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UNITED STATES DEPARTMENT OF AGRICULTURE

Agricultural Research Administration

Bureau of Agricultural and Industrial Chemistry

1.9321
S2Ex8
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Pt.1

EXTRACTION, CHARACTERIZATION, AND UTILIZATION OF GOLDENROD RUBBER

PART 1
SECTIONS I THROUGH VII

Work at the Southern Regional Research Laboratory

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EXTRACTION, CHARACTERIZATION, AND UTILIZATION OF GOLDENROD RUBBER

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EXTRACTION, CHARACTERIZATION, AND UTILIZATION OF GOLDENROD RUBBER
WORK AT THE SOUTHERN REGIONAL RESEARCH LABORATORY

I-INTRODUCTION

The assignment of the Southern Regional Research Laboratory in the study of production of natural rubber from goldenrod was the chemical and chemical engineering research and development work on a practical process for separating and purifying the rubber from the dried plant material, and its preparation in a form suitable for fabrication of rubber products. When work was begun in June 1942, goldenrod of high yielding selections had been planted on fifty acres and represented a potential harvest by September variously estimated at 10-25 tons of dried leaves. The situation as to rubber supplies was in its most uncertain and critical phase, and the desperate need contemplated at the time for additional natural rubber called for the utmost possible expansion of goldenrod plantings in the following year. Under these circumstances it was evident that there would be little time for extensive preliminary laboratory research, and that design and construction of pilot plant equipment should begin almost immediately. Laboratory research and small-scale investigations would have to be carried on concurrently, and keep pace with the demands of pilot plant development for essential operating data. Most important of all, a decision had to be reached at the earliest possible moment as to the general type of process and its major operating steps upon which work would be concentrated.

The situation during the summer of 1942 placed severe restrictions upon the availability of practically every type of material and every sort of accessory equipment required for the construction of a pilot plant of capacity sufficient to process the anticipated production of goldenrod. This inevitably dictated certain limitations of the choice of process operations for isolating the rubber, which was further conditioned by the necessity of developing a process that could have been rapidly expanded to industrial scale under the same restricted availability of construction material, supplies, and facilities. With these considerations in mind, three factors combined to favor preponderantly the decision to concentrate upon a solvent extraction process. First, the only rubber ever isolated from goldenrod in laboratory quantities by Edison thirteen years previously had been obtained by a solvent extraction method; second, the Southern Regional Research Laboratory had an eight cell extraction battery which had been constructed and was in operation for extraction of oil from cottonseed and peanut cake; and third, numerous similar battery type extraction plants were in existence in the Southeast for large-scale commercial extraction of naval stores from pine wood chips, and, in an extreme emergency, might be available for adaptation to a solvent extraction process for producing rubber from goldenrod. Other methods, such as ball milling and hydroseparation, were not eliminated from consideration, but every effort was made to perfect the details of the solvent extraction process as speedily as possible.

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Details of Edison's laboratory extraction method as used by Edison Botanic Research Corporation for extracting 4-pound and 20-pound batches of dry powdered goldenrod leaves were available in a private communication to the Department of Agriculture. Essentially the method consisted of extracting only with benzol the dry leaves which were ground to pass a 30 mesh screen and very evenly sifted through an 8 mesh screen into the extractors. Benzol extracts the rubber, but applied directly to the whole leaf material it simultaneously extracts a larger amount of non-rubber material, partly "resins," and including other leaf constituents. Extraction was effected by two successive periods of soaking, the second and more dilute miscella being reused for the first extraction of a fresh batch of powdered leaves. The extract obtained was concentrated to a sirup by distillation, and residual benzol finally removed by vacuum evaporation in pans. A hard waxy bottom layer of residue from this evaporation could be mechanically separated from the top layer of crude rubbery material, but this raw product was quite impure. It contained chlorophyll, resin, and other acetone soluble substances which were removed only incompletely and with difficulty by long soaking with repeated changes, and final refluxing repeatedly with acetone. At this stage the product containing residual acetone was a paste, to which 1% para aminophenol was added before drying in vacuum at 93° C. Further purification required redissolving in benzol and treatment of the boiling benzol solution with alcoholic caustic soda in an amount insufficient to precipitate the rubber. The rubber was precipitated and the caustic neutralized by pouring the solution into dilute aqueous sulfuric acid, and boiling, allowing the benzol to evaporate. The purified product was again dried in vacuum at 93° C., cooled, and repeatedly sheeted on rolls and alternately washed with warm distilled water until free of acid. Final drying at 93° C. in vacuum resulted in a workable product.

Consideration of the large number of steps in this process, and particularly the repetition of operations and repeated handling of the material made it evident that its adaptation to pilot plant scale would be practically impossible. On a large scale, the use of the indicated amount of alcoholic caustic would be prohibitively expensive, and specially constructed equipment of glass lined or stainless steel required for the subsequent dilute sulfuric acid treatment was unobtainable. While solvent extraction seemed basically the best means of isolating the rubber, a great deal of simplification of the process would be necessary for practical and economical large scale application. The large number of more difficult and repetitive operations were evidently involved in the subsequent purification of the extremely crude material obtained by the initial, relatively simple benzol extraction. The fundamental simplification decided upon was to apply acetone extraction first to remove as completely as possible the non-rubber, acetone soluble impurities - pigments, resins, tannins, etc. Once these substances were largely removed, it should be possible to obtain a comparatively pure rubber extract with benzol, and this proved to be the case. In developing the process on a pilot plant scale, every effort was made to achieve the utmost simplicity in the necessary operations as well as in the design and functioning of the equipment required. The extreme

stickiness and softness of raw goldenrod rubber made it extremely difficult if not impossible to handle in intermediate stages of processing, and the process finally developed involved handling of rubber entirely in solution, which can be done simply and efficiently, up to the final step. As will be shown in what follows, a method was devised for precuring the rubber at this final step and producing a product that could be handled in shipment and further processing.

Most of the rubber produced was extracted from the crop grown in the vicinity of Waynesboro, Georgia, in 1943, and the greater portion of this was from general harvest material processed by the basically simple process of preliminary acetone extraction of resins, benzol extraction of rubber, partial compounding in solution, and precuring. As the dried and ground raw material was not approximately pure leaves, and consequently had a lower rubber content due to inclusion of stems and blooms, a screening operation was employed to enrich the raw material feed to the extractors, and a single reprecipitation step for purification was added to the process to control the final resin content of the rubber. Following the account in Section II of the minimum laboratory and intermediate scale experiments essential to development of the details of this pilot plant process, the basic process as it was finally operated for extraction of the bulk production of usable rubber is described fully in Section III of this report. Simultaneously with the development of the extraction process, work was going forward on vulcanization and physical testing of the rubber, on development of techniques of solution compounding and precuring to produce a product satisfactory for milling, and on further processing and finally, fabrication tests, accounts of which are given in Sections IV and V. Numerous variations of the process were investigated, special lots of raw material were extracted, processed, and tested individually, extensive work was done on the effect of drying conditions on quality of the rubber, tests on grinding and screening of raw material were made, and microscopic studies were employed to guide and control the extraction work. Physical chemical, X-ray, and spectroscopic research for characterizing goldenrod rubber was in progress throughout the work, as well as analytical investigations on the methods for determining rubber and impurities in addition to the very great amount of analytical control work on raw material and products. Some attention was given to the resinous and tarry by-product produced by the preliminary acetone extraction. These phases of the project are separately reported in appropriate sections from VI to XVII.

II-INVESTIGATIONS ON EXTRACTION RATES AND EFFICIENCIES LABORATORY-SCALE AND SINGLE CELL EXTRACTION EXPERIMENTS

The two-solvent extraction method having been decided upon as the most promising for speedy development of a practical process to produce usable rubber from goldenrod in quantity, it was necessary to concentrate most of the research time and effort on perfection of the details of this method. A variety of alternative methods were tried experimentally and leads followed as far as time and available facilities and personnel permitted. These included methods not dependent upon dissolving of rubber described in another Section of this report, as well as many variations of solvent extraction procedures, but the urgency of full pilot plant operation at the earliest possible date required that data essential for plant operation be obtained first and most completely.

Preliminary extraction of resinous and tarry impurities with acetone followed by benzol extraction of rubber appeared to provide the simplest and most practical means of obtaining the rubber, but the properties and behavior of raw material, solutions, and extracted products in various stages of processing and handling, as well as the purity of the rubber obtainable all presented questions which required immediate answers. Some of the major steps of the proposed process depended upon unknown factors which it was necessary to determine before design of pilot plant equipment could be undertaken. At the outset a complete extraction system in glass on a laboratory-scale was assembled as quickly as possible, and all of the operations of the two-solvent process were carried out on this scale as nearly as possible like the projected pilot plant operations, to produce small quantities of rubber.

The glass laboratory extraction system is shown in Fig. 1. It was built around an available large soxhlet type extractor (Corning Catalog No. 3885) with a capacity of 600-700 g. of ground goldenrod leaves, which was modified by the by-pass shown in the figure to permit continuous flow of solvent through the extraction cell. Separate recovery and storage systems were provided for acetone and benzol, with glass piping and cocks to permit introduction of either solvent into the boiler. By using vacuum the concentrated solution in the boiler after each stage of extraction could be drawn directly from the boiler into either the benzol or acetone vacuum evaporators. These were made of standard vacuum distilling pots (Corning Catalog No. 3480) with desiccator type covers permitting the removal of rubber or resinous material left after vacuum distillation of the solvents. A packed fractionating column section, not shown in the figure, was later inserted below the reflux condenser to effect a more rapid separation of acetone displaced from the material when benzol extraction was begun. This arrangement was only partially successful in operation. The small amounts of rubber obtained on this scale were milled and vulcanized, and showed definitely the practicability of producing usable rubber by the two-solvent extraction process.

The results of the first three laboratory extractions on the same

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variety of leaves pointed out the necessity of having a finely ground material for maximum yields of resins and rubber as shown in Table I. In the first experiment a batch of leaves was ground to about 20 mesh in a Bauer disc type mill with the following screen analysis: 11% passed through the 40 mesh screen; 17% was retained on the 40 mesh screen; 26% was retained on the 30 mesh screen; and 46% was retained on the 20 mesh screen. After 24 hours acetone extraction, the resin yield was 13.6% and benzol extraction for the same time gave a rubber yield of 2.9%. Another sample of the same leaves was ground in a Wiley mill which gave the following screen analysis: 100% passed through the 30 mesh screen; 57% was retained on the 40 mesh screen; and 43% passed through the 40 mesh screen. Acetone extraction for 24 hours in this case gave 15.3% resins, while the benzol extraction for the same time yielded 5.7% rubber. A third sample of the same leaves was ground in the Wiley mill so that 100% passed through the 40 mesh screen. In this experiment the resin value after 24 hours acetone extraction was 18.8% and the rubber extracted in 24 hours with benzol was 6.6%. Many other extractions with acetone and benzol were carried out on ground material to determine yields of resins and rubber with respect to fineness of grinding. (See Table I.) These preliminary extractions show that goldenrod leaves should be ground to approximately 30 to 40 mesh for maximum yields of resins and rubber when extracted with acetone followed by benzol.

A metal extractor was constructed with a capacity of approximately 25 pounds of ground leaves. This extractor was used with the boiling, condensing and evaporating setup which was designed for the small glass extractor. It yielded good results with the acetone extract in 48 hours, compared with 24 for the small extractor, but the benzol extract was slower in comparison as shown in Table I, experiment No. 11. In another experiment the resins and rubber were extracted by pouring cold acetone and benzol successively through the ground leaves in the metal extractor at room temperature. Much larger quantities of rubber were obtained from the metal extractor for compounding, vulcanization, and testing and the rubber thus obtained showed promise of development of usable material.

The glass extraction apparatus was used to test other solvents than acetone and benzol for removal of both resins and rubber as shown in Table II. Alcohol was used instead of acetone for resin extraction, and chloroform, toluene, xylene, petroleum ether, and aromatic petroleum fractions with boiling ranges "lighter than xylene," "xylene," and "higher mixed aromatics," were tried instead of benzol. Toluene is somewhat better than benzol as a rubber solvent. Rates of extraction were determined on small samples using boiling benzol, toluene, and xylene. In these tests xylene proved better than benzol or toluene. About 15% more material was extracted from the goldenrod by xylene than by the other two solvents. Absolute alcohol removed the chlorophyll and other pigments more completely than acetone, in fact, more material was extracted. In one extraction chloroform was substituted for benzol to remove the rubber. Petroleum ether was also substituted for benzol in several extractions. (See Table II.) The yield of rubber in the case of chloroform extraction was somewhat higher than with benzol while the petroleum ether extractions gave yields slightly lower. Vulcanizates from these extractions compared favorably with those obtained from the benzol extracts.

II-TABLE I

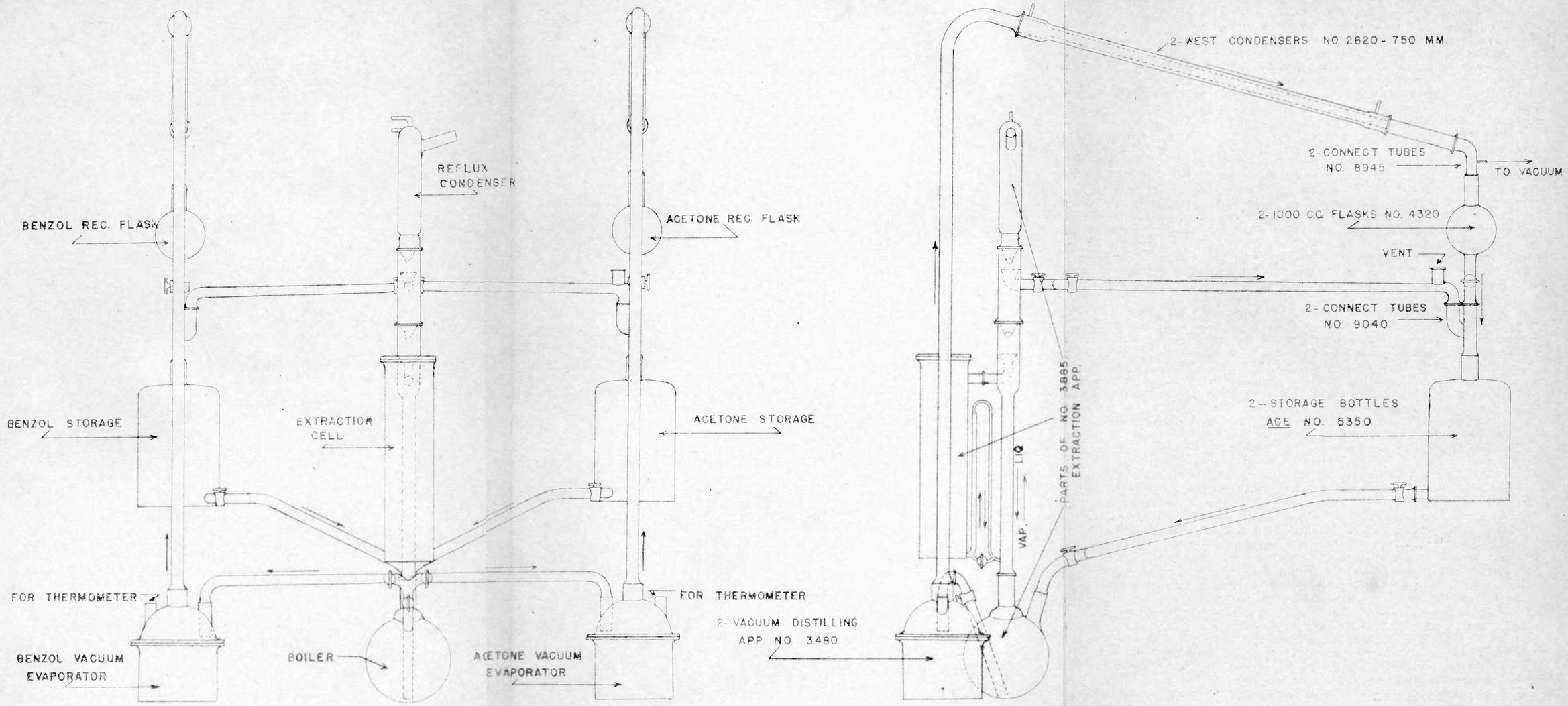
PRELIMINARY LABORATORY EXTRACTIONS WITH ACETONE AND BENZOL

Exp. No.	SOLVENT Time - Hrs. Acetone	Benzol	BOILING TEMPERATURE RANGE 0° C. Resins Boiler	Resins Evaporator	Rubber Boiler	Rubber Evaporator	% EXTRACT Resins	Crude Rubber	Fineness of Material % through Mesh
1	24	24	57.5-61.5	-	75 - 80	-	13.6	2.9	11-40
2	24	24	57	58.5-61.0	74.5-79	80-83.5	15.3	5.7	43-40
3	24	24	57	58 - 61.5	72 - 76	81 - 89	18.8	6.6	100-40
4	24	24	57	57.5-62.5	71-74.5	73-89.	19.3	6.7	100-40
5	24	24	57 - 58	59 - 64	71 - 74	74-89	18.5	5.8	100-40
6	24	24	57 - 58	61.5-64	66 - 80	67 - 89	20.0	5.4	100-40
7	24	26	57 - 58	61 - 66	73.5-79	74 - 89	20.7	5.0	100-40
8	24	26	57.5-58	59 - 81	71 - 77	78-84.5	21.5	4.9	100-40
9	24	26	57 - 58	58 - 87	70.5-75.5	72 - 86	21.8	4.8	100-40
10	24	24	56-- 57	59 - 90	73 - 80	80 - 84	18.2	4.9	100-40
11*	48	57	57 - 58	56 - 80	79 - 80	78 - 87	19.7	3.8	100-40
12	28	24	56.5-57.8	59 - 88	73.5-84	81 - 89	19.0	4.6	100-40
14	26	25	57.1-58	60 - 87	75 - 82	76 - 89	19.9	4.2	100-30
16	24	26	57 - 59	58 - 74	72 - 81	71 - 87	19.2	3.6	100-30
17	24	24	57 - 59	58 - 81	76 - 82	80 - 89	20.8	4.1	100-30
18	24	24	57 - 58	59 - 77	77 - 81	82 - 90	19.2	3.5	100-30
19	24	24	57 - 58	60 - 82	75 - 81	79 - 82	20.5	5.7	100-30
21	24	20	57.5-59	61 - 83	75 - 82	80 - 86	20.7	3.1	100-30
23	24	24	57 - 59	59 - 86	77-81.5	82 - 88	21.4	4.3	100-30
25	24	24	57 - 58	60 - 82	77 - 80	82 - 83	18.8	4.3	100-30
26	26	26	57 - 58	58 - 84	72 - 79	77 - 88	16.8	6.6	100-30
28	24	24	57 - 59	66 - 86	78 - 81	80 - 86	20.5	4.9	100-30
29	24	24	57.5-58	59 - 83	78 - 81	82 - 86	18.7	5.1	100-30

*Metal extractor used.

LABORATORY EXTRACTION

APPARATUS



FRONT ELEVATION

II-FIGURE I

SIDE ELEVATION

II-TABLE II

PRELIMINARY LABORATORY EXTRACTIONS WITH VARIOUS SOLVENTS

Exp. No.	SOLVENT Time	SOLVENT Hrs.	BOILING TEMPERATURE RANGE 0° C. Resins Boiler	Resins Evaprtor.	Rubber Boiler	Rubber Evaprtor.	% Extract Resins	% Extract Crude Rubber	Fineness of Material % Through Mesh
13	Acetone 25	Benzol 43	58.8-61	59.5-79	66-83	69-86	10.5	17.1	100 - 30
20	Acetone 24	Pet.Ether 24	57-58	60-80	63-68	-	20.9	4.3	100 - 30
22	Acetone 24	Pet.Ether 22	57-59.5	60-81	59-68	-	20.5	5.1	100 - 30
24	Acetone 24	Pet.Ether 27	57-59	59-83	59-63	-	19.8	3.9	100 - 30
27	Alcohol 42	Benzol 34	79-81	79-85	71-79	81-89	22.3	5.6	100 - 30
30	Acetone 25	Chloro-form 44	57-59	60-84	65-67	66-67	21.9	7.8	100 - 30
79	Acetone-Skelly B 24	Skelly B 24	20-25	-	68	-	6.2 plus 9.4	1.74	82 - 30
80	Acetone None	Skelly B 24	-	-	67-68	-	-	1.76	82 - 30
81	Acetone-Benzol 24	Benzol 24	-	-	80-81	-	9.3 plus 7.7	2.6	82 - 30

Extractions using mixed solvents were carried out on direct fractional separation in the extraction of goldenrod leaves. (See Table II.) After a short preliminary acetone extraction of the leaves for one hour to dry the ground material, a mixture of 50% petroleum ether (Skellysolve B) and 50% of acetone was circulated for 24 hours at 519 cc. per hour at room temperature. Final extraction of the rubber was done with hot Skellysolve for 24 hours, followed by 15 hours extraction with hot benzol. Pure acetone extracted 6.2% of resins, 50% Skellysolve - 50% acetone extracted 9.4% of resins mixed with some rubber; pure Skellysolve extracted 1.74% of purified rubber, and benzol finally extracted 0.72% of a non-rubber material. The yield was lower than was obtained in the pilot plant with acetone-benzol mixtures. The product on drying was readily peeled from the pot still, and was less sticky than the usual raw rubber produced by unmixed solvents. A vulcanizate with the standard recipe gave 1855 pounds per square inch tensile with 640% elongation.

In another experiment hot Skellysolve was used for extraction for 24 hours without any preliminary acetone extraction, and acetone was added slowly to the concentrated Skellysolve solution up to 50% concentration, to precipitate a purified rubber fraction. The yield was 1.76% of a product similar to that obtained from mixed solvent extraction, which vulcanized with the standard recipe to give 1840 pounds per square inch tensile at 700% elongation. A third experiment was carried out using acetone extraction for one hour at room temperature, followed by extraction with a mixture of 50% acetone and 50% benzol for 24 hours at room temperature. Final extraction of the rubber was done with hot benzol for 24 hours. Pure acetone extracted 9.3% of resins, 50% acetone-50% benzol extracted 7.7% of resins mixed with some rubber. The product on drying was readily peeled from the pot still, and was less sticky than the usual raw rubber produced by unmixed solvents. A vulcanizate with standard recipe gave 1700 pounds per square inch tensile with 840% elongation. These experiments were not practical on account of the low yields of rubber, even though a less sticky product was obtained.

Experiments were carried out using petroleum fractions from the Pan American Refining Corporation in the extraction of rubber from goldenrod leaves. The leaves were ground to 30 mesh and the extractions were made in the dark in small soxhlet extractors employing the standard procedure using 1000 grams of acetone to remove most of the resinous material followed by the rubber extraction. (See Table III.) In these extractions 150 grams of the same batch of ground leaves were used. An average of 21.0% of resins was extracted in 48 hours. Acetone recovered was 80.94% at 25° C. after blowing air through the leaves for five minutes. No acetone was collected in the ice trap (2° C.), therefore, the solvent loss was probably due to that remaining in the leaves.

In 32 hours the "Lighter than Toluol" fraction (b.p. 33-92° C.) extracted 3.86% by weight of the dried leaves after vacuum drying and the rubber obtained appeared to be of good quality. Solvent recovered

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was 64.3% by the 25° C. condenser, while 8.3% was collected in an ice trap at 2° C., thus giving 27.4% of solvent lost in a single extraction. Solvent is easily removed from the leaves but separation from acetone may be difficult because of the similar boiling points. The "xylene" fraction (b.p. 132-142° C.) extracted 9.65% by weight of the dried leaves in 32 hours. This extracted material consisted of rubber and some of the higher boiling ends of the solvent. Solvent recovered was 83.2% by the tap water condenser and none reached the ice trap. Remaining solvent representing 16.8% was lost in the leaves. The "Higher Mixed Aromatics" petroleum fraction (b.p. 133-205° C.) extracted 8.27% by weight of the dried leaves in 32 hours, but the extract was a liquid consisting of the high ends of the solvent and rubber. Vacuum drying of this extract and the xylene extracted rubber was not tried inasmuch as no vacuum drying equipment was available above 100° C. Solvent recovered was 83.2% by the tap water condenser, leaving 16.8% of solvent not removed from the leaves. From considerations of availability, effectiveness in extraction, and ease of removal from the product, acetone and benzol were established as the preferred solvents.

II-TABLE III

EXTRACTIONS WITH ACETONE AND PETROLEUM FRACTIONS

Ground leaves used 150 gms. Acetone extract-48 Hrs.
Acetone used 1000 gms. Petroleum " -32 Hrs.
Petroleum fraction used 500 gms.

Solvent Used	ACETONE EXTRACT			PETROLEUM FRACTION EXTRACT				Condition of Rubber
	Weight of Resins Gms.	Resins %	Solvent Recovered %	Weight of Rubber Gms.	Rubber %	Solvent Recovered %	Solvent Recovered Ice Trap %	
"Lighter than Toluol"	31.4	20.9	82.8	5.8	3.86	64.3	8.3	Good.
"Xylenes"	31.1	20.7	78.9	14.5	9.65	83.2	0	Unsatisfactory mixed with high ends of solvent.
"Mixed Higher Aromatics"	32.0	21.3	81.1	12.4	8.27	83.2	0	Unsatisfactory mixed with high ends of solvent.

Investigations were carried out to determine the effect of particle size on the rate of acetone and benzol extractions. A batch of leaves containing a high yield of rubber was ground in a Ball and Jewell knife type cutter and the various size particles separated on screens. Three samples of 50 grams each of the different particle sizes were extracted in small soxhlet extractors with both acetone and benzol for 24 hour

periods, the rates of extraction being followed, as shown in Table IV. The sample with the largest particles (20 - 30 mesh) was incompletely extracted with both solvents. In case of the intermediate particles (40 - 50 mesh) higher yields of resins and rubber were obtained. The finely ground material (finer than 100 mesh) gave resin values progressively higher with increased extraction time and the rubber was completely removed in less than 12 hours as shown in Figures 2 and 3.

II-TABLE IV

EFFECT OF PARTICLE SIZE ON RATE OF ACETONE & BENZOL EXTRACTIONS

Particle Size	Hours	% Acetone Extract	% Benzol Extract
20 - 30 mesh	0.5	4.6	-
	1	6.0	3.6
	4	9.0	4.6
	12	12.2	5.8
	24	15.4	6.0
40 - 50 mesh	0.5	7.6	-
	1	9.0	6.4
	4	13.0	7.4
	12	15.6	8.2
	24	18.6	8.6
Finer than 100 mesh	0.5	12.4	-
	1	13.6	7.6
	4	16.8	8.4
	12	18.4	9.6
	24	20.2	9.6

In order to determine the optimum extraction time and the effect of various mechanical and chemical treatments of goldenrod leaves, the rates at which the acetone soluble and the benzene soluble portions were extracted were carefully determined and plotted. The rates were determined on 100 g. samples in a soxhlet type extractor siphoning over at the rate of once every 10 to 12 minutes.

The initial studies were made to determine the effect of mechanical treatment of the leaves and to determine the amount of grinding, and the length of time necessary for most efficient extraction. The test samples were prepared as follows:

1. Original leaves as received (crushed but not ground).
2. Sample ground to pass 1/32" screen on a Ball and Jewell mill.
3. Sample ground to pass 1/16" screen on a Ball and Jewell mill. By referring to Table V and Figures 4 and 5 it can be seen that the extraction of the unground leaves was unsatisfactory while the material which passed through the 1/16" screen yielded as much benzol extract as that which passed the 1/32" screen, and the rate of extraction was nearly as rapid. From these data it can be concluded that a relatively coarse grind is all that is necessary to effectively and economically remove the

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major portion of the rubber from goldenrod leaves, by hot benzene extraction. Undoubtedly the finely ground material could be more rapidly and completely extracted if the solvent flow rate can be maintained at the required minimum. These rates were studied in conjunction with pilot plant extractions where it was found that the difficulty of pumping solvent through the material increased with decreasing particle size.

Further studies were made on the rates of extraction of chemically treated goldenrod leaves produced in experiments to be described in Section VIII. A series of these studies made on a representative sample are shown in Table VI and Figures 6 and 7. This series includes:

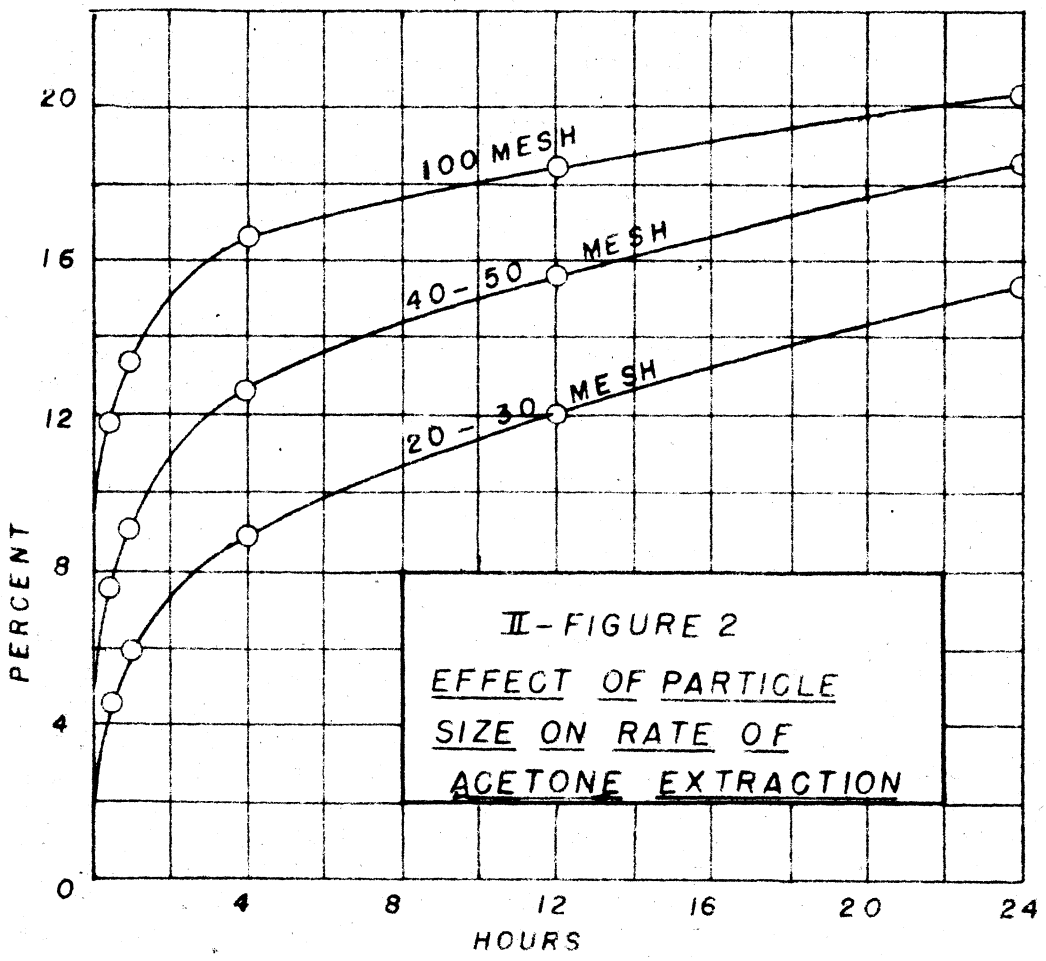
1. Original ground leaves - through 1/16" screen.
2. Original unground leaves.
3. Water cooked leaves, unground.
4. 3% H_2SO_4 cooked leaves, unground.

From previous experiments it had been determined that with chemically treated leaves it was unnecessary to grind the leaves in order to obtain complete extraction. It had also been found in experiments which are described in Section VIII that extraction rate curves of 2% NaOH treated leaves and 2% NaOH plus 3% H_2SO_4 treated leaves were similar to the 3% H_2SO_4 curve shown in Figures 6 and 7. When caustic cooking was used the acetone soluble material was only 4% to 5% instead of 12% to 13% due to the solubility of the resins in 2% NaOH. All of the curves for the treated leaves show a very rapid extraction in the first 10 to 20 minutes and nearly complete extraction in 2 to 3 hours. The untreated leaves and the water cooked leaves still show an appreciable amount of material extracted between 12 and 24 hours, especially in the case of acetone soluble resins.

II-TABLE V

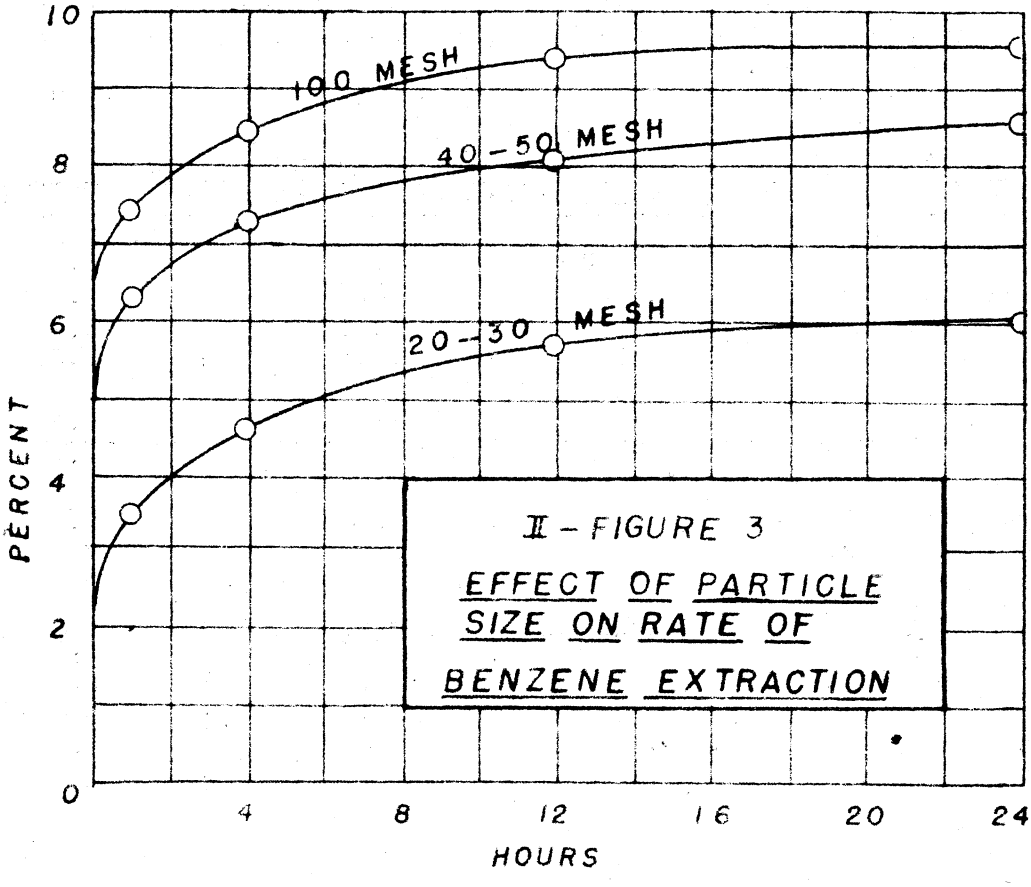
RATES OF EXTRACTION OF UNTREATED GOLDENROD LEAVES

Sample	Time (Hrs.)	% Acetone Extract	% Benzol Extract
As received. (Crushed but not ground.)	0.2	3.3	2.1
	0.5	5.2	3.3
	1	6.6	3.9
	4	10.4	4.6
	12	12.4	5.1
	24	13.9	5.7
Ground to pass 1/32" screen in Ball and Jewell grinder.	0.2	7.6	3.0
	0.5	10.4	5.8
	1	11.8	6.6
	4	15.0	7.0
	12	16.1	7.1
	24	17.6	7.2
Ground to pass 1/16" screen in Ball and Jewell grinder.	0.2	7.7	2.4
	0.5	9.8	5.0
	1	11.1	6.4
	4	13.8	6.9
	12	15.2	7.1
	24	16.6	7.2



II-FIGURE 2

EFFECT OF PARTICLE SIZE ON RATE OF ACETONE EXTRACTION

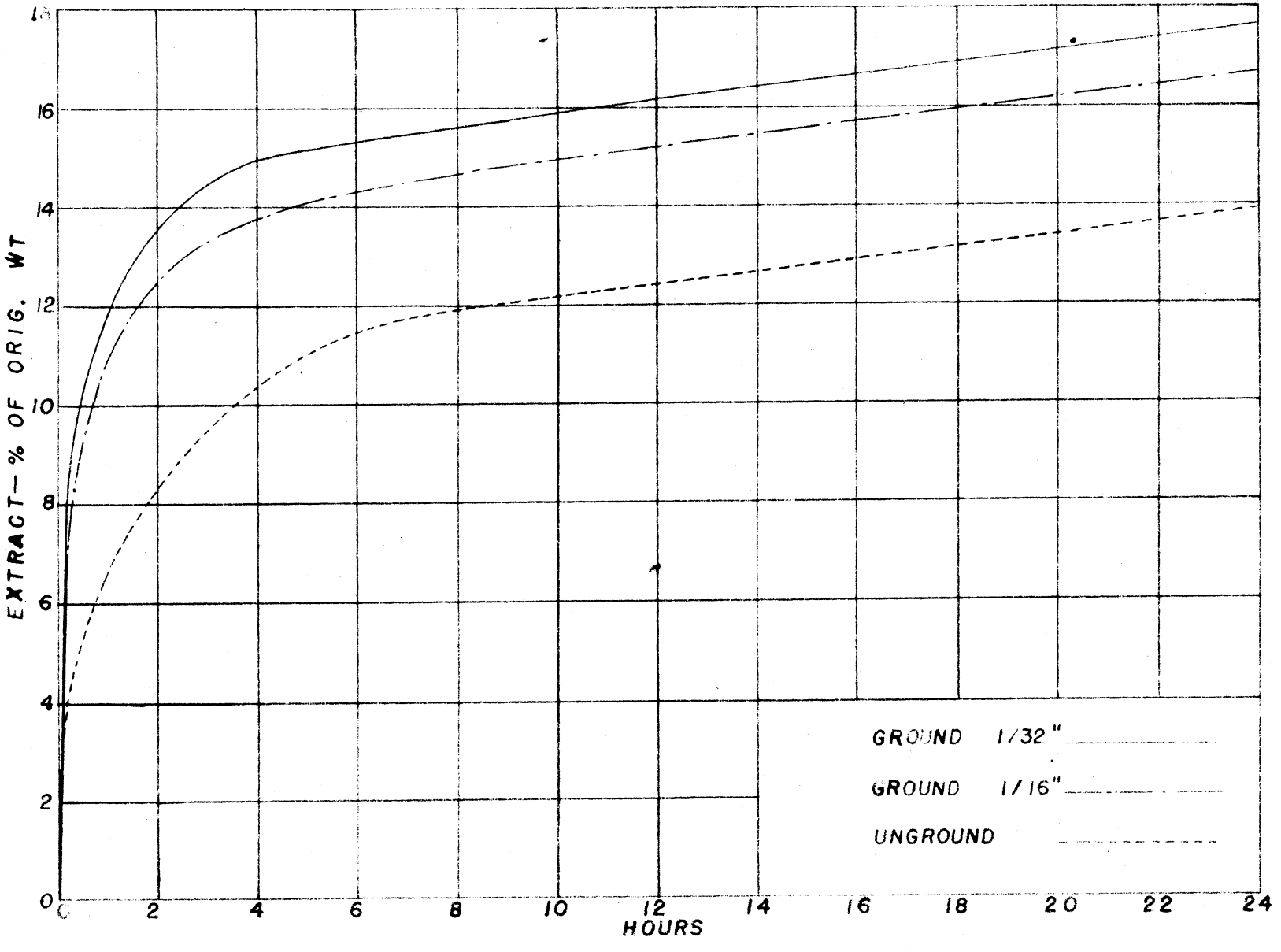


II-FIGURE 3

EFFECT OF PARTICLE SIZE ON RATE OF BENZENE EXTRACTION

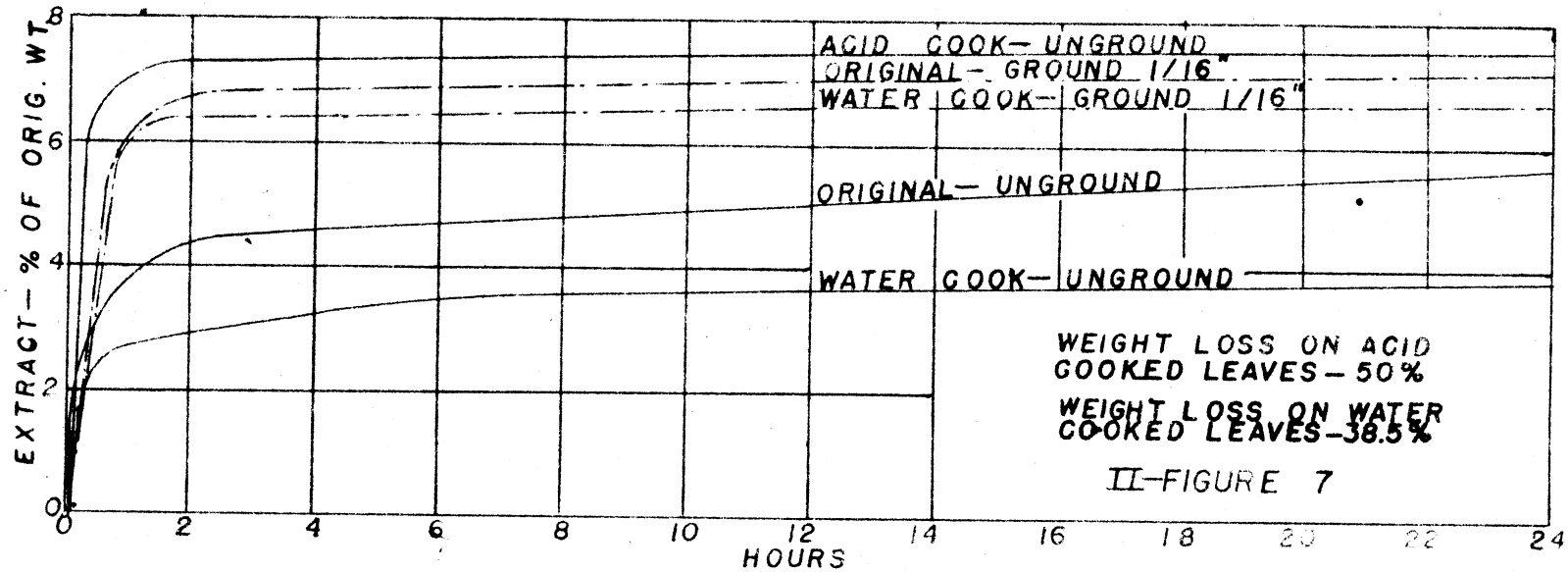
II-FIGURE 4

RATE OF ACETONE EXTRACTION OF UNTREATED GOLDENROD LEAVES



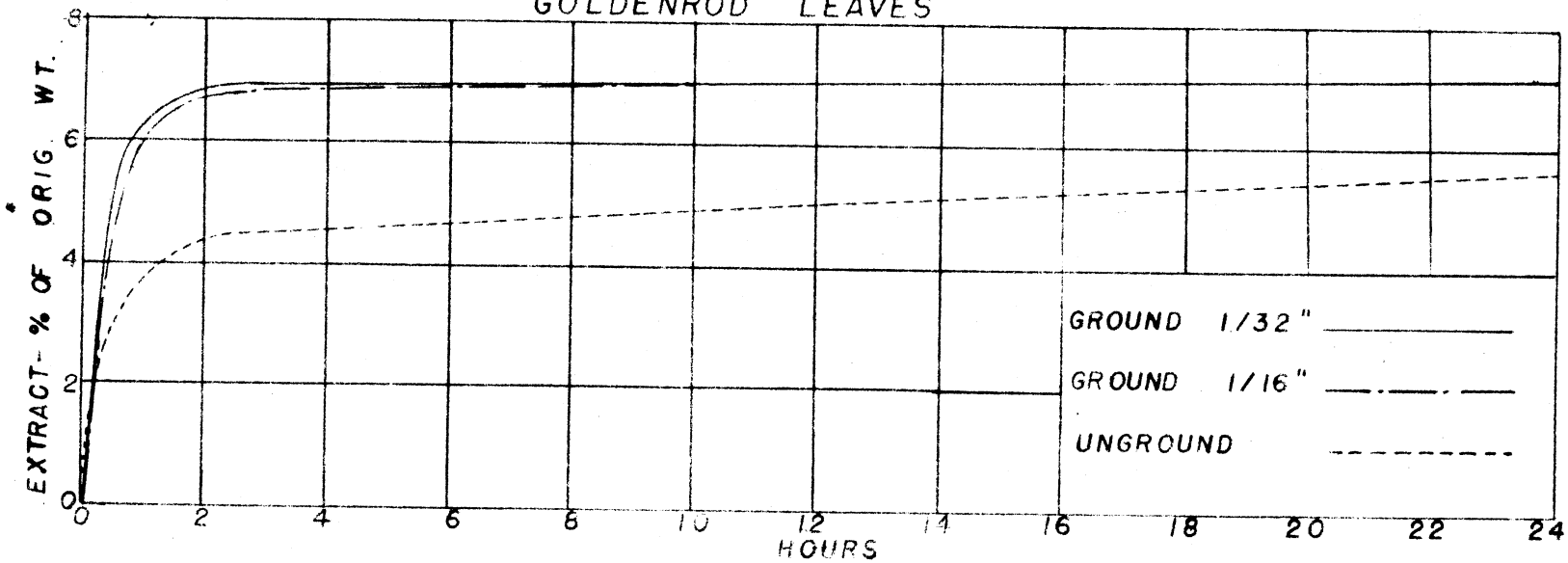
II—FIGURE 7

RATE OF BENZOL EXTRACTION OF TREATED GOLDENROD LEAVES



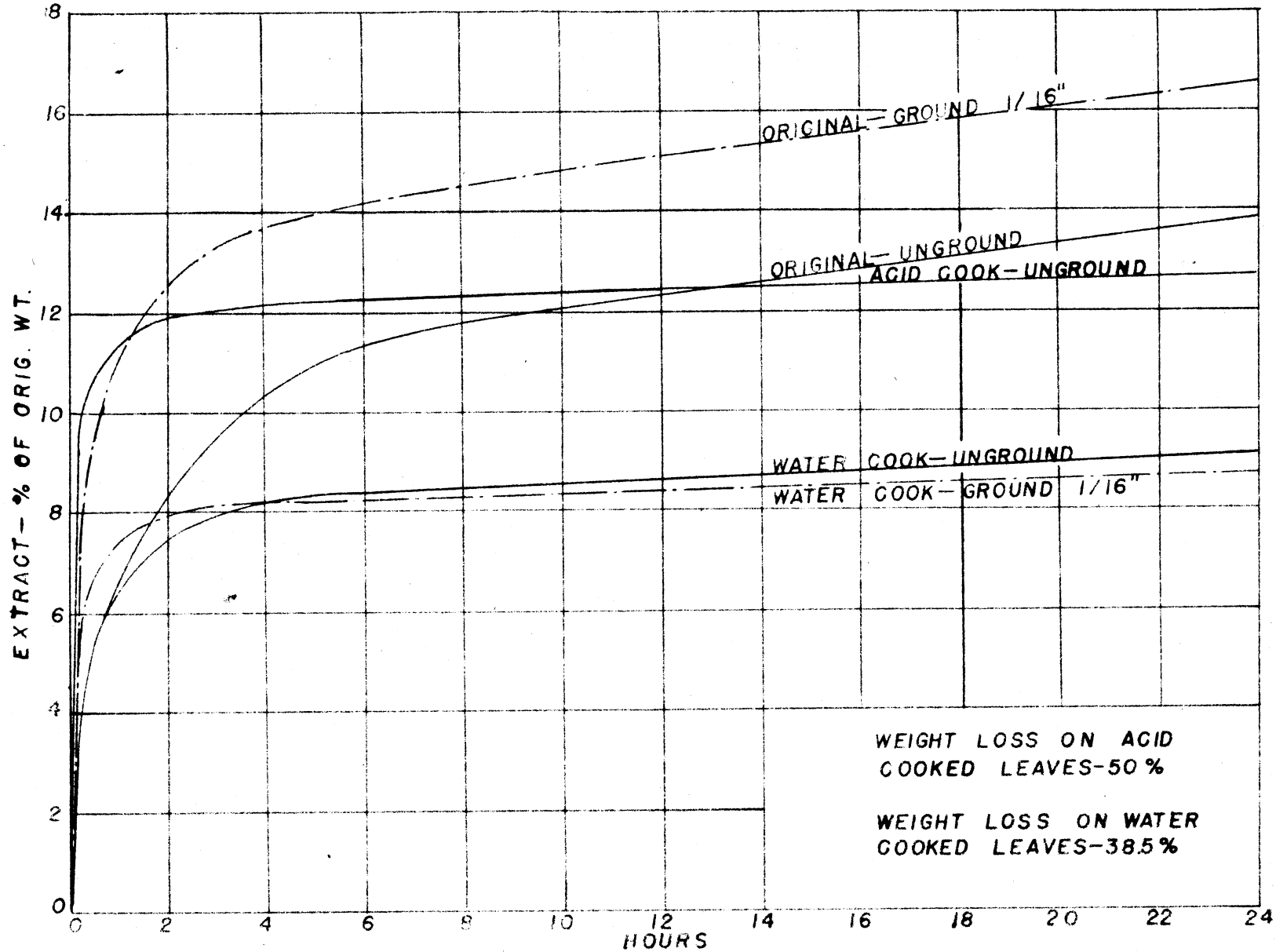
II—FIGURE 5

RATE OF BENZOL EXTRACTION OF UNTREATED GOLDENROD LEAVES



II-FIGURE 6

RATE OF ACETONE EXTRACTION OF TREATED GOLDENROD LEAVES



II-TABLE VI

RATES OF EXTRACTION OF TREATED GOLDENROD LEAVES

Sample	Time (Hrs.)	% Acetone Extract	% Benzol Extract
Original leaves. (Unground.)	0.2	3.3	2.[illegible]
	0.5	5.2	3.3
	1	6.6	3.9
	4	10.4	4.6
	12	12.4	5.1
	24	13.9	5.7
Original leaves. (Ground to pass 1/16" screen on Ball and Jewell grinder.)	0.2	7.7	2.4
	0.5	9.8	5.0
	1	11.1	6.4
	4	13.8	6.9
	12	15.2	7.1
	24	16.6	7.2
Water cooked leaves. (Unground.)	0.2	3.3	1.6
	0.5	5.4	2.4
	1	6.5	2.7
	4	8.2	3.3
	12	8.7	3.7
	24	9.1	3.8
Water cooked leaves. (Ground to pass 1/16" screen on Ball and Jewell grinder.)	0.2	4.3	1.5
	0.5	6.7	3.8
	1	7.3	6.1
	4	8.2	6.5
	12	8.4	6.7
	24	8.7	6.7
3% H_2SO_4 cooked leaves. (Unground.)	0.2	8.0	3.5
	0.5	10.7	6.5
	1	11.3	7.1
	4	12.2	7.4
	12	12.5	7.5
	24	12.7	7.55

Laboratory apparatus was constructed in which the rates of extraction of resins and rubber could be determined at accurately controlled temperatures and rates of flow of solvent over the range from room temperature to the boiling points at atmospheric pressure. Fifty grams of ground leaves from the same sample (87% through 40 mesh screen) were used to charge the extractor for each extraction. The apparatus was so constructed that a constant flow of solvent could be maintained by means of a capillary and the temperature was controlled with a surrounding jacket through which heated water flowed. These experiments showed that hot acetone gave a faster extraction; in fact, at 50° C. the acetone soluble material was removed from the ground leaves approximately eight times as fast as at 30° C. In eight hours at 50° C. the extraction was practically complete as shown in Table VII and Figure 8. No effect was observed at 30° C. or 50° C. in the rate of acetone extraction when the flow was increased above that used in the pilot plant (100 gallons per hour for 85 pounds of leaf material). A large sample of leaves was thoroughly extracted with acetone and dried prior to the benzol extractions. Only two extractions

over

with benzol were made at 27° C. and 70° C. repsectively at the same rate of flow (see Table VII). Hot benzol gave a faster extraction of rubber from the leaves. In six hours at 70° C. the extraction was almost complete as shown in Figure 9. The percent of benzol extract is based on the weight of original leaves used on a moisture free basis.

II-TABLE VII
RATES OF EXTRACTION
CONTROL OF TEMPERATURE & RATE OF FLOW OF SOLVENT

				PERCENT MATERIAL EXTRACTED						
		Flow	Temp.	Hours Extracted						
Run	Solvent	cc/min.	° C.	1	2	4	6	7	7.5	8
1	Acetone	13	30	9.08	10.06	11.21			12.37	
2	"	13	40	10.50	11.71	13.07			14.58	
3	"	13	50	12.42	13.92	15.42				17.24
4	"	27	30	9.47	10.49	11.58				12.83
5	"	27	50	12.42	13.92	15.52				17.02
6	Benzol	10.5	27	5.87	6.30	6.68		6.94		
7	"	10.5	70	8.37	8.65	8.84	8.91			

Conclusions from Laboratory Extraction Experiments. Other solvents than acetone and benzol may be used for removal of both resins and rubber, such as alcohol instead of acetone for resin extraction, and chloroform, toluene, xylene, petroleum ether, aromatic petroleum fractions with boiling ranges of "lighter than xylene," "xylene," "higher mixed aromatics," and mixed solvents instead of benzol for rubber extraction. From considerations of availability, effectiveness of extraction, and ease of removal from the product, acetone and benzol were established as the preferred solvents.

Fineness of grinding not only affects the rate of extraction with acetone and benzol but also the yields of resins and rubber are considerably increased.

Cooked or chemically treated leaves were extracted more rapidly and completely than dried, whole leaf material.

Hot acetone gives a faster extraction of resins. Acetone soluble material was removed from ground leaves approximately eight times faster at 50° C. than at 30° C., however, no effect was observed at 30° C. or 50° C. in the rate of acetone extraction when the flow was increased above 100 gallons per hour for 85 pounds of leaf material. Hot benzol gives a faster extraction of rubber.

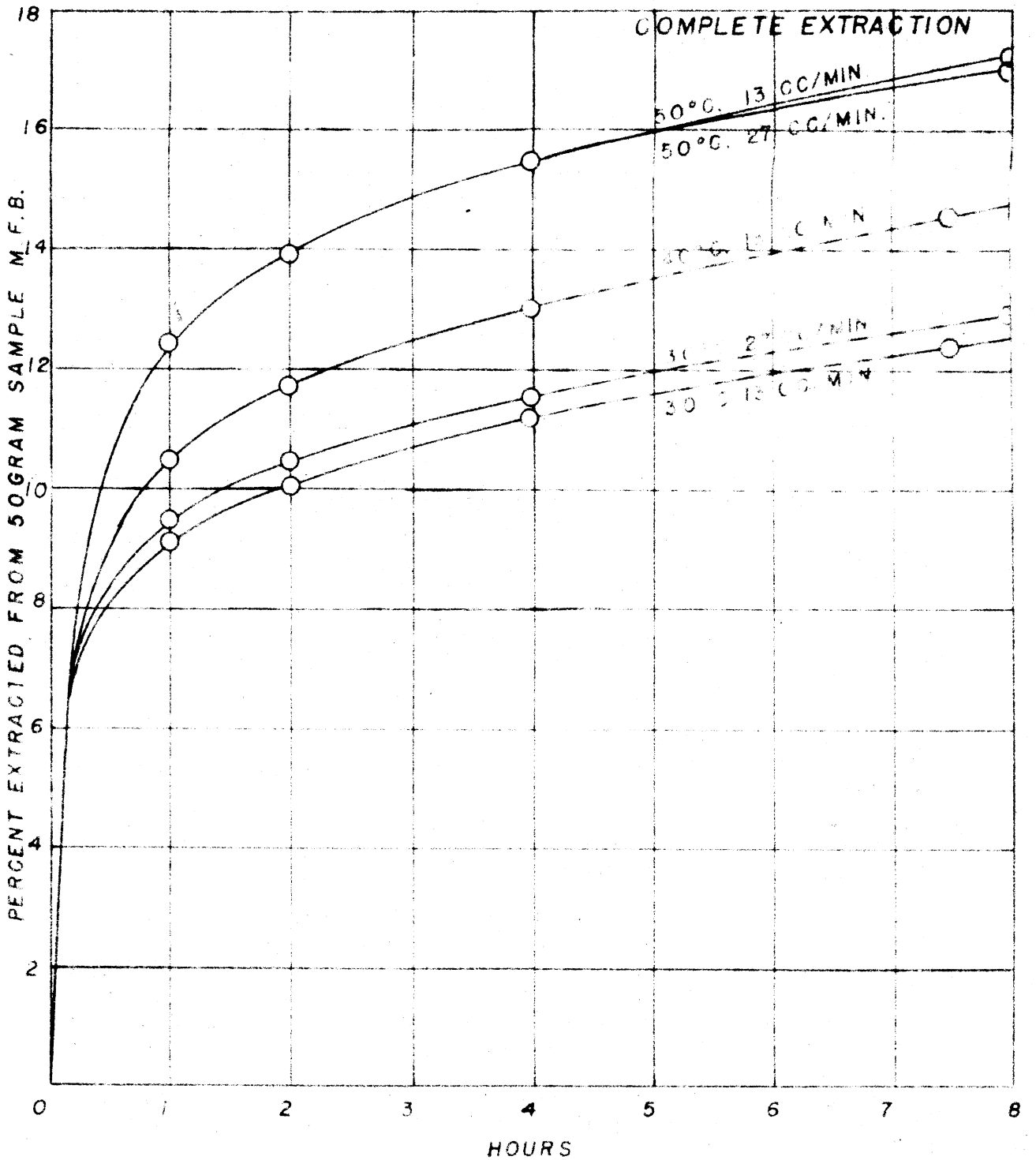
The two-solvent process of extraction with acetone and benzol has been established to be satisfactory for production of usable rubber from goldenrod leaves.

II – FIGURE 8

RATES OF EXTRACTION

CONTROL OF TEMPERATURE AND RATE

OF FLOW OF ACETONE

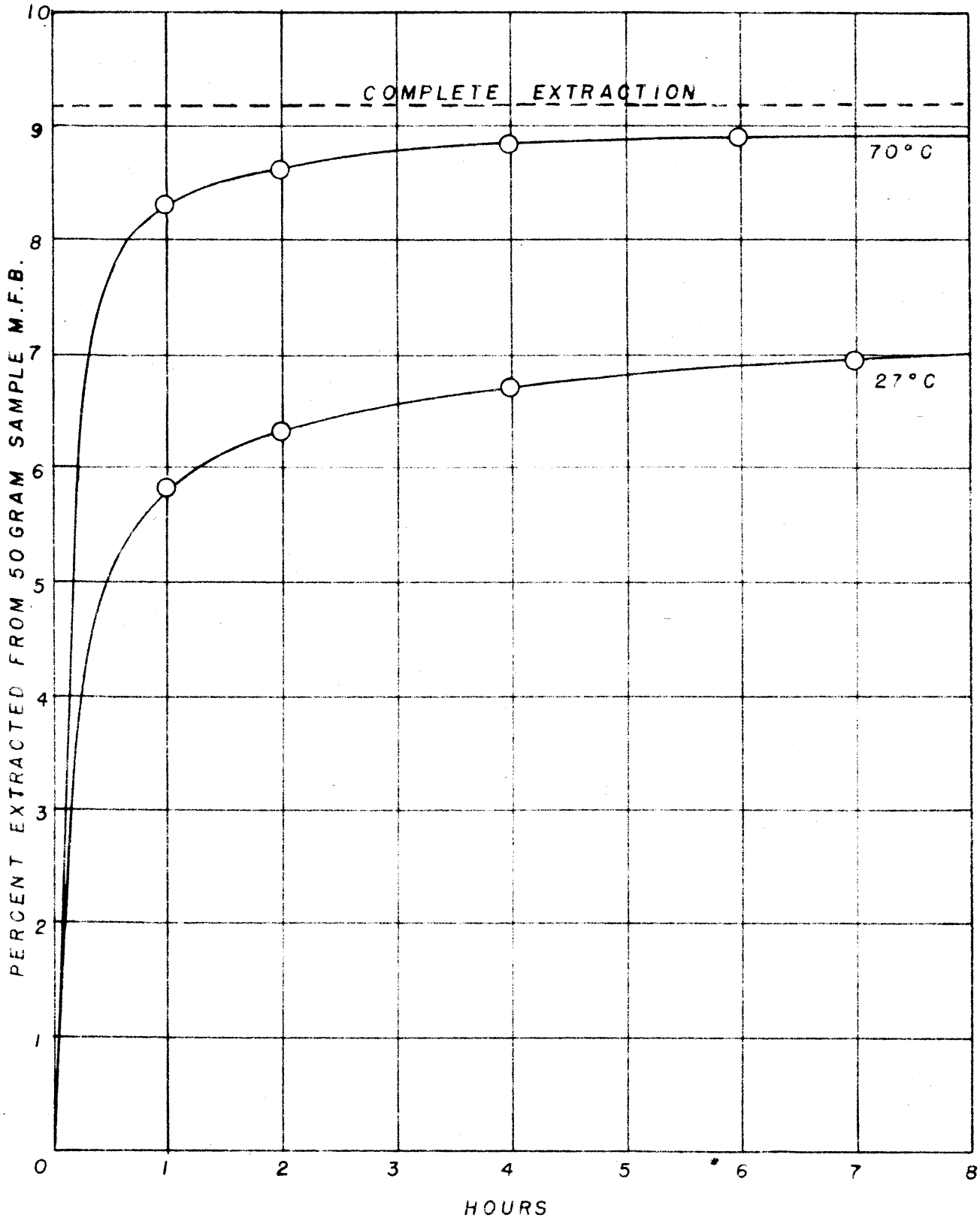


II – FIGURE 9

RATES OF EXTRACTION

CONTROL OF TEMPERATURE AND RATE

OF FLOW OF BENZENE AT 10.5 CC PER MIN.



Single Cell Extraction Experiments. The next step in development of the extraction process on an intermediate scale considerably larger than the laboratory glass extraction equipment was carried out in a single cell extraction system with a capacity of 70 to 80 pounds of ground goldenrod leaves. In this way ample quantities of benzol extract were obtained for the complete evaluation of the goldenrod rubber and information was obtained on the suitability of the extraction process for still larger pilot plant scale production, particularly in regard to behavior of the solutions when processed in metal equipment.

Thirty-five experiments were made in this single cell extraction system, the arrangement of which is shown in Figure 10. For the first 18 experiments the procedure was similar to that used in the laboratory glass extraction system. The ground goldenrod leaves were placed in a cotton sack which fitted inside a jacketed metal extractor 14" in diameter by 38" high, provided with a removable top for loading and unloading. Hot water was circulated through the jacket, which extended to a height of 36", to maintain the contents of the extractor at definite temperatures during extraction with each solvent. The solvent entered near the top of the extractor, and followed a downward path through the ground goldenrod material, passing from the bottom into an overflow leg which maintained the liquid level within 4" of the top so that the charge in the extractor was always covered with solvent. The extract drained from the overflow leg into the evaporator.

The evaporator was a single shell 14" in diameter by 24" high, jacketed to a height of 15" for heating by 25 pound steam. As rapidly as solvent could be distilled from the miscella the vapors were condensed by a water tube condenser and the condensate returned continuously to the extractor. Recirculation was thus effected without a pump, the rate being approximately gaged by a sight glass in the solvent return line. Between the evaporator and condenser there was a 4' section of 8" pipe packed with 1/2" lengths of 12 mm. glass tubing as a ring packing for removal of acetone from the distillate during the first few hours of benzol extraction, since all the acetone could not be drained from the extracted material. A top cut of 15 gallons of distillate containing about 60% acetone was separated and later fractionated to recover the pure solvents. For both the acetone and benzol extractions the evaporator had a capacity of 15 to 20 gallons per hour which was equal to about one solvent change through the extractor per hour.

At intervals, depending upon the concentration of the miscella, it was pumped from the evaporator to either the acetone or the benzol final concentration still. These separate stills, one for resins and the other for rubber solution, were identically constructed of shells 16" in diameter by 24" high, jacketed for 12" of the height for 25 lb. steam heating. Each was equipped with a water tube condenser similar to the one provided for the evaporator. (Details of the design of these condensers and other units are given more completely in Section III.) Recovered solvents were returned to the 50 gallon acetone and benzol storage tanks. The concentrated resin, substantially free of acetone, was sufficiently fluid while hot to be run into 50 lb. lard cans. The benzol extract, at a concentration of 1.0 to 1.5 pounds per gallon, was drained from the

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benzol still into 5 gallon pyrex bottles for storage until further use. These bottles were carefully wrapped to avoid exposure of the solution to light.

For each of the 18 complete experiments made in this system the extraction procedure consisted essentially of a continuous acetone extraction, an acetone draining period of an hour, followed by a continuous benzol extraction. On completion of the benzol extraction, the extractor was drained for one hour, and steamed out to remove the remainder of benzol still absorbed by the goldenrod material. The benzol-water mixture steamed from the extractor was condensed by means of a single pass, water cooled, double pipe condenser, and the benzol layer was siphoned from the settled mixture and reused without drying or redistillation.

The evaporator, stills, and extractor were all constructed of welded 14 gauge galvanized iron. The piping, filling, solvent, and extract valves were all black iron and either 1/2 or 3/4" in size, pipe joints being sealed with litharge and glycerine.

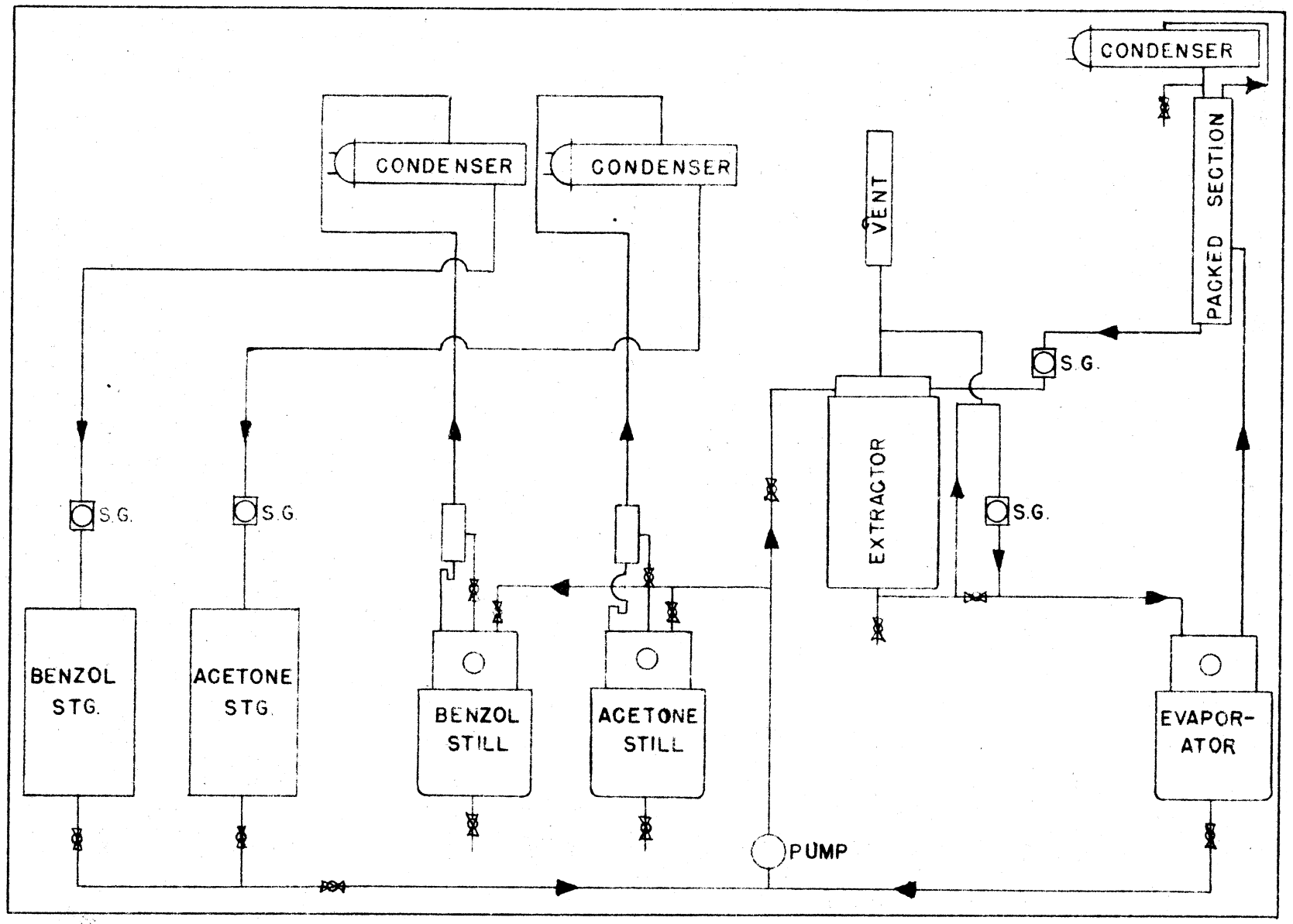
After completion of the first 18 extractions the extraction system was altered to permit determination of the effect of varying conditions such as rate of flow, temperature, and pressure, and to provide upward flow of solvent through the extractor. The solvent was pumped to the extractor by means of a small gear pump instead of flowing by gravity from the condensers. The jacketed extractor was replaced by an extraction cell of the type used in the eight cell pilot plant battery, details of which are shown in Figure 11. It was constructed of a 54" length of 12" pipe with a 12" welding neck flange at the top and a 12" welding cap at the bottom. A side access 6" x 12' was provided near the bottom of the extractor for discharging. Cover plates for the top and side openings were bolted, and made solvent and vapor tight by gasketing with vegetable fiber sheet material (Pac-Oil) coated with a starch-glycerine sealing compound. In this welded extraction cell pressures above atmospheric and correspondingly higher temperatures could be used. The entire extractor, with the exception of the cover plates, was insulated with a 2" layer of 85% magnesia.

To provide for either upward or downward flow of solvent filters were used at both top and bottom of this extractor. The top filter frame was 15" x 10", covered with a cotton filter cloth, and was inserted vertically in the extractor. By means of a pipe connection through the extractor to this filter, either solvent could be pumped through the filter to the goldenrod material for top feed, or the extract could pass through the filter into the pipe outlet when bottom feed was used. The bottom filter frame was circular and was covered with a cotton filter cloth. This frame rested horizontally across the bottom of the extractor, and was held in position by means of a tightly fitted ring which was set directly on top of the filter. Valves were provided so that the solvents could be pumped either upward or downward through the material in the extractor. Solvent inlet pipes were jacketed near the inlet in either case for steam heating of entering solvents.

II- FIGURE 10

FLOW CHART

SINGLE CELL EXTRACTION SYSTEM

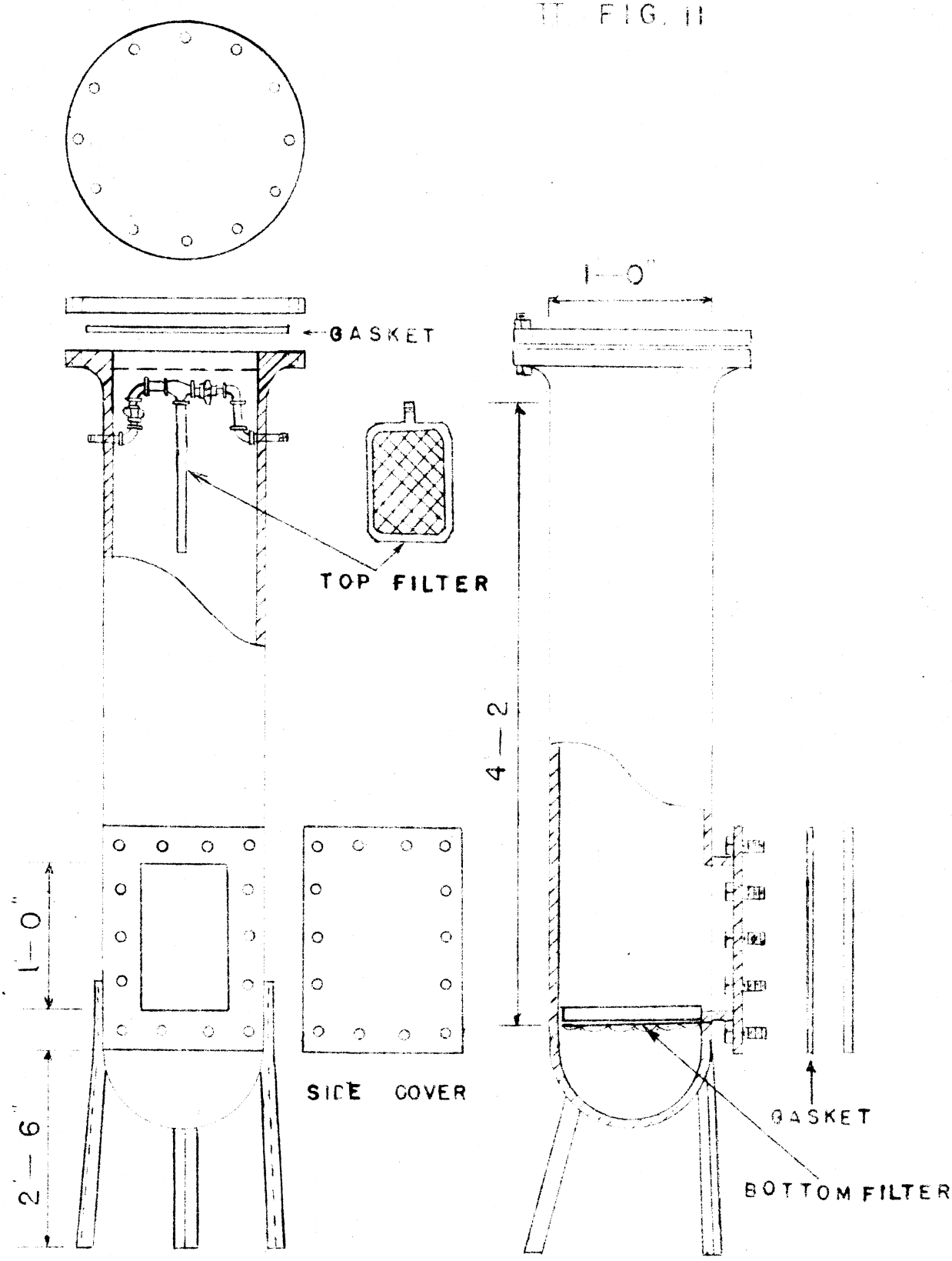


II. Fig. 10A. General view of jacketed single cell extractor and auxiliaries, as used in the pilot plant for producing larger amounts of rubber by the laboratory procedure, and for preliminary large-scale experiments. (Refer to Fig. 10.)

TOP COVER

EXTRACTION CELL

FIG. 11



The acetone and benzol stills were operated continuously during both the acetone and benzol extractions. The jacketed extractor previously used was converted into an evaporator and was connected to a condenser similar to those used with the stills. This evaporator was used for preliminary concentration of both acetone and benzol miscella, and could be connected for discharge to either the acetone or benzol recovery and final concentration stills.

The resins and benzol extract obtained from the stills were handled in the same manner as for the earlier experiments. The smaller evaporator used in the earlier experiments was used as a vented receiver for the solvent returning from the condensers, from which either acetone or benzol was pumped for recirculation. The rearranged system had an evaporative capacity of 60 gallons per hour of acetone, and about 50 gallons per hour for benzol.

For each of the 17 experiments carried out in this rearranged extraction system, the stages of operation were: (1) continuous acetone extraction; (2) acetone draining period for one hour; (3) continuous benzol extraction; (4) benzol draining period for one hour; and (5) steaming out for five hours to recover benzol remaining in the residue.

Results of all of the single cell extraction experiments are summarized in Tables VIII to XVII, inclusive, in which they are grouped according to the numerous variations of the procedure which were studied. The principal factors varied were temperature, rate of solvent flow, total time of extraction, and upward as compared to downward flow through the material. All of the goldenrod used was hand-stripped, dried leaf material containing a negligible amount of stems or blooms, which was shipped from Savannah in moisture-proof paper sacks for grinding at the Southern Regional Research Laboratory. It was all from the 1942 crop except a small quantity of 1941 material used in experiments 1, 2, 15, and 16. Consideration was given to the differences in rubber content and quality of leaf material of different selections and from different fields in selecting lots for use in the various series of experiments.

Experiments listed in Table VIII. Experiments 1 and 2 were preliminary extractions performed chiefly to obtain several pounds of goldenrod rubber. Experiment 3 was the first continuous extraction made with finely ground goldenrod leaves. The acetone and benzol extractions were each conducted over a long period of continuous operation. The goldenrod leaves used for this experiment were considered to be of a very good grade.

Experiments listed in Table IX. These experiments were made with the same lot of goldenrod leaves, and the same rate of acetone and benzol was used for each extraction. However, the effect of fine grinding (Exp. 4) versus coarse grinding (Exps. 5-8) and of variations in extraction temperature and time are indicated in the results given in the table.

For both the acetone and benzol extractions, experiments 6 and 7, rate studies of completeness of extraction versus time were made and are

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plotted in the form of curves in Figure 12 for Experiment 6 and Figure 13 for Experiment 7.

Experiments listed in Table X. These experiments, 9, 10, and 11, were each made from the same lot of goldenrod material. In addition the conditions for extractions; namely, the rate, temperature, and extraction time, were practically identical for all three experiments, to determine consistency and reproducibility of results.

Experiments listed in Table XI. The material for these experiments was taken from different lots of goldenrod leaves. For these experiments, the acetone extraction time was considerably longer than for experiments in the preceding table. The benzol extraction time for Exp. 12 was one-half as long as for 13 and 14. For all these experiments the material was coarsely ground. In fact the ground material for Exp. 13 was somewhat coarser than for the other two. Benzol extract from Exp. 13 was divided into three fractions and tested separately to evaluate the rubber from each fraction. The first fraction was the extract from the first three hours of extraction, second fraction, extract from next three hours, and third fraction contained the extract from the last eighteen hours.

Experiments listed in Table XII. Although the original material for these two experiments was from the same lot, the leaves for Exp. 15 were given an acid treatment, and the leaves for Exp. 16 were given an alkaline treatment before extractions.

For experiment 15, 113 pounds of goldenrod leaves were divided equally into two batches. Each batch was cooked together with 45-1/2 gallons of water for three hours. The pH was maintained at approximately 4.4 by the addition of small amounts of sulfuric acid. Cooking was done by means of steam introduced directly into the suspension of solids. At the end of three hours the water was drained off through a 120 mesh screen, and the leaves were washed three times, rescreening each time. The wet leaves were dried in a tray drier for 24 hours at a temperature of 130° to 134° F. By means of this procedure the original 113 pounds were reduced 39.6% in weight. The dried leaves were ground in a knife type mill.

For experiment 16, 87 pounds of goldenrod leaves were divided equally into two batches. Each batch was cooked separately with 35 gallons of 1/2% sodium hydroxide solution for three hours by means of direct steam. Then the solution was drained off through a 120 mesh screen. Approximately 35 gallons of water were added to the drained leaves, and the mixture was brought to a boil and once again drained. A second 35 gallons were added and drained as before. A third 35 gallons were added and 10 cc. of concentrated sulfuric acid were poured into the mixture. This solution was drained off and a fourth 35 gallons of wash water added, boiled, and drained. Then the wet leaves were placed in the tray drier for 24 hours at a temperature of 130 to 135° F. By means of this procedure the original 87 pounds was reduced 47.5% in weight.

Analytical determinations on the original material gave 18.5% acetone extract and 3.3% benzol extract, while on the acid treated leaves the values were 15.8% acetone extract, 5.05% benzol extract, and on caustic treated leaves 15.7% acetone extract and 7.13% benzol extract. For these two experiments the extraction time, rate, temperature, and fineness of grinding was practically the same. For the acetone extraction of Exp. 16, and for the benzol extraction of Exps. 15 and 16 studies of rate of extraction versus time were made and were plotted in the form of a curve. The curves are illustrated in Figure 14 for the acetone extraction of Exp. 16, and in Figure 15 for the benzol extraction of Exps. 15 and 16.

Experiments listed in Table XIII. This table contains the results of Exps. 17 through 20. Since the first 18 extractions were made in the original single cell extraction system and the last 17 experiments were made in the rearranged system, the table contains two complete experiments for each system. Experiments 17, 18, and 19 were all made from the same lot of material which was considered to be a good selection of leaves, while Experiment 20 was made from a lot of material somewhat inferior when compared to that used for the other experiments in this group. For all four experiments the goldenrod leaves were given a coarse grinding. Experiments 17 and 18 were made with relatively long acetone and benzol extraction of the same duration for both experiments. One percent para amino phenol was added to the rubber product as an antioxidant, instead of 0.5% of Flectol H. The rates and temperatures of extraction were identical for both experiments. The only difference between these two runs was that relatively pure acetone was used for the acetone extraction of Experiment 18, while the solvent used for the acetone extraction of Experiment 17 contained 25% benzol. In this way some of the lower molecular weight rubber was fractionated out, and the yield was consequently lower.

The conditions for Experiment 19 were irregular due to filter trouble within the extractor. However, the material was given a relatively long acetone and benzol extraction, and satisfactory results were obtained.

For extraction 20, the rate of solvent flow through the charge was greatly increased. In the jacketed extractor, used for previous experiments, the rate of flow of solvent was 15 gallons per hour, while in the new unit the rate was increased to 120 gallons per hour, however, approximately 75% of the 120 gallons was recirculated extract and only 30 gallons was fresh pure solvent.

Experiments listed in Table XIV. For these experiments a composite batch of leaves was used, since these experiments were conducted to study various factors which might affect the rate and completeness of extraction, and the final quality of the goldenrod rubber. All five runs had the same number of hours of acetone and benzol extraction. Experiment 21 was made with normal extraction temperature and pressure as used in the preceding experiments. Experiments 22 and 23 were runs in which the solvent action was that obtained in soxhlet type extraction. Of the 20 gallons of solvent pumped into the charged extractor, 10 gallons were drained off after 25 to 35 minutes of standing in

over

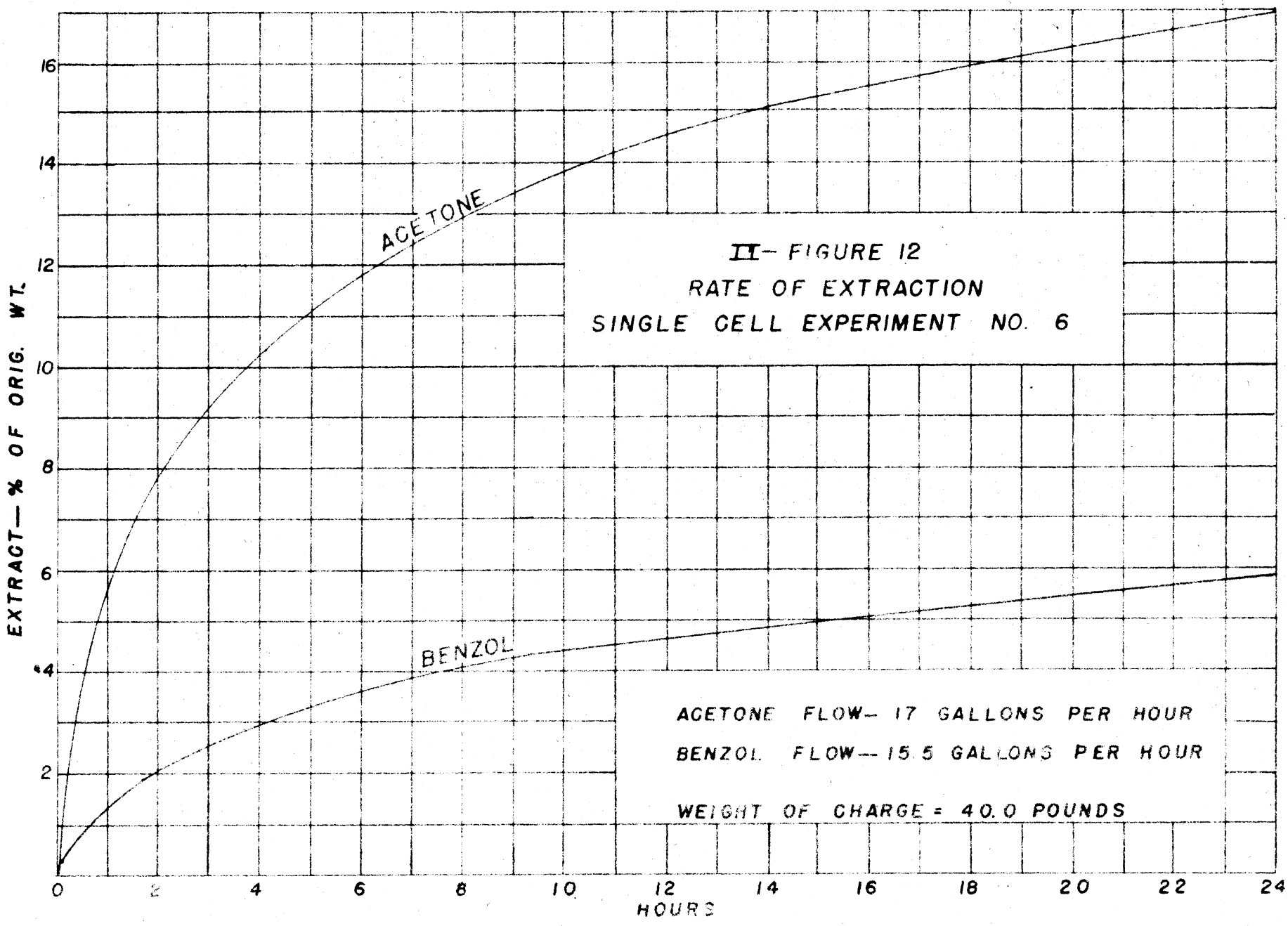
contact with leaves at 110° to 115° F. A complete cycle required approximately one hour, and after 24 cycles the extraction was discontinued. In Experiment 24 the acetone was maintained at a temperature of approximately 150° F. (16 lb. gauge) and the benzol temperature at 170° F. (25 lb. gauge) instead of the usual temperatures 10°-15° F. below the boiling points of the solvents. For Experiments 21 and 24, the flow to the extractor was 120 gallons per hour, 75 gallons of recirculated extract and 30 gallons of pure solvent. In Experiment 28, a higher temperature was used during acetone extraction, but during the benzol extraction the temperature was maintained at 10° to 15° F. below boiling point. However, for this extraction the solvent was pumped into the bottom and the extract removed from the top outlet of the extractor. This procedure was the reverse of the solvent flow used for the other experiments in this group. The rate of flow was 60 gallons per hour for the acetone extraction, and 50 gallons per hour for the benzol extraction.

Experiments listed in Table XV. For each of the experiments in this group the material for extraction was taken from separate lots of goldenrod leaf material, and all were given a rather coarse grinding. Similar to experiments in the preceding tables, these experiments were conducted to determine the effect of increased temperature and pressure during acetone and benzol extraction, upon the completeness of extraction. For Experiments 26 and 27 the acetone extraction was for 36 hours while the extraction time was somewhat shorter for the other two runs. The benzol extraction time was not less than the equivalent of 24 hours of continuous extraction for all four runs. In Experiments 25, 26, and 27, the solvent entered the extractor at the top while in Experiment 29 the solvent entered at the bottom. For Experiment 25 the flow to the extractor was 120 gallons per hour (90 gallons recirculated extract and 30 gallons pure solvent). In Experiments 26, 27, and 29, the acetone was pumped at 60 gallons per hour and the benzol at 50 gallons per hour.

In the product of Experiment 25, 0.5% of JZF was added as an antioxidant instead of the usual 0.5% Flectol H.

Experiments listed in Table XVI. The same lot of material was used for these two runs. The extraction procedure, the temperature, rate of extraction, and hours of continuous acetone and benzol extraction were practically identical for both of these extractions. The essential difference was that for Experiment 29 the material was coarsely ground, and for Experiment 30 the material was finely ground.

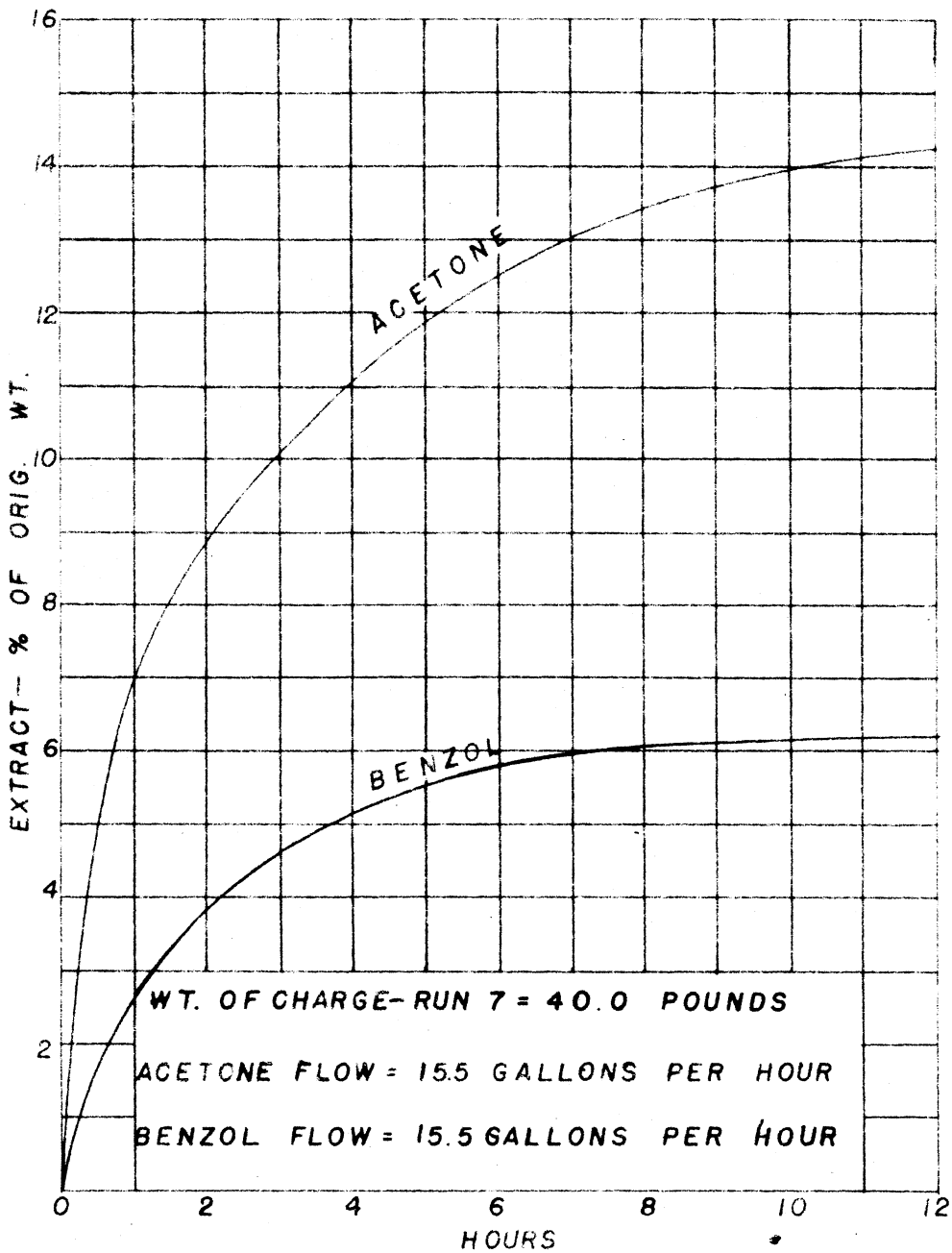
Experiments listed in Table XVII. Extractions were made with the same lot of material for experiments 32 and 33, while different lots were used for Experiments 34 and 35. All the material for these four runs was ground in a hammer mill and the grinding was comparatively finer than that for most of the preceding experiments. Extraction procedure, temperature, rate, and time were essentially the same for all four experiments, and the chief factor studied in this group was the effect of fineness of grinding upon completeness of extraction.


II- FIGURE 12
RATE OF EXTRACTION
SINGLE CELL EXPERIMENT NO. 6
ACETONE
BENZOL
ACETONE FLOW- 17 GALLONS PER HOUR
BENZOL FLOW-- 15.5 GALLONS PER HOUR
WEIGHT OF CHARGE = 40.0 POUNDS
EXTRACT— % OF ORIG. WT.
HOURS
0
2
4
6
8
10
12
14
16
18
20
22
24

II- FIGURE 13

RATE OF EXTRACTION

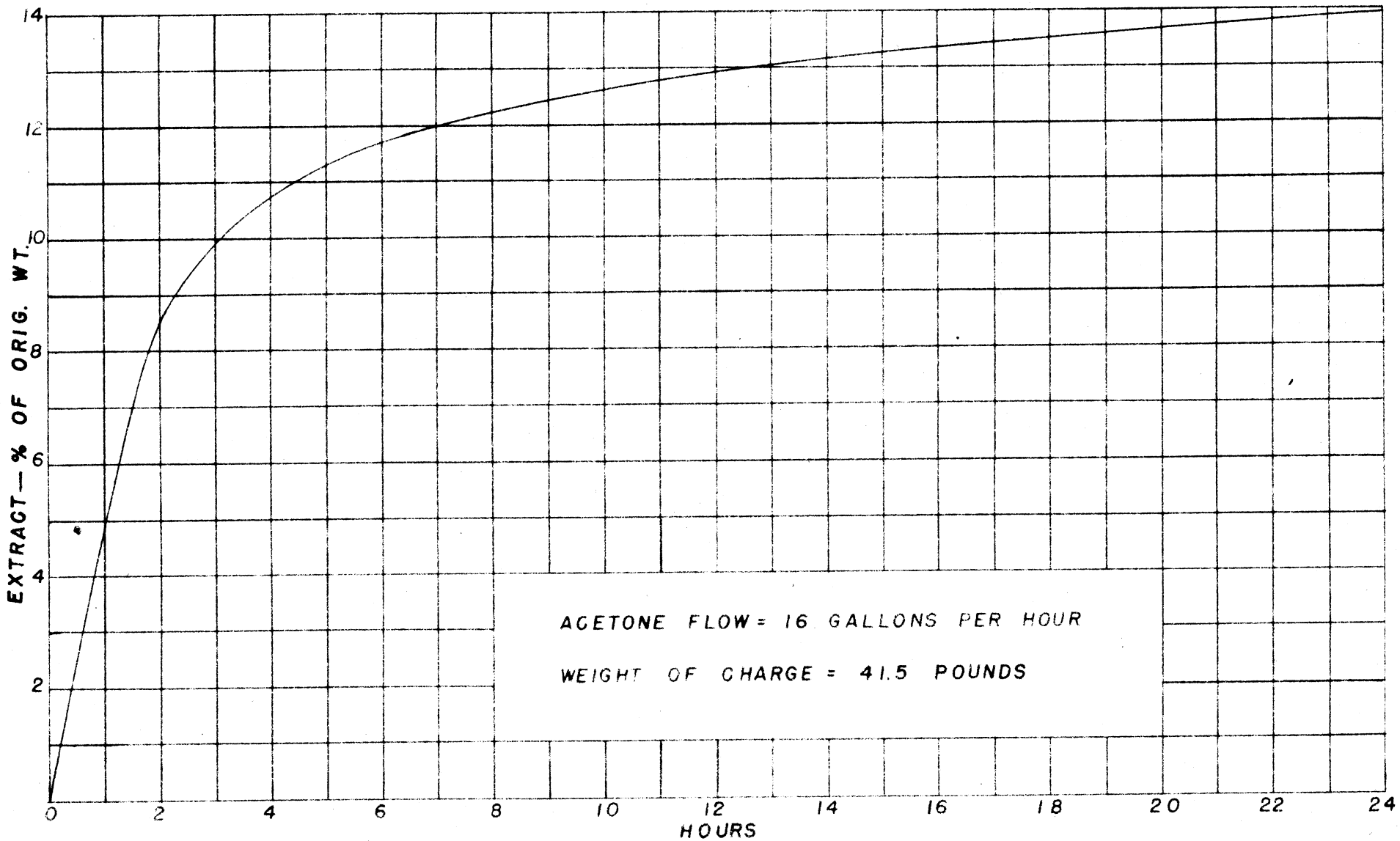
SINGLE CELL EXPERIMENT NO. 7



II— FIGURE 14

RATE OF ACETONE EXTRACTION

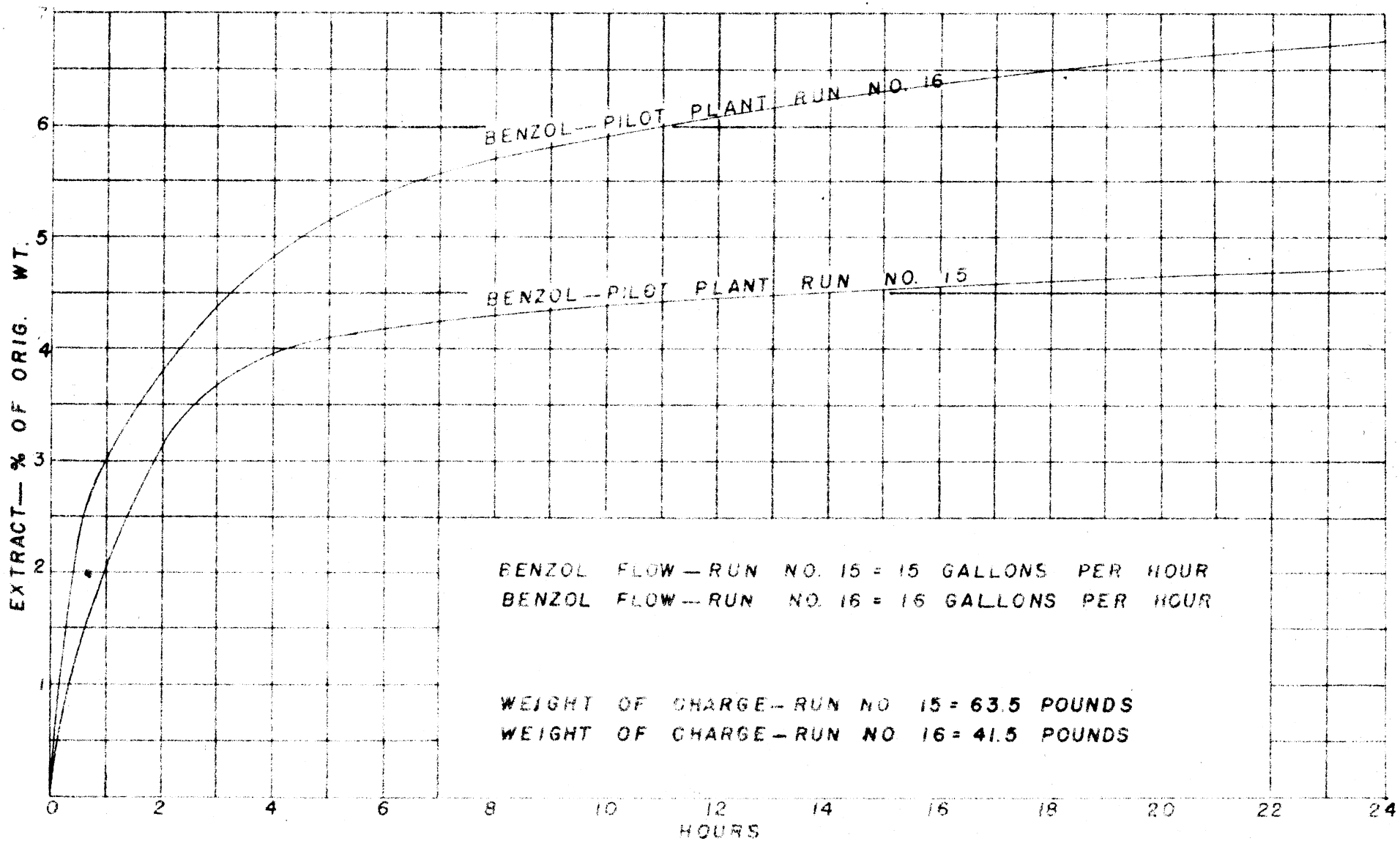
SINGLE CELL EXTRACTION EXPERIMENT NO. 16



II—FIGURE 15

RATE OF BENZOL EXTRACTION

SINGLE CELL EXTRACTION EXPERIMENTS—NOS. 15 & 16



For vulcanization and testing of the goldenrod rubber from all 35 experiments, representative samples of the crude benzol extract and also the acetone precipitated material were precured in pot stills one to six hours with the following chemicals added in solution:

Rubber	100.0 parts
Zinc Stearate	5.5
Thiotax	1.0
Flectol H	1.0
Sulfur	3.5

In both cases a sufficient sample was taken to produce approximately 50 gms. material into which 5.5 parts Zinc Oxide were then milled on cold rolls. In all cases, except where p-aminophenol or JZF were substituted, the material produced in the pilot plant contained 0.5% Flectol H, based on rubber.

over

II-TABLE VIII

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
1	Knife cutter	30 mesh	-	-	-	-	-	-	67.2	-
2	" "	30 "	-	-	-	-	-	-	65.7	8.57
3	" "	1/16 & 1/32	-	-	-	-	80.6	100.0	77.8	6.68

	ACETONE EXTRACTION: Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F	Press. #'s/sq.in.	BENZOL EXTRACTION: Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
1	At top	-	15	120	None	At top	-	12	140	None	-
2	" "	-	15	120	"	" "	-	12	150	"	Flectol H
3	" "	38	15	120	"	" "	28	12	150	"	" "

	SINGLE CELL EXTRACTION RESULTS: Acetone Resins Lbs.	Acetone Resins %	Vol. Ext. Gals.	Tot. Sld. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Rubber #'s Resin-free	Yield % *	RAW MATERIAL: Analytical Ext. Acetone % *	Analytical Ext. Benzol % *	Efficiency of Extraction
1	12.9	19.2	-	-	-	2.84	-	4.22N	20.1	5.42	-
2	13.0	19.8	2.08	.1740	-	3.01	-	4.58N	18.35	4.41	-
3	11.8	15.2	3.86	.1415	5.0T	4.568	4.34	5.59	15.43	5.82	95.9

	OPTIMUM VULCANIZATION AND TESTING DATA: Crude Benzol Extract Titr. c.c.	Vis. c.p.	Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Acetone Precipitated Resins %	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %
1	-	-	-	-	-	-	-	-	-	-	-
2	5.30	-	-	-	-	-	-	-	-	-	-
3	-	-	30	260	2060	775	-	-	-	-	-

*-Percent based on total weight.
N-Yield based on weight of crude rubber (%).
T-Estimated resins.

II-TABLE IX

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Weight of Charge # Total	% Moisture
4	Knife cutter	1/16 & 1/32	-	17.1	22.6	44.6	91.3	100.0	84.3	7.22
5	" "	1/16	-	6.8	9.2	17.9	43.2	98.8	80.5	7.22
6	" "	1/16	-	6.8	9.2	17.9	43.2	98.8	40.0	7.22
7	" "	1/16	-	6.8	9.2	17.9	43.2	98.8	40.0	7.22
8	" "	1/16	-	6.8	9.2	17.9	43.2	98.8	74.0	7.22

Exp. No.	ACETONE EXTRACTION Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F	Press. #'s/sq.in.	BENZOL EXTRACTION Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F	Press. #'s/sq.in.	Anti-oxidant
4	At top	35	15	120	None	At top	26	12	160	None	Flectol H
5	" "	32	16	122	None	" "	26	15	155	None	" "
6	" "	24	17	120	None	" "	24	14.5	140	None	" "
7	" "	12	15.5	128	None	" "	12	15.5	140	None	" "
8	" "	14	21	130	None	" "	12	12	135	None	" "

Exp. No.	SINGLE CELL EXTRACTION RESULTS Acetone Resins Lbs.	Acetone Resins %	Vol. Ext. Gals.	Tot. Solids Gms/c.c.	Benzol Resins % *	Rubber # Crude	Rubber # Resin-free	Yield % *	RAW MATERIAL Analytical Ext. Acetone % *	Benzol % *	Efficiency of Extraction
4	13.8	16.4	5.00	.1424	5.3	5.95	5.62	6.67	14.3	5.86	114.0
5	13.0	16.2	2.46	.2205	6.0T	4.55	4.28	5.32	14.3	5.86	90.8
6	6.8	17.0	1.92	.1295	6.7	2.07	1.93	4.825	14.3	5.86	82.5
7	6.0	15.0	1.82	.1375	15.8	2.09	1.76	4.40	14.3	5.86	75.1
8	13.0	17.6	3.73	.1090	13.4	3.56	3.08	4.17	14.3	5.86	71.5

Exp. No.	Crude Benzol Extract Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Acetone Precipitated Resins %	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %
4	4.30	-	30	260	1950	750	-	40	260	1780	750
5	4.30	-	-	-	-	-	-	-	-	-	-
6	4.35	-	45	260	1540	735	-	75	260	1780	785
7	4.25	-	75	260	840	800	-	105	260	1920	735
8	4.30	-	135	260	1000	750	-	60	260	1790	800

*-Percent based on total weight. T-Estimated resins.

II-TABLE X

Exp. No.	Mill: Type of Mill	Mill: Screen	Mill: Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH: 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
9	Knife cutter	1/16	-	7.6	11.2	20.7	52.0	97.3	80.0	8.15
10	" "	1/16	-	7.6	11.2	20.7	52.0	97.3	73.0	8.15
11	" "	1/16	-	7.6	11.2	20.7	52.0	97.3	74.5	8.15

	ACETONE EXTRACTION: Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	BENZOL EXTRACTION: Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
9	At top	28	20	120	None	At top	24	15	135	None	Flectol H
10	" "	24	20	125	"	" "	24	16	135	"	" "
11	" "	24	22	100	"	" "	24	18	135	"	" "

	SINGLE CELL EXTRACTION RESULTS: Acetone Resins Lbs.	Acetone Resins %	Benzol Vol. Ext. Gals.	Benzol Tot. Slds. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Rubber #'s Resin-free	Yield % *	RAW MATERIAL Analytical Ext.: Acetone % *	Benzol % *	Efficiency of Extraction
9	15.0	18.8	3.29	.1360	12.0	3.73	3.28	4.10	15.8	5.89	69.7
10	14.0	19.2	3.84	.1127	11.2	3.61	3.21	4.40	15.8	5.89	74.8
11	12.3	16.5	3.52	.1090	11.5	3.189	2.82	3.79	15.8	5.89	64.5

	Crude Benzol Extract: Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA: Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Resins %	Acetone Precipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %
9	4.30	.689	90	260	1010	790	-	75	260	2010	725
10	4.25	.692	30	260	1650	715	-	90	260	1490	700
11	4.40	.698	75	260	1110	750	-	120	260	1620	735

*-Percent based on total weight.

II-TABLE XI

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
12	Knife Cutter	1/16	-	8.5	12.0	22.4	56.8	98.2	71.5	8.93
14	" "	1/16	27.8	5.5	8.8	18.0	52.0	98.8	71.5	9.35
13	" "	1/16	-	3.2	4.8	10.4	38.2	96.2	74.0	8.31

	ACETONE EXTRACTION					BENZOL EXTRACTION					
	Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
12	At top	30	16	125	None	At top	12	15	140	None	Flectol H
14	" "	36	15	130	"	" "	24	15	150	"	" "
13	" "	36	15	130	"	" "	24	15	145	"	" "

	SINGLE CELL EXTRACTION RESULTS									RAW MATERIAL		
	Acetone		Benzol							Analytical Ext.		Efficiency of Extraction
	Resins Lbs.	Resins %	Vol. Ext. Gals.	Tot. Slds. Gms/cc.	Resins % *	Rubber #'s Crude	Rubber #'s Resin-free	Yield % *		Acetone % *	Benzol % *	
12	12.5	17.5	3.09	.1260	6.80	3.24	3.06	4.28		15.5	5.85	73.3
14	12.0	16.8	2.87	.1260	12.55	3.01	2.63	3.68		17.73	5.04	73.0
13A	12.6	17.0	1.06	.1810	6.25	1.605	1.500	)				
B			.31	.1760	22.20	.455	.354	)3.38		14.5	5.39	62.7
C			1.09	.0782	25.20	.856	.642	)				

	Crude Benzol Extract		OPTIMUM VULCANIZATION AND TESTING DATA								
			Unprecipitated				Acetone Precipitated				
	Titr. c.c.	Vis. c.p.	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Resins %	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %
12	4.50	.697	45	260	1665	750	-	75	260	1800	765
14	4.35	.692	60	260	1415	750	-	60	260	1845	735
13A	4.35	.765	45	260	1660	775	-	60	260	1795	750
B	4.45	.695	45	260	1215	690	-	60	260	1720	810
C	4.55	.655	45	260	380	540	-	60	260	1295	660

*-Percent based on total weight.

II-TABLE XII

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
15	Knife cutter	1/16	20.7	1.7	7.2	17.3	51.5	98.8	63.5	9.46
16	" "	1/16	19.8	3.8	7.5	17.0	52.2	96.5	41.5	9.49

Exp. No.	ACETONE EXTRACTION Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	BENZOL EXTRACTION Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
15	At top	24	16	126	None	At top	24	15	146	None	Flectol H
16	" "	24	16	127	"	" "	24	16	150	"	" "

Exp. No.	SINGLE CELL EXTRACTION RESULTS Acetone Resins Lbs.	Acetone Resins %	Benzol Vol. Ext. Gals.	Benzol Tot. Slds. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Benzol Rubber #'s Resin-free	Benzol Yield % *	RAW MATERIAL Analytical Ext. Acetone % *	RAW MATERIAL Analytical Ext. Benzol % *	Efficiency of Extraction
15	10.5	16.6	1.29	.2520	17.75	2.72	2.24	3.53	15.8	5.05	70.0
16	6.65	16.2	1.41	.1864	19.05	2.20	1.78	4.29	15.7	7.13	60.2

Exp. No.	Crude Benzol Extract Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Resins %	Acetone Precipitated Time Mins.	Temp. °F.	Tensile #/sq. in.	Elongation %
15	4.75	.663	75	260	510	700	-	45	260	885	655
16	5.00	.648	45	260	570	685	-	45	260	785	710

*-Percent based on total weight.

II-TABLE XIII

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
17	Knife cutter	1/16	27.2	4.8	7.5	14.8	43.9	96.8	72.0	7.07
18	" "	1/16	27.2	4.8	7.5	14.8	43.9	96.8	72.0	7.07
19	" "	1/16	27.2	4.8	7.5	14.8	43.9	96.8	67.0	7.07
20	" "	1/16	24.9	5.4	7.3	13.1	36.2	94.2	66.0	9.55

Exp. No.	ACETONE EXTRACTION Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq. in.	BENZOL EXTRACTION Solv. in Extractor	Time Hrs.	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
17	At top	35	16	128	None	At top	24	14.5	150	None	P. A. P.
18	" "	35	15	127	"	" "	24	14	140	"	" " "
19	" "	-	-	-	"	" "	-	-	-	"	Flectol H
20	" "	24	T 30S-90E	122	1.5	" "	24	T 30S-90E	140	1.5	" "

Exp. No.	SINGLE CELL EXTRACTION RESULTS Acetone Resins Lbs.	Acetone Resins %	Benzol Vol. Ext. Gals.	Benzol Tot. Slds. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Benzol Rubber #'s Resin-free	Benzol Yield % *	RAW MATERIAL Analytical Ext. Acetone % *	Analytical Ext. Benzol % *	Efficiency of Extraction
17	11.0	15.3	2.76	.0905	9.12	2.08	1.89	2.63	14.8	4.83	54.5
18	10.5	14.6	3.11	.1030	7.10	2.69	2.50	3.50	14.8	4.83	72.5
19	10.5	15.7	4.27	.0743	8.20	2.65	2.43	3.63	14.8	4.83	75.2
20	9.25	14.0	2.35	.0714	26.50	1.40	1.03	1.56	13.4	2.79	55.8

Exp. No.	Crude Benzol Extract Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Acetone Precipitated Resins %	Time Mins.	Temp. °F.	Tensile #/sq. in.	Elongation %
17	4.40	.722	30	260	2355	750	-	30	260	2605	750
18	4.45	.692	30	260	1985	725	1.1	30	260	2130	750
19	4.35	.698	45	260	1640	700	0.9	60	260	1995	765
20	4.60	.663	90	260	1310	700	1.7	15	260	1780	735

*-Percent based on total weight. T 30S-90E = 30 gallons solvent, 90 gallons extract.

II-TABLE XIV

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
21	Knife cutter	1/16	22.5	5.2	7.0	12.7	35.5	93.8	60.0	9.73
22	" "	1/16	22.8	5.8	7.6	13.4	36.4	93.8	62.5	10.15
23	" "	1/16	22.7	4.9	6.6	11.9	34.8	93.7	63.5	9.83
24	" "	1/16	22.4	5.6	7.4	12.8	35.3	93.8	60.0	6.48
28	" "	1/16	22.4	5.0	6.4	11.5	33.8	93.7	60.0	9.79

Exp. No.	ACETONE EXTRACTION Solv. in Extractor	Time Hrs.	Rate Gals./Hr.	Temp. °F.	Press. #'s/sq.in.	BENZOL EXTRACTION Solv. in Extractor	Time Hrs.	Rate Gals./Hr.	Temp. °F.	Press. #'s/sq. in.	Anti-oxidant
21	At top	24	30S-90E T	122	2.0	At top	24	30S-90E T	148	2.0	Flectol H
22	" "	24	1 Hr.-C.	110	1.5	" "	24	1 Hr.-C.	115	1.5	" "
23	" "	24	1 Hr.-C.	105	1.5	" "	24	1 Hr.-C.	110	1.5	" "
24	" "	24	30S-90E T	150	16.0	" "	24	30S-90E T	170	25.0	" "
28	" Bottom	24	60	154	23.0	At Bottom	22	50	158	1.5	" "

Exp. No.	SINGLE CELL EXTRACTION RESULTS Acetone Resins Lbs.	Acetone Resins %	Benzol Vol. Ext. Gals.	Benzol Tot. Slds. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Benzol Rubber #'s Resin-free	Benzol Yield % *	RAW MATERIAL Analytical Ext. Acetone % *	Benzol % *	Efficiency of Extraction
21	8.50	14.2	1.59	.1060	26.1	1.40	1.03	1.72	13.1	2.87	60.1
22	8.40	13.5	1.85	.0746	27.0	1.15	0.84	1.34	13.75	2.69	49.8
23	8.75	13.8	2.69	.0639	30.8	1.44	0.996	1.57	13.6	2.71	58.0
24	8.65	14.4	2.06	.0862	30.5	1.48	1.03	1.72	13.7	2.67	64.5
28	8.35	13.9	1.85	.0824	15.65	1.27	1.07	1.78	13.3	2.67	66.7

Exp. No.	Crude Benzol Extract Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Acetone Precipitated Resins %	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %
21	4.45	.665	150	260	1250	750	2.8	45	260	1470	700
22	4.60	.652	105	260	1090	715	2.8	30	260	1770	700
23	4.55	.680	90	260	565	650	7.5	30	260	1210	700
24	4.55	.663	60	260	765	725	2.5	30	260	1160	650
28	4.80	.670	45	260	1420	650	2.9	45	260	1270	700

*-Percent based on total weight. C= 1-hour cycle - intermittant solvent drainage.
T= 30S-90E = 30 gallons solvent, 90 gallons extract.

II-TABLE XV

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
25	Knife cutter	1/16	24.1	4.15	5.5	9.9	30.1	93.0	67.5	7.96
26	" "	1/16	27.73	6.42	8.62	16.8	45.5	97.5	70.0	8.56
27	" "	1/16	29.1	8.76	10.4	16.2	39.0	96.5	69.0	8.68
29	" "	1/16	24.3	5.57	7.07	12.64	35.1	93.9	68.0	8.88

Exp. No.	ACETONE EXTRACTION Solv. in Extractor	Time Hours	Rate Gals./Hr.	Temp. °F.	Press. #'s/sq.in.	BENZOL EXTRACTION Solv. in Extractor	Time Hours	Rate Gals./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
25	At top	24	30S-90E T	162	20.5	At top	30	30S-90E T	188	24	JZF
26	" "	36	60	144	23.5	" "	24	50	188	23.5	Flectol H
27	" "	36	60	156	21.5	" "	24	50	148	2	" "
29	At Bottom	19½-3N	60	150	16	At Bottom	22-2N	50	143	6	" "

Exp. No.	SINGLE CELL EXTRACTION RESULTS Acetone Resins Lbs.	Acetone Resins %	Vol. Ext. Gals.	Tot. Slds. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Benzol Rubber #'s Resin-free	Yield % *	RAW MATERIAL Analytical Ext. Acetone % *	Benzol % *	Efficiency of Extraction
25	10.25	15.2	2.72	.1070	23.67	2.43	1.85	2.74	14.31	4.31	63.6
26	10.75	15.4	2.11	.1450	6.85	2.556	2.38	3.40	13.26	5.37	63.2
27	10.2	14.8	1.05	.1965	4.95	1.72	1.635	2.37	10.73	5.06	46.7
29	10.2	15.0	2.59	.1170	14.2	2.53	2.17	3.19	13.7	4.60	69.4

Exp. No.	Crude Benzol Extract Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA UNPRECIPITATED Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	ACETONE PRECIPITATED Resins %	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %
25	4.50	.680	75	260	1820	750	2.2	30	260	2020	750
26	4.45	.703	30	260	1500	775	0.7	45	260	1660	700
27	4.55	.692	15	260	1560	750	1.3	30	260	1420	700
29	4.45	.683	45	260	1550	725	1.5	30	260	1420	700

*-Percent based on total weight. T 30S-90E = 30 gallons solvent; 90 gallons extract.
N=Overnight soaking.

II-TABLE XVI

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
30	Knife cutter	1/16	25.6	5.15	7.06	14.12	39.8	95.2	64.5	8.39
31	" "	1/16& 1/32	35.4	14.7	20.0	28.5	94.5	100.0	70.0	6.91

	ACETONE EXTRACTION					BENZOL EXTRACTION					
	Solv. in Extractor	Time Hours	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Solv. in Extractor	Time Hours	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
30	At Bottom	20-2N	60	136	7	At Bottom	24-4N	50	150	8.5	Flectol H
31	" "	16½-2N	60	124	6	" "	19-2N	50	152	13.5	" "

	SINGLE CELL EXTRACTION RESULTS									RAW MATERIAL		
	Acetone				Benzol					Analytical Ext.		Efficiency of Extraction
	Resins Lbs.	Resins %	Vol. Extr. Gals.	Tot. Slds. Gms/cc.	Resins % *	Rubber #'s Crude	Rubber Resin-free	Yield % *		Acetone % *	Benzol % *	
30	11.75	18.1	2.50	.1390	7.25	2.95	2.73	4.17		17.3	6.46	64.6
31	12.0	17.2	4.46	.1350	3.50	5.03	4.85	6.93		16.3	6.90	100.2

	Crude Benzol Extract		OPTIMUM VULCANIZATION AND TESTING DATA									
			Unprecipitated				Acetone Precipitated					
	Titr. c.c.	Vis. c.p.	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Resins %	Time Mins.	Temp. °F.	Tensile #/sq.in.	Elongation %	
30	4.35	.716	30	260	1210	700	1.4	45	260	1290	700	
31	4.40	.695	30	260	1210	700	0.9	45	260	1290	650	

*-Percent based on total weight.

N= Overnight soaking.

II-TABLE XVII

Exp. No.	Type of Mill	Mill Screen	Density #/cu. ft.	SCREEN ANALYSIS-% PASSED THROUGH 100 Mesh	80 Mesh	60 Mesh	40 Mesh	20 Mesh	Wt. of Charge #'s Total	% Moisture
32	Hammer	1/32	37.5	8.4	8.9	46.1	96.0	99.8	100.0	6.60
33	"	1/32	37.5	8.4	8.9	46.1	96.0	99.8	80.0	6.60
34	"	1/32	33.7	40.7	47.5	72.8	98.8	100.0	90.0	8.92
35	"	1/16	32.6	15.7	19.4	30.7	72.7	99.8	80.0	9.99

Exp. No.	ACETONE EXTRACTION Solv. in Extractor	Time Hours	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	BENZOL EXTRACTION Solv. in Extractor	Time Hours	Rate G./Hr.	Temp. °F.	Press. #'s/sq.in.	Anti-oxidant
32	At Bottom	16-2 N	60	130	9	At Bottom	12-2 N	50	150	9	Flectol H
33	" "	12-2 N	60	132	10	" "	12-2 N	50	145	9	" "
34	" "	16-1 N	60	135	10	" "	16-2 N	50	150	8	" "
35	" "	16-1 N	60	135	10	" "	16-2 N	50	155	11	" "

Exp. No.	SINGLE CELL EXTRACTION RESULTS Acetone Resins Lbs.	Acetone Resins %	Benzol Vol. Ext. Gals.	Benzol Tot. Slds. Gms/cc.	Benzol Resins % *	Benzol Rubber #'s Crude	Benzol Rubber #. Resin-free	Benzol Yield % *	RAW MATERIAL Analytical Ext. Acetone % *	Analytical Ext. Benzol % *	Efficiency of Extraction
32	16.5	16.5	3.91	.1387	14.8	4.53	3.86	3.86	15.8	5.59	68.0
33	13.5	16.9	3.29	.1570	4.3	4.31	4.12	5.15	15.8	5.59	92.3
34	13.9	15.5	3.83	.1370	6.7	4.38	4.09	4.54	14.2	5.65	80.3
35	10.75	13.5	3.30	.0870	16.4	2.40	2.01	2.51	11.3	2.79	90.0

Exp. No.	Crude Benzol Extract Titr. c.c.	Vis. c.p.	OPTIMUM VULCANIZATION AND TESTING DATA Unprecipitated Time Mins.	Temp. °F.	Tensile #/sq.in.	Elong. %	Acetone Precipitated Resins %	Time Mins.	Temp. °F.	Tensile #/sq. in.	Elongation %
32	4.50	.681	45	260	800	750	3.2	45	260	1115	700
33	4.60	.690	45	260	1210	700	1.8	45	260	1300	700
34	4.45	.687	60	260	1460	650	1.8	60	260	1680	675
35	4.45	.682	60	260	1460	675	2.4	45	260	1510	650

*-Percent based on total weight. N= Overnight soaking.

Conclusions: From the results obtained for these 35 single cell experiments it is evident that the most important factor affecting extractability of the resins and rubber was the fineness of grinding of the goldenrod leaf material. Grinding or disintegration of the goldenrod leaf material must be sufficiently extensive to expose all rubber-containing cells to solvent action. The variation of any other operating conditions such as rate and direction of solvent flow, intermittant solvent drainage, elevated temperatures, and longer extraction cycles had considerably less effect on the completeness of extraction. In the order of their effectiveness the variable conditions for extraction can be listed as follows: (1) fineness of grinding; (2) temperature of material in extractor during extraction; (3) time of extraction cycles; (4) rate of solvent flow to extractors.

For the operation of the extraction process on a large scale it was concluded that the following conditions should be adopted: (1) the fineness of grinding should be such that 90% to 95% of the material passes through a 40 mesh screen, and 40% to 50% through a 60 mesh screen; (2) upward flow of solvent through the extractor should be used because it minimizes channelling, packing, and aids in the extraction of finer material since there is less resistance to the movement of the solvent through the extractor; (3) for both the acetone and benzol extractions the temperature of the material during extraction should be held not lower than 10° to 15° F. below the boiling point of the solvent, nor is it necessary to maintain the temperature much higher than the boiling point of the solvents; (4) the rate of solvent to the extractor for both the acetone and benzol extraction should be maintained at the rate of one gallon per hour per pound of material in the extractor; (5) although for some of the experiments conducted continuous acetone extraction for as long as 36 hours was necessary to obtain a very low resin content in the benzol extract, there is sufficient evidence to warrant the use of an acetone extraction period of twelve continuous hours, provided that a very good grade of leaf material is available. For some cases, depending upon the grade of goldenrod material used for extraction, it may be necessary to purify the product by acetone precipitation to reduce the resin content if the material is only acetone extracted for 12 hours; (6) the benzol extraction time should not be longer than 12 continuous hours because extending the benzol extraction time any longer than this period yields very little additional rubber and only increases the percent of resins present in the benzol extract.

Although the lots of goldenrod leaves which were considered to be the better part of the 1942 crop were used for the earlier experiments, there is a possibility that the goldenrod leaves might have undergone some deteriorating changes during storage over several months. A more comprehensive study must be made in the future to determine definitely whether the observed poorer quality of the last batches of rubber produced in these experiments was due to deterioration in storage, or to initially lower grade leaf material available for the later experiments.

The results of microscopic examination of representative samples of residue fairly accurately indicated the percent rubber left in the residue after extraction. In general where the efficiency of extraction was between 90% and 100% no appreciable amount of rubber was detected in the residue, and where poor efficiency of extraction was obtained, microscopic analysis indicated a large quantity of rubber still present in the extracted material. It can be concluded that this method of examining the residue for rubber content is a fairly accurate one for estimating the completeness of extraction of the goldenrod leaf material.

III-PILOT PLANT OPERATIONS

In the pilot plant wing of the Southern Regional Research Laboratory there was available an eight-cell extraction battery previously used for solvent extraction of oil from cottonseed and peanut meal and cake. The individual extractors in this battery were made of 12" diameter steel pipe about five feet high, holding about 100 pounds of cottonseed or peanut meal each.

The design of this extraction battery was based largely upon existing industrial installations extracting rosin, turpentine, and similar materials from pine stumps. The total capacity of all these pine stump extraction plants is about 4500 tons per 24 hours.

During 1942 and for some time later these pine stump extractors were not being operated at full capacity for a number of reasons. A portion of their extensive capacity was therefore considered available for extracting rubber from goldenrod should a suitable solvent process be developed.

Preliminary results from laboratory determinations and single cell extractions showed that the rubber in goldenrod could be satisfactorily extracted and processed to a precured form, easy to handle and suitable for vulcanization. In order to develop the process to a larger scale from the single cell extraction system and to obtain information concerning the suitability of the acetone-benzol extraction process for large-scale plant production, the eight-cell pilot plant extraction battery was redesigned, modified, and operated at the Southern Regional Research Laboratory over a period of seven months. Approximately 850 pounds of goldenrod rubber were produced.

Before discussing the equipment and process used in the pilot plant it should be pointed out that further development of the pilot plant two-solvent extraction process was necessary. Based on the results obtained from the extractions of 1942 leaf material (Section II - Single-Cell Runs 3-35), it was originally decided to start extracting the goldenrod material from 1943 general harvest in the eight-cell extraction battery, using a continuous acetone extraction for 12 hours, followed by a continuous benzol extraction for 12 hours. The result of initial operations, extracting over 12,000 pounds of 1943 goldenrod material, by means of this procedure, was that a yield of rubber, on a resin-free basis, of only 1.36% was obtained; and the average resin content of the benzol rubber solution was 18% to 20%. The weighted average analysis of the 12,000 pounds of material was only 1.87% benzol extract on total weight basis, and hence the overall efficiency of extraction was 73%. Several attempts were made to precure, compound, and vulcanize some of this high resin content rubber, but the resulting product was inferior in quality. Previous laboratory experiments had shown that tensile strength and other properties of the rubber are adversely affected by resin contents in excess of 5%.

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Unfortunately, the bale shipments of 1943 goldenrod material, as well as the two carloads of ground material packed in paper bags shipped from Waynesboro, Georgia, contained very little leaf material. In fact, the average 1943 goldenrod material from General Harvest contained only 20% to 25% leaf material. The rubber is found only in the leaves. The balance, 75% to 80%, was made up of stems, twigs, bloom, and seed. Since the goldenrod material contained only 20% to 25% of leaf material, it is obvious why such a low yield of rubber was obtained. Also the inclusion of the large percentages of stems, seed, stalk, and bloom in the material used for extraction resulted in a resin content of the benzol rubber solution considerably higher than that obtained from pure leaf material extracted under similar conditions the previous year.

The goldenrod material used for the extraction during the early stages of the operation of the eight-cell extraction battery was reprocessed with an air-box type of separator which removed a large percentage of large stems and stalks. The processed material was ground in a hammer mill with 1" hammers, and 1/16" holes in the screen plate.

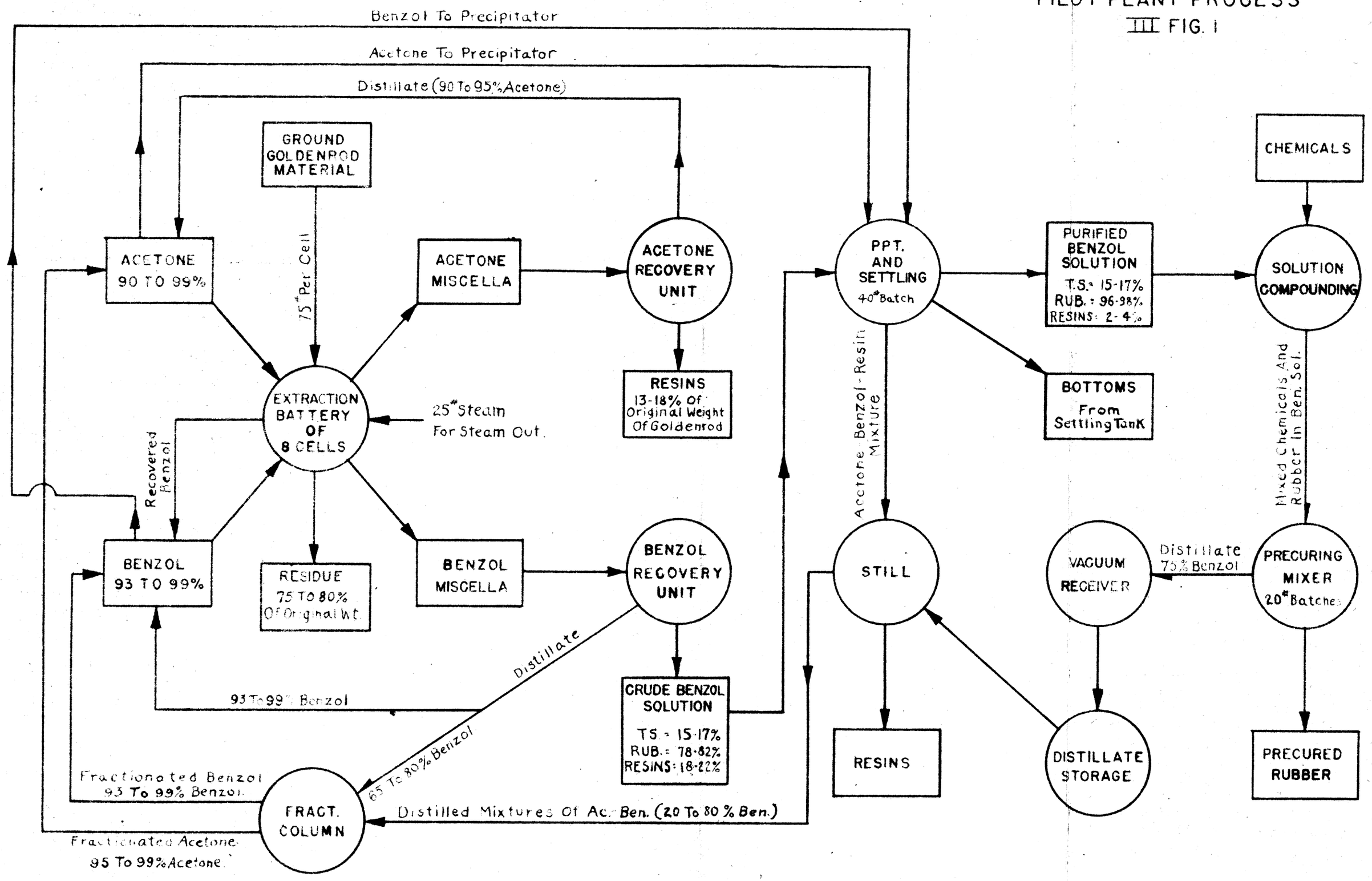
Since all the ground goldenrod material shipped in paper bags from Waynesboro, Georgia, had a rubber content of 1% to 2%, and contained only 20% to 25% leaf material, steps had to be taken to obtain a higher rubber content in the material used for extraction and to reduce the resin content in the concentrated rubber solution. The former was accomplished by the use of a screening procedure developed at the Southern Regional Research Laboratory, and the latter by reducing the resin content in the benzol rubber solution by means of an acetone precipitation.

The screening procedure is described in detail in Section VII. The screening process provided a fraction which was about 42% by weight of the original material, considerably richer in rubber content than the unscreened material. The rubber content of the unscreened material ranged somewhat over 1% while that of the screened fraction was 2.4% to 2.9%. The balance of the processing in the pilot plant, with the exception of such special lots as ensilage and retted, was performed with this screened fraction used as raw material for the extraction process.

The acetone precipitation procedure was developed by laboratory experiments (Section XII), and was adopted as a step in the pilot plant process for reducing the resin content of the benzol rubber solution obtained in the extraction process. This step in the process is fully described and discussed in a later part of this Section.

A simplified flow chart of the pilot plant process used is presented in III-Figure 1. This shows, in schematic form, the flow of goldenrod plant material, acetone and benzol; the methods used in handling acetone and benzol miscellae; the recovery of resins and rubber from the miscellae; the recovery, fractionation, and return of the solvents to the extraction process; the precipitation and purification of the rubber solution; the solution compounding operations; and the final preparation of precured rubber.

SIMPLIFIED FLOW CHART
OF
PILOT PLANT PROCESS
III FIG. 1



Some of the more important data on quantities, concentrations, yields, and sizes of batches are also given. A careful study of the simplified flow chart will be of considerable benefit in comprehending the detailed flow chart, III Figure 2.

In the detailed flow Chart III, Figure 2, an attempt has been made to present as far as possible all of the detailed operations. The arrangement of the chart followed from a desire to have everything on a single page, convenient for binding in the final report.

The interconnecting flow lines show the flow of the solvent used and the extract produced in the process. The chart is not drawn to scale and actually some of the equipment is at an elevation higher or lower than designated on the chart.

FLOW CHART KEY

The following tabulation is a key to the numbers used to designate the equipment shown in the flow chart (III-Fig. 2):

Extraction Battery of Eight Cells
Acetone Recovery and Recirculation Unit

Number	
1 - 8	: Individual extraction units.
9	: Underground tank for storage of large quantities of acetone.
10	: Solvent storage tank for supplying acetone to extractors.
(P-0)	: Motor pump arrangement for draining an extractor at the completion of acetone extraction.
(P-1)	: Motor pump arrangement for delivery of acetone to extractors.
11	: Orifice flow meter for measuring rate of flow of acetone to extractors.
12	: Heat exchanger for automatically controlling temperature of acetone pumped to the extractors.
13	: Surge tank between extractors and stills for acetone miscella.
14	: Acetone evaporator for first stage of concentration of acetone miscella.
15	: Acetone evaporator for second stage of concentration of acetone miscella.
16	: Acetone still for final concentration of acetone extract.
17	: Condenser and after coolers for recovery of acetone from evaporators and still.
18	: Distillate receiver.

Benzol Recovery and Recirculation System

19	: Underground benzol storage tank.
20	: Solvent storage tanks for supplying benzol to extraction system.
(P-2)	: Motor pump arrangement for pumping benzol to extractors.

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21 : Orifice flowmeter for measuring rate of benzol to extractors.
22 : Heat exchanger for automatically controlling temperature of benzol to extractors.
23 : Intermediate storage tank for benzol miscella.
(P-3) : Motor pump arrangement for pumping miscella from intermediate storage tank to surge tank.
24 : Filter.
25 : Surge tank for holding benzol miscella.
26 : Evaporator for first stage of concentration of benzol miscella.
27 : Condenser and after cooler for recovery of benzol distilled from evaporator.
(P-4) : Motor pump arrangement for pumping benzol miscella from evaporator to storage.
28 : Rotometer for measuring rate of flow of miscella from benzol evaporator.
29 : Storage tank for benzol miscella from first evaporator.
30 : Benzol still for final concentration of benzol miscella.
31 : Condenser and after cooler for recovery of benzol still.
32 : Storage tanks for crude concentrated benzol miscella.
33 : Condenser and separator for recovery of benzol from the steaming-out of the extractors.
34 : Sump tank.
35 : Separator used for reclaiming benzol from sump tank.
(P-5) : Motor pump arrangement for draining extractor at end of benzol extraction, and also used for pumping benzol-water mixtures to separator from sump tank.

Precipitation, Settling, and Solvent Recovery Unit

(P-6) : Motor pump arrangement for pumping concentrated benzol miscella to precipitation tank for circulation of crude benzol miscella, and for transferring precipitated and purified rubber solution from settling tanks to storage tanks for the precuring process.
36 : Precipitation tank with motor-driven stirrer.
37 : Acetone-benzol-resins-storage tanks.
(P-7) : Motor pump arrangement for pumping acetone-benzol-resin mixtures from first storage tank to second storage tank .
38 : Still for distilling acetone-benzol mixture from resins.
39 : Condenser for still (38).
40 : Storage tank for distillate from condenser.
41 : Settling tank for precipitated and purified rubber solution.
42 : "Bottoms" storage tank.

Precuring Unit

43 : Storage tank for precipitated and purified rubber solution.
(P-9) : Motor pump arrangement for circulating precipitated and purified rubber solution.
44 : Chemical mixing tank.
45 : Condenser for mixing tank.

46 : Loomis mixer.
47 : Condenser for solvent vapor from Loomis mixer.
48 : Vacuum receiver for distillate.
49 : Distillate storage tank.
(P-8) : Motor pump arrangement for transferring distillate from receiver to storage tank, and for transferring distillate to be redistilled in still (38).

Fractionation Unit

50 : Storage tanks for acetone-benzol mixtures to be fractionated.
51 : No. 1 acetone-benzol fractionation column.
52 : Reboiler for Column No. 1.
53 : Condenser for Column No. 1.
54 : No. 2 acetone-benzol fractionation column.
55 : Reboiler for Column No. 2.
56 : Condenser for Column No. 2.
57 : Cooler for fractionated benzol from reboilers.
(P-10): Feed pump from Column No. 1.
(P-11): Benzol cut (bottoms) pump for Column No. 1.
(P-12): Benzol cut (bottoms) pump for Column No. 2.
(P-13): Feed pump for Column No. 2.

For producing a precured rubber from the ground goldenrod material, the operating steps conducted in the pilot plant system were: (1) the removal of most of the resiniferous conponents in the goldenrod material by means of an acetone extraction; (2) production of a concentrated benzol miscella containing the rubber, together with a high percentage of resiniferous material; (3) precipitation of the rubber from the benzol miscella to reduce its resin content to a minimum; (4) redissolving the purified and precipitated rubber in benzol and processing this rubber solution to a precured form which could be easily vulcanized. In addition, provision was made for fractionating mixtures of acetone-benzol, accumulated during operation of the system, into relatively pure individual components. For performing the above operations, the pilot plant system contained the following units which are clearly indicated on the flow chart given in III-Fig. 2: (1) extraction battery of eight cells; (2) acetone recovery and recirculation unit; (3) benzol recovery and recirculation unit; (4) precipitation, settling, and solvent recovery unit; (5) precuring unit; (6) fractionation unit.

The capacity of the pilot plant system was originally based on the volumetric capacity of the existing battery of eight extractors previously described. Modification of procedure and variation in the composition of the ground material decreased the capacity of the plant from the standpoint of rubber production. However, the pilot plant system as finally operated handled 600 pounds of ground goldenrod plant material per 24 hour day, or 3000 pounds per week of 120 hours.

The entire pilot plant occupied a space measuring 64' long x 25' wide, parts of which were three stories high. Most of the extraction equipment

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was located on the ground floor with the exception of the benzol still and concentrated benzol extract storage tanks which were located on a third floor balcony and a second floor balcony respectively. The majority of the precipitation equipment was located on the second floor balcony with the exception of the settling tank which was on the first floor balcony. The entire precuring unit was located on the ground floor adjacent to the extraction system. A few photographs of the pilot plant are included.

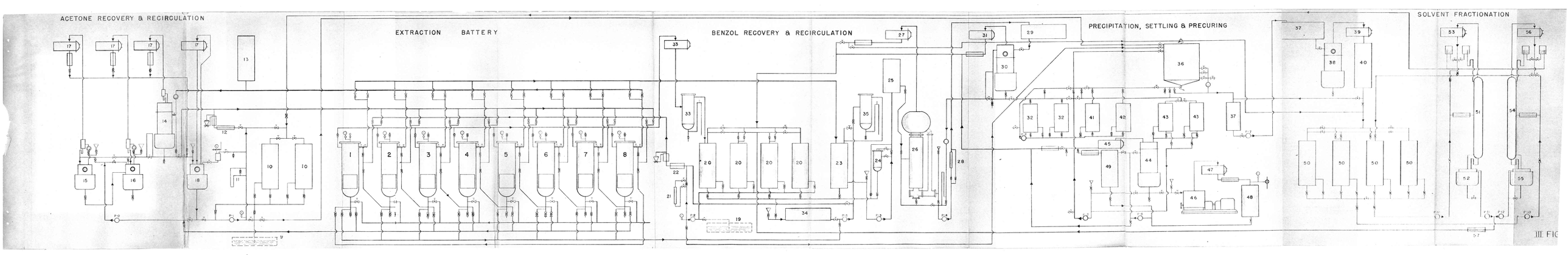
The Extraction Battery of Eight Identical Cells (Flow Charts Nos. 1 through 8). The type of extractor used in the extraction battery is illustrated in Section II, Figure 11. The size, shape, and general dimensions of the extractor are indicated on this drawing. The body of the extractor was made from a section of standard 12" steel pipe. At one end, as a top, was welded a 12" welding neck flange, and at the other end was welded a standard welding cap for a bottom. A side opening with rectangular cover plate was provided for unloading the extractor. Loading was done through the top of the extractor. To facilitate loading and unloading of the extractor, both top and side cover plates were completely removable. These plates were securely fastened to the extractor by means of 3/4" nuts and bolts. A gasket made from 1/8" vegetable fiber gasket material (Pac-oil) was inserted between the flanged face openings and the cover plates. In this way these openings were made vapor tight during extraction.

The solvents flowed upwards through the extractor during the extraction process, and the extractor, at the end of both the acetone and benzol extraction cycles, was drained. Hence provisions were made to prevent any of the ground material from getting out of the extractor. This was accomplished by placing a removable filter at the top and bottom of the extractor. After the completion of every extraction these filters were removed from the extractor, thoroughly cleaned with water and steam, and dried before they were reused.

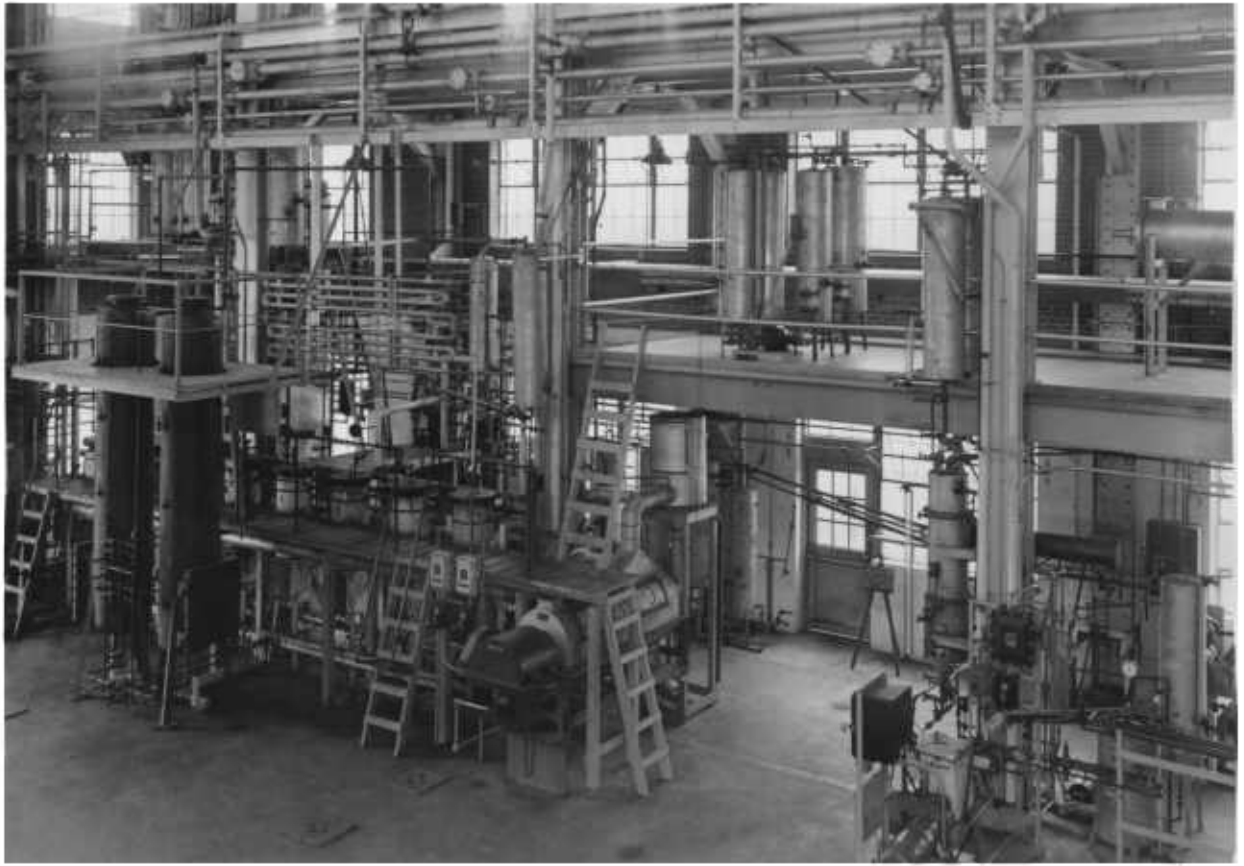
The top and bottom filter arrangements are shown in Section II, Fig. 11. The top filter consisted of an outer frame, measuring 12" x 10", made from 1/2" pipe. Welded on both sides of the frame was 1/2" heavy wire mesh screen. On the inner side of the pipe frame were several 1/4" holes through which the filtered miscella left the extractor. The entire frame was covered with Style 145CH filter cloth made to conform to the shape of the frame. The bottom filter was a circular frame which was cut out of 1/2" heavy wire mesh screen similarly covered. In addition to this filter, cotton was tamped around the inside wall of the extractor and on top of this was inserted a 12" ring which held the whole bottom filter arrangement in place.

Eight such extractors as the one described above composed the battery of extractors used for the goldenrod rubber pilot plant system.

The extractors were arranged in a single row, with their side openings all facing the outer side of the pilot plant system. On the opposite side (called inner side) all valves and manifold lines were

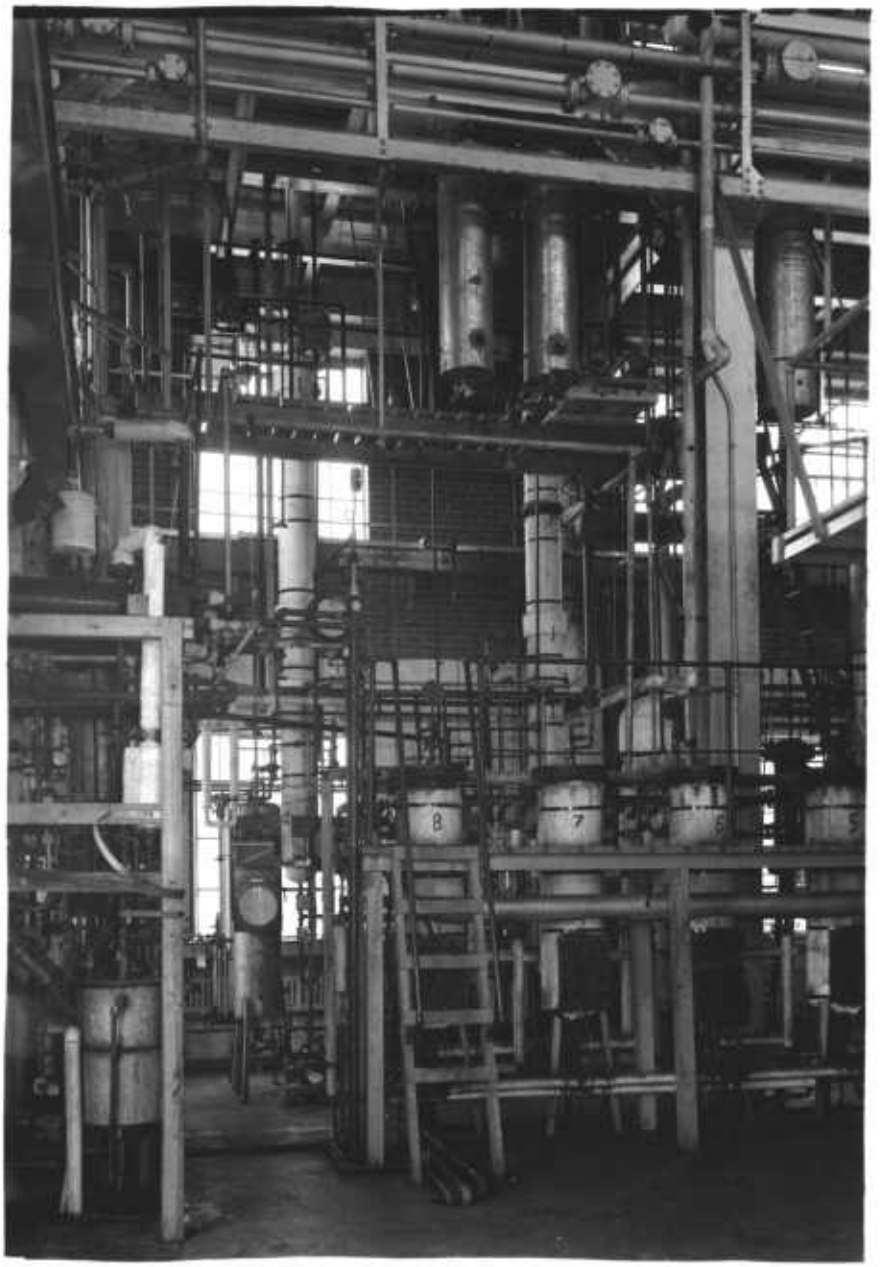

ACETONE RECOVERY & RECIRCULATION
EXTRACTION BATTERY
BENZOL RECOVERY & RECIRCULATION
PRECIPITATION, SETTLING & PRECURING
SOLVENT FRACTIONATION

III FIG



III. Fig. 3. General view of Pilot Plant (except upper floor).

III. Fig. 4. Upper floor of Pilot Plant.
Left - Benzol Still for final concentration of Benzol Miscella.
Center - Precipitation Tank.
Background - Evaporator for distilling acetone-benzol mixtures from resins.



III. Fig. 5. East End of Pilot Plant. Acetone stills at extreme left - fractionation columns in background - extractors 5 to 8 at right.

III. Fig. 6. Chemical Mixing and Precuring Installation.

located. Since the extractors were charged with material through the top, and the residue left after extraction was unloaded through the side opening in the extractor, the outer side was cleared of all equipment which might cause inconvenience in loading and unloading of the extractors. Because the tops of the extractors were seven feet above the floor, a platform 5' 6" high extended the full length of the bank of the extractors along the outer side, for convenience in loading and unloading.

Seven manifold lines extended across the length of the bank of extractors on the inner side, and from top to bottom the order of these lines was as follows: (1) steamed-out benzol line; (2) benzol miscella; (3) acetone miscella; (4) benzol solvent; (5) acetone solvent; (6) acetone drain; (7) benzol drain. Each extractor was connected to all seven manifold lines. All valves, fittings, and interconnecting pipe lines were 3/4" in size and of black iron construction. To and from each extractor, as indicated on the flow chart, necessary pipe connections were made and valves installed for placing any of the eight extractors as the first, intermediate, or last extractor in either the acetone or benzol cycle, and for filling, draining, venting, and steaming out an extractor. In the interconnecting line between extractors a 3/4" flow glass was placed for observing the liquid flow from one extractor to another.

Description of Equipment in the Acetone Recovery and Recirculation Unit

Flow Chart No. 9. Underground storage tank. Capacity 1000 gallons. Diameter 5' 0". Length 6' 0". Buried underground adjacent to identical tank used for benzol storage. Constructed from 1/4" iron plate; welded construction used. Suction and discharge pipe connected this tank with acetone system.

Flow Chart No. 10. Solvent storage tanks in acetone cycle. Two identical tanks were used for this purpose. Capacity 60 gallons. Diameter 1' 2", height 5' 0". Fabricated from 14 gage iron, welded construction used, and galvanized both inside and outside. Mounted on 18" long legs, and equipped with calibrated level gages.

Flow Chart No. (P-1). Motor pump arrangement for pumping acetone to extractors. Mounted on suitable base, a small spur gear pump, operated at variable speed by means of variable speed changes, driven by fractional horsepower, A.C., explosion-proof motor. V-belts used for transmitting power from motor to speed reducer and from speed reducer to pump. Speed range from 400 r.p.m. to 900 r.p.m. Capacity up to 300 gallons per hour. In addition to pumping acetone to extractors, this pump was used to draw acetone from underground storage, and to deliver acetone to precipitation system.

Flow Chart No. (P-0). Motor pump arrangement for draining extractors at end of acetone extraction. Mounted on a suitable base, a small spur gear pump. Operated at constant speed (below 900 r.p.m.). Driven

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by fractional horsepower, A. C., explosion-proof motor, V-belt drive between motor and pump. Capacity 120 gallons per hour.

Flow Chart No. 11. Orifice flowmeter for measuring the rate of flow of acetone to extractors. This flowmeter was located in the acetone solvent line to extractors, with pressure points on both sides of orifice plate connected to ends of a mercury manometer. The scale on the manometer was calibrated in gallons per hour, and the meter had an operating range of 0 to 130 gallons per hour. Rate was manually controlled by 3/8" needle valve located in solvent line before orifice plate. A spring loaded relief valve prevented overloading the pump motor.

Flow Chart No. 12. Heat exchanger for automatically heating acetone pumped to extractors. Heat exchanger was located in solvent line between acetone pump and extractors. Type - single pass, double pipe heat exchanger. Measurements - length 5'-0", inside pipe 3/4", outside pipe 1-1/4", 25 pounds steam used as a source of heat. Temperature automatically controlled by means of bellows type temperature regulator. The element of the regulator was placed in contact with heated solvent and actuated the valve controlling the steam to heat exchanger. A temperature recorder was used to indicate the temperature of the acetone before it entered the first extractor in the acetone cycle.

Flow Chart No. 13. Surge tank between extractor and stills for storage of acetone miscella. Capacity 40 gallons. Diameter 1'-2". Height 5'-0". Mounted vertically above extractors. Fabricated from 14 gage iron, welded construction, galvanized inside and outside, and equipped with calibrated level gages.

Evaporators and Stills, Condensers and Coolers for Concentrating Acetone Miscella by Means of Evaporation of Acetone Which Was Condensed for Reuse. Two evaporators and one still were used to concentrate the acetone miscella from the extractors. These three pieces of equipment were operated in series and their total evaporative capacity was between 100 and 120 gallons per hour of acetone.

The evaporators and still were fabricated from sections of 14 gage range boilers, and welded construction was used.

Flow Chart No. 14. First evaporator. Height 5'-0". Diameter 14". Jacketed height 2'-0". Jacket diameter 18". The evaporator was equipped with a calibrated level gage. The evaporator held 8 to 10 gallons of extract during continuous operation and had an evaporative capacity of 50 to 60 gallons per hour. The light extract from the extractors entered the evaporator near the top and the extract was given its first stage of concentration in this evaporator. Through an overflow leg which maintained a constant level of not less than six gallons of extract in the evaporator, the extract flowed by gravity into the second still for the second stage of concentration.

Flow Chart No. 15. Second evaporator. Height 2'-0". Diameter 1'-4". Jacket height 1'-0". Jacket diameter 1'-6". Operating capacity 8 gallons. Acetone evaporative capacity 30 to 40 gallons per hour. Steam heated

baffle coil inserted inside the evaporator near the top to prevent foaming. Side port holes with Pyrex glass covers were provided for observing the boiling conditions within the evaporator. The acetone miscella was given its second stage of concentration in this evaporator. The operating pressure of this evaporator was 1-1/2 pounds per square inch higher than that for the still and the partially concentrated miscella could be forced through an interconnecting pipe line to the still for final concentration.

Flow Chart No. 16. Still. Height 2'-0". Diameter 1'-4". Jacket height 1'-0". Jacket diameter 1'-6". During continuous operation the still held 8 to 10 gallons, and had an evaporative capacity of 20 to 30 gallons. A steam heated baffle coil was inserted inside the still near the top to prevent foaming. Port holes with Pyrex sight glasses were installed for observing the boiling of the contents of the still. In this still final removal of the acetone from the resins was accomplished. A 1" gate valve was located at the bottom of this still for removing the concentrated resiniferous material extracted.

Flow Chart No. 17. A condenser and after cooler were provided for condensing the distillate from each of the two acetone evaporators and from the acetone still. All three condensers and after coolers were of identical design and construction. The condenser was of the tube and shell type, and the outer shell made from a 3' section of standard 8" pipe. The hairpin shaped tubes were made of 1/2" standard pipe through which the cooling water passed. The after cooler was a single pass, double pipe type. The length of this after cooler was 4', the inner pipe 3/4", and the outer 1-1/4" in diameter. Connections for cooling water were so arranged that the condenser and after cooler could either be connected in series or in parallel. When connected in series, the cooling water first entered the after cooler and then passed through the condenser.

Flow Chart No. 18. Distillate receiver. Diameter 14", height 2'-0", capacity 12 gallons. Made from section of 14 gage range boiler, and fitted with calibrated level glass. For condensing any vapors which might rise from the solvent in this receiver, a water-jacketed vent condenser was provided. The distillate from the three after coolers in the acetone evaporative system drained into a manifold line which was connected to this distillate receiver. From this receiver the acetone was recirculated to the extractors in the acetone cycle.

Description of Equipment in Benzol Recovery and Recirculation System

Flow Chart No. 19. The benzol underground storage tank was identical to the acetone underground storage tank. Both were located outside the pilot plant. The two tanks rested horizontally on a concrete slab which was located approximately seven feet underground. The tanks were anchored by means of 2" steel straps to the concrete slab. For measuring the contents of these two tanks in gallons, an air-actuated, manometer type of tank gage was provided. Suction and discharge pipe lines connected the underground benzol storage tank to the benzol solvent and recirculation unit.

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Flow Chart No. 20. Solvent storage tanks. Four tanks were used for this purpose. Capacity of first two was 50 gallons each, diameter 1' 4", and height 5'-0". The third had a capacity of 40 gallons, with a diameter of 1'-2", and height of 5'-0". The fourth held 30 gallons, was 12" in diameter, and 5'-0" high. All four tanks were constructed from 14 gage iron, with welded construction used, and inside and outside surfaces were heavily galvanized. The tanks were mounted on 18" long legs and were fitted with calibrated level gages. The two fifty gallon and the thirty gallon tanks were used for the storage of benzol to and from the benzol extraction cycle. In addition, these tanks received benzol from the fractionation system.

The forty gallon storage tank was used for storage of benzol recovered from steaming out of an extractor.

All four tanks were so connected that solvent pumped from the underground supply could be placed in any of the tanks.

Flow Chart No.(P-2). Identical arrangement of motor and pump was used for pumping benzol to extractors as was described (Flow Chart No. (P-1)) for pumping acetone to the extractors in the acetone cycle.

Flow Chart No. 21. Orifice flowmeter for measuring rate of benzol to extractors.

The meter was located in the benzol solvent line to extractors, and its construction was identical to the one used for measuring the rate of flow of acetone in the acetone cycle. In addition to the orifice flowmeter, a rotameter was used to check solvent flow of benzol to extractors.

Flow Chart No. 22. Heat exchanger for automatically controlling temperature of benzol to extractors. This heat exchanger was located in the solvent line between benzol pump and extractors. The heat exchanger was of the double pipe, single pass design, and measured 10' long. The inside pipe through which the heated benzol flowed was 3/4" in diameter and the outside pipe was 1-1/4" in diameter. Steam, at 25 pound pressure, flowed between the two pipes and heated the solvent to the desired temperature. The temperature was automatically controlled by a bellows type regulator. The element of the regulator was placed in contact with the heated benzol, and actuated the valve controlling the steam to the heat exchanger. A temperature recorder was used to indicate the temperature of the benzol before it entered the extractor.

Flow Chart No. 23. Intermediate storage tank for benzol miscella. Capacity 50 gallons, diameter 1' 4", height 5'-0". Fabricated from 14 gage iron, welded construction used, and galvanized inside and outside. Mounted vertically on 18" long legs, and equipped with calibrated level gages. The benzol extract from the extractors flowed into this tank. This tank was provided with two outlets. One outlet was on the side of the tank 6" from the bottom, and the other in the center of the dished bottom of the tank. For the next step in the benzol cycle the miscella in this tank was withdrawn through the side outlet. In this way sufficient room was allowed for the settling of small particles of foreign matter

which might come over with the miscella from the extractors. Through the bottom outlet, the contents of this intermediate tank (approximately six gallons) were periodically drained into a sump tank. In this way any settled material accumulated in the bottom of the tank was washed out into the sump tank. The recovering of the benzol transferred to the sump tank as a result of this procedure will be discussed under the functions of the sump tank.

Flow Chart No. (P-3). Motor pump arrangement for pumping miscella from intermediate benzol miscella tank through filter into benzol miscella surge tank. This unit consisted of a small spur gear pump operated at a constant speed (800 r.p.m.), mounted on a suitable base, and driven by a fractional horsepower, A. C., explosion-proof motor. V-belt drive was provided between the motor and the pump. Capacity of the unit was 120 gallons per hour.

Flow Chart No. 24. Filter. The filter consisted of an iron pipe shell 12" in diameter by 20" high, with a bolted top cover plate. Inside the filter were two 8" x 16" filter frames covered with filter cloth. Each frame had an outlet through the top cover plate. The benzol miscella was pumped into the space between the shell and the filter frames, and passed out through the filter frames into the line to the benzol miscella surge tank.

Flow Chart No. 25. Surge tank for holding feed to benzol evaporator. Capacity 50 gallons, diameter 1' 4", height 5'-0", fabricated from 14 gage iron, welded construction used, and galvanized inside and outside. Equipped with calibrated level gages and mounted above benzol evaporator. The benzol miscella from the intermediate benzol miscella storage tank was pumped through a filter (Flow Chart No. 24) into this surge tank. Like the intermediate benzol miscella storage tank, this surge tank was provided with a bottom and a side outlet 6" from the bottom. The benzol miscella flowed out of the side outlet to the evaporator. Periodically the contents (about 6 gallons) of the surge tank were drained through the bottom outlet into the sump tank for removing any settled material which might have accumulated in the bottom.

Flow Chart No. 26. Evaporator for first stage of concentration of benzol miscella. The concentration of the benzol miscella from the extractors was performed in two stages. This evaporator (Flow Chart No. 26) was used for the first stage of concentration. The evaporator consisted of a single tube calandria constructed from a 6' section of standard 8" pipe, jacketed to a height of 5' by another section of 10" pipe. On the top there was mounted a 24" diameter dome. Inside at the center of the dome was a baffle plate to control foaming. At the bottom of the calandria section was bolted a standard 4" cross. A four inch diameter return leg connected the baffle dome with the cross at the bottom of the evaporator so that circulation of the miscella inside the evaporator could be accomplished. The evaporator was mounted on three 18" long legs, and the overall height was 9-1/2 feet. While in continuous operation, the evaporator held approximately 14 gallons of

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miscella, and had an evaporative capacity of 75 to 90 gallons per hour when 25 pounds of steam were used to heat the jacket. The evaporator was fitted with a 4' length of calibrated level gage glass. The miscella feed to the evaporator entered at the bottom through a 3/4" pipe which extended 18" upwards inside the calandria tube. The partially concentrated benzol miscella was pumped from the bottom of the evaporator.

The temperature of the vapor, and the pressure within the evaporator were measured by a recording thermometer and a compound pressure gage respectively.

Flow Chart No. 27. Condenser and after cooler. For condensing the distilled benzol from the evaporator a condenser of identical design to the ones used in the acetone system was mounted above the evaporator. The vapor pipe between the condenser and evaporator was 2" in diameter.

For cooling the distillate from the condenser, a 4-pass, double pipe cooler was installed. Each pass was 8' long, and the inner pipe, through which the distillate flowed, was 3/4" in diameter, while the outer pipe was 1-1/4" in diameter. The cooled distillate drained from this cooler directly into one of the four benzol storage tanks.

The cooling water first passed through the after cooler and then into the condenser.

Flow Chart No. (P-4). This is the motor pump arrangement for pumping the benzol miscella from evaporator to storage tank where it is held before final concentration.

This small spur gear pump, operated at variable speed (400 to 900 r.p.m.) by means of speed reducer, driven by a fractional horsepower, A. C., explosion-proof type motor, was arranged on a suitable base. V-belt drive was provided between motor and reducer, and reducer and pump. Capacity up to 120 gallons per hour.

Flow Chart No. 28. In the line between the pump and storage tank a rotameter was installed for measuring the rate of flow of miscella pumped from the benzol evaporator for further concentration.

Flow Chart No. 29. Storage tank for benzol miscella from evaporator. Capacity 65 gallons, diameter 1'-6", height 5'-0", fabricated from 14 gage iron, welded construction used, and galvanized both inside and outside. Equipped with calibrated level gage. Mounted above the benzol still.

A 2" Y-type strainer with a 100 mesh screen was installed in the line between the benzol miscella storage tank and the benzol still.

Flow Chart No. 30. Benzol still for final concentration of the benzol extract. The still consisted of a section of range boiler 14" in diameter by 5' high, jacketed to a height of 18", equipped with calibrated level gages, vapor and liquid thermometer, and steam pressure gage. A steam heated baffle coil was inserted inside the still near the top to

prevent excessive foaming during operation. Side port holes with Pyrex glasses were provided for observing boiling condition within the still. The still was fabricated from 14 gage, galvanized iron, welded construction used. During continuous operation, the still held eight gallons of miscella and had an evaporative capacity of 20 to 30 gallons per hour when steam at 25 pounds pressure was supplied to the jacket of the still.

Flow Chart No. 31. Condenser and after cooler. The condenser for the above still was of the same design and construction as the one used for the benzol evaporator. The after cooler was a single pass, double pipe type made from standard black iron pipe. The length was 12', the inside pipe was 3/4" through which the distillate flowed, and the outside pipe was 1-1/4". The cooling water first passed through the after cooler and then into the condenser.

Flow Chart No. 32. Storage tank for benzol extract from benzol still. Two identical tanks used for this purpose, each having a capacity of 40 gallons, a diameter of 14", and a height of 5'. Fabricated from 14 gage iron, welded construction used, and inside and outside surfaces heavily galvanized. Both tanks were equipped with calibrated level gages, and were vertically mounted on 18" long legs. Concentrated benzol miscella was stored in these two tanks until it could be purified by precipitation.

Flow Chart No. 33. Condenser and separator for the recovery of benzol from steaming out of extractors. For condensing the benzol-water vapors from the extractor during the steaming out of the extractors at the end of the benzol cycle, an 8-pass double pipe cooler was used. Each pass was 8' long; the inside pipe was 1-1/4" in diameter through which the vapors and condensate flowed, and the outside pipe was 2" in diameter.

The separator was constructed from a 32" section of standard 8" pipe with a standard 8" flanged welding neck welded to the top end, and an 8" welding cap welded to the bottom. A cover plate was bolted to the welding neck flange. The water-benzol mixture from the condenser entered the separator at its middle; the water was removed from the bottom of the separator through a 1-1/4" diameter, adjustable overflow leg and the separated benzol flowed out of an outlet near the top of the separator into the 40 gallon benzol storage tank (Flow Chart No. 20).

Flow Chart No. 34. Sump tank. Capacity 20 gallons, diameter 12", length 36", horizontally mounted at an elevation below bottom of all benzol storage tanks so that the bottoms from these tanks could be drained into it. Fabricated from 14 gage iron, welded construction used, and heavily galvanized on inside and outside surfaces. In addition to the benzol storage tank, the intermediate benzol miscella tank and the benzol miscella surge tank could be drained into this sump tank. From this sump tank, the contents were pumped to a separator for reclaiming the benzol from any water which might have been mixed together with the benzol delivered to the sump tank.

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Flow Chart No. 35. Separator for reclaiming benzol and benzol miscella from sump tank. The separator was constructed from a 32" section of standard 10" pipe with a standard 10" welding neck flange welded to the top, and a 10" welding cap welded to the bottom. A cover plate was bolted to the welding neck flange. Mixtures from the sump tank were pumped into this separator through a connection in the side of the separator near its middle. The water, and any dirt or foreign matter suspended in the water which separated from the top layer (benzol layer) in the separator, was removed from the bottom of the separator through a 1-1/4" diameter adjustable overflow leg. The water from the overflow leg flowed to the sewer. The benzol reclaimed flowed out of an outlet near the top of the separator through a pipe line to the intermediate benzol miscella tank.

Flow Chart No. (P-5). Motor pump arrangement for draining extractors at end of benzol extraction, and for pumping contents of sump tank into separator. This consisted of a small spur gear pump, operated at constant speed (800 r.p.m.), driven by fractional horsepower, A. C. explosion-proof motor. V-belt drive was provided between motor and pump. Capacity 120 gallons per hour. Since the draining of the extractor at the end of the benzol extraction period and the pumping of the contents of the sump tank to the separator were intermittant operations, the same pump could be used for both purposes.

Description of Precipitating, Settling, and Solvent Recovery Unit

Flow Chart No. (P-6). Motor pump arrangement. This unit consists of a small spur gear type motor mounted on a suitable base, driven by fractional horsepower motor, at a speed of 700 r.p.m. V-belt drive is provided. This pump was used to circulate concentrated benzol miscella in the storage tanks, for pumping this miscella to the precipitator, and for pumping precipitated, settled rubber solution from settling tank to storage tanks for the precuring process.

Flow Chart No. 36. Precipitating tank. The precipitating tank was 30" in diameter by 36" high, with a 20° conical jacketed bottom, and was welded from 1/4" iron plate. A 1[illegible] gage iron cover was bolted to the top of the tank, and made vapor tight by means of a gasket placed between the cover and tank. In this cover was an 8" diameter access opening with a removable cover for viewing the contents of the tank during precipitation. Below the top cover was a 3/4" coil through which cooling water flowed to minimize vapor loss during precipitation. Two dial type thermometers were placed in the wall of the tank, one at the top for measuring the vapor temperature, and the other near the bottom for measuring the liquid temperature. On the side wall of the tank, near the bottom, were located three 3/4" outlets 4" apart for draining off the acetone-benzol-resin mixtures after the rubber was precipitated. The precipitating tank was equipped with a single, vertical type paddle agitator which rotated at 125 r.p.m. Coupled to the agitator was a fixed ratio speed reducer which was driven by a 3/4 horsepower, A. C., explosion-proof motor. To the jacket of the precipitating tank either steam or water could be supplied.

A condenser was connected to the precipitating tank by means of a 1" vapor pipe for condensing any vapor which might escape past the cooling coil inside the precipitator. The condenser was of the same design as the ones used for condensing acetone and benzol in the extraction process. The condensed vapors were returned to the precipitator.

Flow Chart No. 37. Acetone-benzol-resin storage tanks. Two tanks were provided for this purpose. One had a capacity of 40 gallons, was 14" in diameter by 5' high; the other held 65 gallons, was 18" in diameter by 5' high. Both tanks were welded from 14 gage iron, galvanized on the inside and outside surfaces, and equipped with calibrated level gages.

Flow Chart No. (P-7). Motor pump arrangement for pumping acetone-benzol-resin mixtures from first storage tank to second storage tank. This unit, mounted on a suitable base, consisted of a small belt driven spur gear pump, which was operated at a speed of 800 r.p.m. and had an output delivery of approximately 200 gallons per hour. The pump was driven by a fractional horsepower, A. C., explosion-proof type motor. The acetone-benzol-resin mixture drained by gravity from the precipitator (No. 36) to the first tank and had to be pumped to the second tank which acted as gravity feed to the still (No. 38).

Flow Chart No. 38. Still for the recovery of solvent mixtures from precipitation process. The still was made from a section of a range boiler, 14" in diameter by 5' high, jacketed to a height of 16". The still was welded from 14 gage iron and was galvanized inside and outside. Inside of the still, one foot from the top, there was a 3/4" steam heated baffle coil for preventing excessive foaming. The still was equipped with two dial type thermometers, one for vapor temperature, and the other for liquid temperature, steam pressure gage, and calibrated liquid level gages. During operation the still held six gallons of acetone-benzol-resin mixture, and when 25 pounds of steam were supplied to the jacket of the still the evaporative capacity of the still was 10 to 12 gallons per hour of the solvent mixture.

Flow Chart No. 39. Condenser for Still (38). Same design as the condenser (27), for the benzol evaporator.

Flow Chart No. 40. Storage tank for distillate from still. This tank had a capacity of 65 gallons; was 18" in diameter by 5' high; was welded from 14 gage iron, galvanized inside and outside. The tank was equipped with calibrated level gages and was vertically mounted on 18" legs.

Flow Chart No. 41. Settling tank for holding purified and precipitated rubber solution from the precipitator. Same design and construction as distillate storage tank (Flow Chart No. 40.)

Flow Chart No. 42. "Bottoms" storage tank. Same design and construction as the 40 gallon acetone-benzol-resin storage tank. Used to hold "bottom" portions from the settling tank.

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Description of Equipment in Precuring Unit

Flow Chart No. 43. Storage tanks for precipitated benzol extract from settling tank. Two identical tanks were used for this purpose, each having a capacity of 40 gallons; a diameter of 14", and a height of 5'. The tanks were welded of 14 gage iron, galvanized inside and outside, and were equipped with calibrated level gages. Both tanks were mounted above the chemical mixing tank (No. 44).

Flow Chart No. (P-9). Motor pump arrangement for circulation of the precipitated and purified rubber solution in the storage tanks (No. 43). This arrangement consisted of a small gear pump, V-belt driven by a fractional horsepower, A. C., explosion-proof motor. The speed of the pump was approximately 700 r.p.m. and at this speed the pump had a capacity of 200 gallons per hour.

Flow Chart No. 44. Chemical mixing tank. This tank was made from a section of range boiler 14" in diameter by 5' high; jacketed by two independent sections as follows: the bottom section was 4" high and directly above this section a 16" section was placed. Independent steam connections were provided for each jacket section. This mixing tank was welded from 14 gage iron, galvanized inside and outside, and equipped with calibrated level gages, compound pressure gage, and two dial type thermometers, one for measuring vapor temperature, and the other liquid temperature. A valved funnel inlet for the addition of vulcanizing chemicals was provided at the top.

Flow Chart No. 45. Condenser. A condenser of identical design to the ones used for condensing solvent at other stages of the process was mounted directly above the chemical mixing tank. A 2" vapor line connected the chemical mixing tank to this condenser. In addition to the condenser, a 4' single pass, double pipe after cooler was provided. The inner pipe was 3/4" in diameter through which the distillate flowed, and the outer pipe was 1-1/2" in diameter. The distillate could either be sent back to the chemical mixing tank or delivered to the distillate storage tank.

Flow Chart No. 46. Loomis mixer. This mixer was of the bottom discharge type for vacuum operation, having a total volume of 13 gallons, equal to a working capacity of approximately 5 gallons or 20 pounds of processed rubber. The trough of the mixer was 12" wide x 14" long x 19" deep, and was provided with a cover with a quick opening device. The trough was constructed of Mechanite metal, and the other parts of the mixer were either cast iron or steel. The mixer trough was jacketed on the front, rear, and bottom, and the sigma type mixing arms were drilled and provided with flexible connections so that heating and cooling could be accomplished using the jackets or mixing blades or both. The 7" diameter mixer arms turned at constant speeds of 31 r.p.m. for the front arm, and 56 r.p.m. for the rear arm. The mixer was designed to withstand full vacuum. An inlet opening was provided in the trough for adding the solution of chemicals and rubber from the solution compounding tank. Also a vacuum outlet connection was provided for the removal of solvent vapor during processing.

Discharge was accomplished by lowering the central bottom of the trough which acted as a poppet valve. The mechanism for this purpose was operated by a hand wheel located at the side of the machine. Roller bearings were provided throughout with double thrust bearings to absorb the thrust loads from the mixer blades; also the mixer was equipped with vacuum and oil seals. The mixer was coupled to a totally enclosed gear reducer which was driven by a 3 horsepower, 60 cycle, 3 phase, 220 volt motor. The entire assembly was mounted on a single base.

For measuring the temperature inside the mixer during processing, a potentiometer type temperature recorder was used.

Flow Chart No. 47. Condenser for vapor from Loomis mixer. This condenser was a two-pass double pipe type, with each pass 4' long, the inner pipe was a 1-1/4" standard black iron pipe through which the distillate flowed and the outer pipe was a standard 2" black iron pipe. The vapors from the Loomis mixer were condensed by means of this condenser and flowed directly to the receiver (No. 48) for the distillate.

Flow Chart No. 48. Distillate receiver. The capacity of this receiver was 36 gallons, the diameter 18", and the height 36". The receiver was welded from 14 gage galvanized iron, and was internally braced to withstand reduced pressure. A calibrated level gage was installed on the side of this tank, and a vacuum pressure gage fitted in the top of the tank. An ejector operated by steam or water was connected to the receiver so that reduced pressure could be maintained inside the tank. This provided more rapid evaporation of the solvent from the rubber in the Loomis mixer. Normally the system was operated at absolute pressure between 15" and 20" of mercury.

Flow Chart No. 49. Distillate storage tank. This tank had a capacity of 40 gallons, a diameter of 14", and a height of 5'. It was constructed from a section of 14 gage galvanized iron range boiler, and equipped with calibrated level gage. Distillate from the receiver was pumped into this tank.

Flow Chart No. (P-8). Motor pump arrangement. This arrangement consists of a small gear type pump, mounted on a suitable base, V-belt driven by means of a fractional horsepower, A. C., explosion-proof motor. The pump rotated at 750 r.p.m. and delivered approximately 200 gallons per hour. This pump was used to transfer distillate from the receiver to the storage tank, and from the storage tank to the fractionation storage tanks.

Design and Analysis of Fractionating Columns

1. Design. The extraction and evaporation operations of the proposed pilot plant process result in a mixture of acetone and benzol which have to be separated for reuse, necessitating the use of a fractionating column (No. 51 on Flow Chart). The packed type was selected because of simplicity of construction and the availability of pipe sufficiently large for the required design capacity.

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Results of laboratory and pre-pilot plant tests indicated that a mixture of approximately 34% acetone by weight would have to be fractionated. Subsequent design calculations showed a capacity of 75 pounds per hour of 30% acetone or 37.5 pounds per hour of 60% acetone possible if the 8" pipe on hand were used. These capacities were considered ample, and calculations were made for both feed compositions.

The equilibrium curve used was based on data obtained from Landolt-Bornstein.(1) The number of theoretical plates required was determined by the well known McCabe-Thiele graphical method.(2) The design was based on the above mentioned feed compositions at 75° F., product compositions of 98% by weight acetone and benzol, a reflux ratio of 10 (lb. reflux/lb. product), and vapor velocity of 1.5 ft./sec. (unfilled cross-section).(3,4) A 3/8" Raschig ring packing was selected.

No data was found in the literature relative to design constants for the acetone-benzol system, indicating that this system is not commonly encountered in distillation practice. An Hp (Height equivalent to a Theoretical Plate) of 10" was assumed, after a survey of values for other liquid systems, although some extra height was added for liquid distribution.

The design resulted in a rectifying section of 6 feet, a stripping section of 4 feet, and an intermediate feed section of 2 feet with facilities for introducing feed at three points 7" apart - made of 8" standard pipe throughout. A 14" reboiler, 25" high, with a 16" diameter jacket 18" high was selected as suitable. A condenser similar in design to those used in evaporator operations was employed. All equipment was constructed in the Southern Regional Research Laboratory shops. Upon erection, the condenser was placed sufficiently high to allow for any future increase in column height should circumstances require it. Standard 1" thick x 8" 85% magnesia insulation was used.

Flowmeters were designed and calibrated to measure feed, reflux, and top product rates. Control was manual.

A mercury manometer measured pressure at the bottom of the packing. Vapor temperature at top of the column was measured by a 50°F. - 220° F. vapor pressure type recording thermometer. A multipoint Micromax recorder was used to measure reflux, boiler vapor, and feed temperatures. A Fulton-Sylphon regulator in the steam line to the reboiler controlled the vapor rate into the column.

(1) Landolt-Bornstein, Physikalisch-Chemische Tabellen, III, Part 3, p.2483.
(2) Badger, W. L. & McCabe, W. L., Elements of Chemical Engineering, pp. 344-357 (1936)
(3) Peters, W. A. Jr., Ind. & Eng'g. Chem., 14, 476 (1922).
(4) Pierce, D. E., Chemical Engineering for Production Supervision, p. 148 (1942).

A column was similarly designed for fractionation of acetone-water mixtures (No. 54 on Flow Chart). The rectifying section was 3 feet shorter than that for the acetone-benzol column, all other dimensions being the same, however, subsequent pilot plant operations and the processing of goldenrod leaf material drier than originally contemplated showed that this column was unnecessary. The addition of an acetone precipitation step to the operations constituting the pilot plant process called for more acetone-benzol fractionating capacity, and accordingly the rectifying section was increased to 6 feet, making this second column available for additional acetone-benzol fractionation.

2. Analysis. The absence in the literature of design information for the acetone-benzol system necessitated an assumption for the height equal to a theoretical plate. It was decided to operate the column at various feed rates, reflux ratios, and vapor rates, and determine H_t (Height of a Transfer Unit) for several sets of conditions as a check of the assumption made in design, so that reliable information would be available for calculations on large columns of capacity ample for industrial scale production.

Rates, temperatures, and pressures were measured as indicated in the discussion on column design. Readings were taken when conditions had approached constancy. Top and bottom products and feed were analyzed for composition by the density-refractive index method of Honold and Wakeham; [5] according to these analyses, small amounts of water (up to 2% by weight) persisted in the feed, nearly all of the water appearing at the top in some runs, and nearly all in the bottom in other runs. Rectifying and stripping calculations were made with compositions on a dry basis. To what extent the results were affected by this small amount of water is not known, but it is a fact that this is an actual feed condition in pilot plant operation.

Since "m" (the average slope of the equilibrium curve between the equilibrium compositions of vapor entering and leaving the column) has been found to be important as an operating variable in column performance [6,7,8] it was calculated and included in the results.

Results for H_t and "m" were calculated for rectifying and stripping sections separately as well as for the column as a whole.

H_t was calculated in each case by the well known method of Chilton and Colburn.[9] Graphical integrations were made by planimeter. To determine

(5) Honold, E. and Wakeham, H., Analysis Data for the Ternary System: Acetone-Benzol-Water, Ind. & Eng'g. Chem. (In Press).
(6) Colburn, A. P., Trans. Am. Inst. of Chem. Engrs., 35, 211 (1939).
(7) Furnas, C. C. & Taylor, M. M., Trans. Am. Inst. of Chem. Engrs., 36, 135 (1940).
(8) Duncan, D. W., Koffolt, J. H. & Withrow, J. R., Trans. Am. Inst. of Chem. Engrs., 38, 259 (1942).
(9) Chilton, T. H. & Colburn, A. P., Ind. & Eng'g. Chem., 27, 255 (1935).

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compositions of vapors at bottom of packing, a perfect plate was stepped off for the reboiler, as analysis was made of the reboiler liquid. The values of "m" were calculated graphically by the method used by Duncan, Koffolt, and Withrow, [8] although tangents were drawn and located by eye.

Operating lines were constructed and vapor and liquid rates were calculated by the methods of Badger and McCabe. [2]

The reflux ratios reported are corrected for condensation of vapor due to cold reflux and heat loss through insulation. Heat losses through insulation were calculated by the formula of Stoever. [10]

The results of 12 runs appear in Table I.

(10) Stoever, H. J., Applied Heat Transmission, p. 200 (1941).

III-TABLE I

ANALYSIS OF ACETONE-BENZOL FRACTIONATING COLUMN

Run No.	1	2	3	4	5	6	7	8	9	10	11	12
Column as a Whole:												
Feed, Lb./Hr. (F)	0	41.1	68.5	25.8	68.4	25.7	41.1	68.6	25.8	41.1	41.0	25.7
Feed Temp., °F.	-	92	92	88	94	92	95	94	90	92	95	90
Concentrations, mol-fraction Acetone:												
Vapor from col. (Y_2)	0.998	0.997	0.978	0.998	0.822	0.852	0.856	0.843	0.676	0.997	0.774	0.998
Vapor into col. (Y_1)	0.083	0.266	0.187	0.426	0.266	0.582	-	0.458	0.056	0.443	0.482	0.152
Feed (x_f)	-	0.542	0.542	0.540	0.550	0.555	0.542	0.529	0.529	0.54	0.547	0.542
Reflux Ratio (R_D)	∞	14.82	8.22	56.5	2.41	6.19	6.8	4.12	7.57	13.95	1.35	45.2
Height of Transfer Unit, Ft. (H_t)	0.908	0.983	1.286	0.981	3.12	4.87	4.81	3.862	4.09	0.997	5.165	0.918
Av. Slope Equil. Curve ("m")	1.01	0.651	0.759	0.583	0.686	0.538	-	0.584	1.276	0.582	0.593	0.809
Pressure Drop/Ft. (Lb./sq.in.)	0.121	0.121	0.121	0.121	0.020	0.010	0.020	0.020	0.020	0.121	0.010	0.121
Rectifying Section:												
Vapor Velocity (Col. Cross-Section), Ft./Sec.	1.77	1.73	1.65	1.74	0.75	0.50	0.86	0.82	0.89	1.70	0.38	1.74
Vapor-Liquid Ratio (Vn/Ln)	1	1.07	1.12	1.02	1.41	1.16	1.15	1.24	1.13	1.07	1.74	1.022
Height of Transfer Unit, Ft. (H_t)	-	0.700	1.017	0.649	4.12	3.205	3.04	3.26	10.04	0.666	6.48	0.663
Av. Slope Equil. Curve ("m")	-	0.548	0.548	0.55	0.534	0.534	0.541	0.536	0.557	0.552	0.541	0.551
Stripping Section:												
Vapor Velocity (Col. Cross-Section), Ft./Sec.	1.77	1.73	1.67	1.72	0.81	0.53	0.90	0.87	0.93	1.69	0.42	1.73
Vapor-Liquid Ratio (Vm/Lm)	1	0.946	0.909	0.946	0.852	0.888	0.883	0.814	0.966	0.948	0.887	0.949
Height of Transfer Unit, Ft. (H_t)	-	3.216	2.363	8.18	2.177	44.65	∞	5.66	2.032	6.86	3.83	2.708
Av. Slope Equil. Curve ("m")	-	0.766	0.913	0.687	0.776	0.625	-	0.688	1.391	0.679	0.667	0.989

Column Cross-Section	50.027 Sq. In.	Height of Packed Column	12.00 Ft.
Packing Used	3/8" Raschig Rings	Height Rect. Section	7.58 Ft.
Percent Free Space	68	Height Stripping Section	4.42 Ft.

Minor Auxiliary Equipment and Other Features of the Pilot Plant Not Included in Flow Chart III-Figure 2

A single tube, double pipe arrangement in which cooling water was passed through the annular space between the pipes was used as a vent condenser. Five such condensers were installed in the pilot plant, several pieces of equipment being connected to the same condenser. In this manner all solvent condensers, solvent storage tanks, acetone and benzol miscella tanks, and extract tanks were vented.

Gaskets for top and bottom plates of the extractors were cut from 1/8" "Pac Oil" packing. A specially prepared soluble starch-glycerine compound applied to the surfaces of the gasket greatly increased the life of the gasket and eliminated solvent loss through the gasket.

Sight glass flow fittings were made vapor-tight by placing an asbestos graphite gasket on the solvent side of the sight glass and a rubber gasket on the outer side of the glass. A thin metal ring was inserted between the outer gasket and the thread ring which locked the whole arrangement in place.

Either "Pac Oil" gaskets or lead ring gaskets were used where needed to make sections of evaporators, stills, and condensers vapor-tight.

Level glass fittings were kept vapor and liquid-tight by using Neoprene washers as packing for these fittings.

For solvent and miscella flow, 3/4" black iron pipe fittings, and all iron gate valves were used to connect one piece of equipment to another. All thread connections were made vapor-tight with a mixture of litharge in glycerine, or Crane's plastic sealing compound.

On all steam outlets from evaporators and stills, a standard impulse type trap was used. A strainer with a 1/80 mesh screen was inserted in the line ahead of each steam trap.

Steam and water valves were either standard brass, globe, or gate valves, depending upon the particular use of each valve. Steam lines were of black iron construction while water lines were all galvanized pipe and fittings.

Pilot Plant Procedure

The ground goldenrod material from the general harvest as received from Waynesboro, Georgia, was separated into two fractions by means of a screening procedure performed at the Southern Regional Research Laboratory. This screening procedure is fully described in Section VII, and produced a fraction enriched in rubber content over that of the unscreened material. This enriched fraction was used for pilot plant extractions.

As processed, the enriched material was packed in paper bags, containing 25 pounds each. Three bags were used for each extractor, since 75 pounds were the maximum amount of this material the extractor could hold.

This goldenrod material was manually poured into the extractors.

Table II is an illustration of the typical extraction schedule used for the acetone and benzol extraction of the goldenrod material in the 8-cell battery of extractors. By means of this schedule one could readily determine the processing stage of any one of the extractors at any time during continuous operation. Further, the schedule indicates that at all times two extractors were in the acetone extraction cycle while three were in the benzol extraction cycle. The other three extractors were either in the process of acetone draining, benzol draining, steaming out, unloading, loading, or were filled and ready to be placed in the acetone cycle.

By following such a schedule, 3000 pounds of material were processed in 120 hours of continuous extraction each week. During this period 40 cells were completely extracted, with a new extractor placed in the system once every three hours.

The length of time for each operation in the processing of an extractor was as follows: (1) loading and holding - one hour; (2) acetone extraction - 6 hours; (3) acetone drain - 1 hour; (4) benzol extraction - 9 hours; (5) benzol drain - 1/2 hour; (6) steaming out - 4 hours; (7) unloading and cleaning - 1 hour. As scheduled, the time for a complete cycle for an extractor was 22-1/2 hours, and once every 24 hours the extractor started a new cycle.

Acetone Extraction Procedure. In starting up the acetone unit, first an extractor was placed in the cycle, followed three hours later by a second one. From this point on there were always two extractors in the acetone cycle. When first placed in the cycle a charged extractor had to be filled with approximately 20 gallons of acetone pumped from an acetone storage tank (Flow Chart No. 10). This operation only took about ten minutes, and once the extractor was filled cyclic operation of the acetone unit could be maintained.

The acetone to the two extractors in the acetone cycle was heated to 140° F. automatically by means of the heat exchanger (Flow Chart No. 12), and pumped to the first extractor at a rate of 100 gallons per hour. This gave a solvent change in the extractor equal to about five times per hour. The heated acetone entered at the bottom of the first extractor and had an upward path through the extractor. The resulting acetone miscella left the first extractor from an outlet near the top and passed through the second extractor in the same manner as for the first extractor. The acetone miscella from the second extractor flowed to the acetone miscella surge tank. The average temperature inside the first extractor was 135° F., and for the second 130° F. The pressure in the solvent line at the point of entry of the solvent to the first extractor ranged from 15 to 20 pounds per square inch.

The acetone miscella from the acetone miscella storage tank flowed by gravity continuously through a sight glass into the first evaporator

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III-TABLE II

TYPICAL EXTRACTION SCHEDULE FOR PILOT PLANT OPERATION

Extraction #	Extractor #	Lot # & Lbs.	Loading Beg.	Loading End	Acetone Extraction Beg.	Acetone Extraction End	Acetone Drain Beg.	Acetone Drain End	Benzol Extraction Beg.	Benzol Extraction End	Benzol Drain Beg.	Benzol Drain End	Steaming Out Beg.	Steaming Out End	Unloading Beg.	Unloading End
315	1	Lot 9 75#	Thu. 3:30 AM	Thu. 4:30 AM	Thu. 6:00 AM	Thu. 12:00 N.	Thu. 12:00 N.	Thu. 1:00 PM	Thu. 1:00 PM	Thu. 10:00 PM	Thu. 10:00 PM	Thu. 10:30 PM	Thu. 10:30 PM	Fri. 2:30 AM	Fri. 2:30 AM	Fri. 3:30 AM
316	2	Lot 9 75#	Thu. 6:30 AM	Thu. 7:30 AM	Thu. 9:00 AM	Thu. 3:00 PM	Thu. 3:00 PM	Thu. 4:00 PM	Thu. 4:00 PM	Fri. 1:00 AM	Fri. 1:00 AM	Fri. 1:30 AM	Fri. 1:30 AM	Fri. 5:30 AM	Fri. 5:30 AM	Fri. 6:30 AM
317	3	Lot 9 75 #	Thu. 9:30 AM	Thu. 10:30 AM	Thu. 12:00 N.	Thu. 6:00 PM	Thu. 6:00 PM	Thu. 7:00 PM	Thu. 7:00 PM	Fri. 4:00 AM	Fri. 4:00 AM	Fri. 4:30 AM	Fri. 4:30 AM	Fri. 8:30 AM	Fri. 8:30 AM	Fri. 9:30 AM
318	4	Lot 9 75 #	Thu. 12:30 PM	Thu. 1:30 PM	Thu. 3:00 PM	Thu. 9:00 PM	Thu. 9:00 PM	Thu. 10:00 PM	Thu. 10:00 PM	Fri. 7:00 AM	Fri. 7:00 AM	Fri. 7:30 AM	Fri. 7:30 AM	Fri. 11:30 AM	Fri. 11:30 AM	Fri. 12:30 PM
319	5	Lot 9 75#	Thu. 3:30 PM	Thu. 4:30 PM	Thu. 6:00 PM	Thu. 12:00 M	Thu. 12:00 M	Fri. 1:00 AM	Fri. 1:00 AM	Fri. 10:00 AM	Fri. 10:00 AM	Fri. 10:30 AM	Fri. 10:30 AM	Fri. 2:30 PM	Fri. 2:30 PM	Fri. 3:30 PM
320	6	Lot 9 75#	Thu. 6:30 PM	Thu. 7:30 PM	Thu. 9:00 PM	Fri. 3:00 AM	Fri. 3:00 AM	Fri. 4:00 AM	Fri. 4:00 AM	Fri. 1:00 PM	Fri. 1:00 PM	Fri. 1:30 PM	Fri. 1:30 PM	Fri. 5:30 PM	Fri. 5:30 PM	Fri. 6:30 PM
321	7	Lot 9 75#	Thu. 9:30 PM	Thu. 10:30 PM	Thu. 12:00 M.	Fri. 6:00 AM	Fri. 6:00 AM	Fri. 7:00 AM	Fri. 7:00 AM	Fri. 4:00 PM	Fri. 4:00 PM	Fri. 4:30 PM	Fri. 4:30 PM	Fri. 8:30 PM	Fri. 8:30 PM	Fri. 9:30 PM
322	8	Lot 9 75#	Fri. 12:30 AM	Fri. 1:30 AM	Fri. 3:00 AM	Fri. 9:00 AM	Fri. 9:00 AM	Fri. 10:00 AM	Fri. 10:00 AM	Fri. 7:00 PM	Fri. 7:00 PM	Fri. 7:30 PM	Fri. 7:30 PM	Fri. 11:30 PM	Fri. 11:30 PM	Sat. 12:30 AM
323	1	Lot 9 75#	Fri. 3:30 AM	Fri. 4:30 AM	Fri. 6:00 AM	Fri. 12:00 N.	Fri. 12:00 N.	Fri. 1:00 PM	Fri. 1:00 PM	Fri. 10:00 PM	Fri. 10:00 PM	Fri. 10:30 PM	Fri. 10:30 PM	Sat. 2:30 AM	Sat. 2:30 AM	Sat. 3:30 AM

(Flow Chart No. 14) where the acetone miscella was given its first stage of concentration while the evaporator distilled off 50 to 60 gallons of acetone per hour. The bottom of the first evaporator was slightly higher than the top of the second evaporator allowing the partially concentrated acetone extract to flow from the overflow leg of the first evaporator through an interconnecting pipe into the second evaporator (Flow Chart No. 15). Here the extract was given its second stage of concentration while this second evaporator distilled off 30 to 40 gallons of acetone per hour. Since the pressure inside the second evaporator was maintained approximately 1-1/2 pounds per square inch higher than the acetone still (Flow Chart No. 16), which was of similar design and located on the same level, the concentrated extract from the second evaporator continuously flowed through an interconnecting pipe into the still where the acetone extract was given its final concentration. The evaporative capacity of this still was 20 to 30 gallons per hour of acetone. The resins (concentrated acetone extract) were concentrated until no acetone remained in them, and these resins were discharged from an outlet in the bottom of the still approximately once every 2 to 3 hours. The resins were collected in cans which held about 65 pounds.

The two acetone evaporators and the acetone still had a combined evaporative capacity of more than 100 gallons per hour. The distilled acetone from each of these pieces of equipment was condensed and the resulting distillate was further cooled by means of the condensers and after coolers (Flow Chart No. 17). The distillate from all three after coolers flowed into a manifold line which terminated at the distillate receiver (Flow Chart No. 18). In this receiver the distilled acetone was reheated and then pumped back to the extractors.

As scheduled, at the end of every three-hour period, the first extractor was taken out of the acetone cycle and the extractor next in line (charged with material), was placed in the cycle.

The quantity of solvent in the acetone cycle during normal continuous extraction was approximately 80 gallons and can be accounted for as follows: in the two extractors there were 40 gallons; in the distillate tank 8 gallons; in the surge tank 1 gallon, in the first evaporator 10 gallons, in the second evaporator 8 gallons, in the concentrating still 6 gallons, and in the interconnecting pipe lines and condensers 7 gallons.

The composition of the solvent used for acetone extraction contained, on the average, 88% to 95% acetone, 4% to 11% benzol, and 1% to 4% water.

At the completion of the acetone extraction (6 hours), each extractor was drained for one hour by means of a small gear pump arrangement (Flow Chart No. (P-0)) which discharged the drained solvent into the second evaporator. The vent valve on top of the extractor was kept closed until the pressure inside the extractor was reduced to zero, and when this condition was obtained it was opened for the remainder of the draining period. The amount of acetone which could be drained from the extractor was approximately 10 gallons. Since originally 20 gallons of acetone

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were needed to fill the extractor, there were approximately 10 gallons of acetone still absorbed by the material in the extractor. The removal of this acetone from the extractor will be discussed in the benzol extraction procedure.

Benzol Extraction Procedure. During normal extraction there were three extractors as scheduled, in the benzol cycle. Each extractor was given a benzol extraction for nine continuous hours. Since every three hours the first extractor in the cycle was taken out of the system, the next extractor in line (acetone extracted and drained) was placed last in the cycle.

Once all the acetone from the last extractor in the benzol cycle was removed by means of the procedure outlined in the following paragraph, the benzol extraction unit was operated in a cyclic manner. Benzol from the storage tanks (Flow Chart No. 20) was heated automatically to 175° F. by means of the heat exchanger (Flow Chart No. 22) and pumped at a rate of 50 to 75 gallons per hour to the extractors. The three extractors were connected in a series and the benzol miscella flowed upward through each extractor. The average temperature of the material in the first extractor was 150° F. to 155° F., in the second 140° F. to 145° F., and in the third 130° F. to 135° F. The miscella leaving the last extractor flowed to the intermediate benzol miscella storage tank (Flow Chart No. 23), which allowed some settling of the benzol miscella before it was pumped to the benzol miscella surge tank (Flow Chart No. 25) by means of the pump arrangement (Flow Chart No. (P-3)). From the surge tank the benzol miscella flowed by gravity into the benzol evaporator (Flow Chart No. 26) where it was given its first stage of concentration while 50 to 60 gallons per hour of benzol were distilled. By means of the condenser and after cooler (Flow Chart No. 27) located above the evaporator, the distilled benzol was condensed and cooled, and returned to the benzol storage tanks for recirculation in the extraction process. From the evaporator the partially concentrated benzol miscella (about 3% total solids) was pumped by means of a pump arrangement (Flow Chart No. (P-4)) to a storage tank (Flow Chart No. 29) above the benzol still (Flow Chart No. 30). From this storage tank the extract flowed by gravity through a fine strainer into the benzol still (Flow Chart No. 30). Here the extract was concentrated to approximately 15% total solids and was dropped at regular intervals to the benzol miscella storage tanks (Flow Chart No. 32).

Every three hours an extractor which was acetone extracted and drained was placed as the last extractor in the benzol cycle, and provision had to be made to remove from the benzol cycle the acetone which remained in this extractor (approximately 10 gallons) while the rubber was being extracted from the material in the extractors. These two operations were simultaneously accomplished by pumping to the first extractor in the cycle benzol heated to a temperature of 175° F. and at a rate of 50 gallons per hour from benzol storage tanks. Since these extractors were connected in a series, the extract leaving the last extractor contained a considerable amount of acetone. About 25 to 35 gallons of miscella had to be pumped through the last extractor in order to take practically all the acetone out of the cycle. This gave a mixture of 35 to 45 gallons

of miscella which was concentrated in the first benzol evaporator. The distilled solvent mixture from this miscella was condensed, cooled, and transferred to the storage tanks (Flow Chart No. 50) in the fractionation unit. This part of the benzol extraction process usually took 45 minutes to one hour, and during this time the benzol miscella was concentrating in the first benzol evaporator. In the beginning when a new extractor was placed in the benzol cycle, the acetone content in the miscella was not high enough to precipitate out any large quantity of rubber. Usually, when starting to evaporate, the first miscella which came over, the boiling point of the mixture in the evaporator was 146° F. to 150° F. After 35 to 45 gallons had been evaporated, the vapor temperature rose to 170° F. to 172° F.

Once the acetone was removed from the cycle, the distillate from the after cooler of the evaporator was transferred to benzol storage (Flow Chart No. 20) for the remainder of the three hour interval. Only the first benzol evaporator (Flow Chart No. 26) was in the cycle while the acetone was being removed since no miscella was pumped from the benzol evaporator to the second still (Flow Chart No. 30) for further concentration. While the acetone was being removed from the benzol cycle, the second still (Flow Chart No. 30) was used to concentrate to 15%, in batches of 3 to 3-1/2 gallons, the benzol miscella obtained for a six hour interval of extraction. Since the concentration of the benzol extract occurred once every six hours, and acetone was removed every three hours from the system, this still was shut down during half of the periods when the removal of acetone from the benzol cycle was in progress.

As stated in the description of equipment of the benzol unit, the intermediate benzol miscella tank and the benzol miscella surge tank were provided with an additional outlet located in the side of these tanks, so that any foreign matter in the benzol miscella could settle. Since these outlets were about 6" from the bottom, there were always at least 6" of miscella in these two tanks during continuous extraction. When a new extractor was placed in the benzol cycle both intermediate storage tank and surge tank were completely drained into the sump tank. While these two tanks were being drained, heated benzol was pumped to the first extractor in the cycle. In this way the last extractor in the cycle was filled with miscella from the second extractor. Within ten minutes the extractor was filled and the miscella began to enter the empty intermediate storage tank. When the level of the miscella in this tank was up to the side outlet, the miscella was pumped to the surge tank, and from the surge tank the miscella flowed to the evaporator and distillation of the acetone-benzol rubber solution was started, as described in the preceding paragraph.

By dropping the bottoms from the intermediate storage and surge tanks into the sump tank, the acetone-benzol mixture returning from the extractor in the benzol cycle did not become diluted with additional benzol before reaching the evaporator. This procedure was adopted in order to keep from sending more solvent mixture to the fractionating unit than necessary. In addition, accumulation of settlings in these two tanks was avoided. The benzol miscella dropped into the sump tank was reclaimed

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through the separator (Flow Chart No. 35) which was provided for this purpose. This operation was always performed while the benzol system was in cyclic operation. The benzol from the separator flowed to the intermediate benzol miscella tank. The separator was provided with an additional water feed so that at all times there was enough water entering with the liquid from the sump for proper action within the separator. By sending the benzol mixture to the separator, any insoluble particles were washed out of the benzol miscella and passed out of the separator suspended in the water routed to the sewer.

Another procedure tried was to send the benzol miscella from the last extractor directly to the evaporator, with a surge tank only in the line between the extractors and evaporator. This procedure required less handling of the benzol miscella before reaching the benzol evaporator and was satisfactory provided a suitable strainer was provided in the benzol miscella line before the evaporator.

An antioxidant (Flectol H) was added to the miscella on the basis of .5% of the rubber present. On this basis, 2 grams of Flectol H, dissolved in 500 cc. of benzol, were added to the benzol miscella before it reached the evaporator at intervals of 1-1/2 hours during continuous extraction.

The quantity of solvent in the benzol cycle during normal continuous extraction, excluding that in the benzol storage tank, was approximately 100 gallons and can be accounted for as follows: in three extractors there were 60 gallons; in intermediate benzol miscella tank six gallons; in surge tank six gallons; in benzol evaporator 12 gallons; in benzol still eight gallons; in condensers and after coolers five gallons; and in pipe lines three gallons.

The composition of solvent used for benzol extraction contained from 93% to 100% benzol, and 0% to 7% acetone. Now and then a trace of water was present in the solvent.

At the completion of the nine hours of benzol extraction, the extractor was taken out of the cycle, and drained for 1/2 hour, by means of the same gear pump arrangement used to pump out the sump. Approximately eight to ten gallons of benzol were drained out of the extractor and added to the benzol pumped to the extractors.

After an extractor was drained of benzol, steam at 20 to 25 pounds pressure was directly passed thru the extractor at a bottom connection. In this way the remainder of benzol left in the extractor was steam distilled and passed through the top filter inside the extractor into a manifold line which was connected to the multipass, double pipe condenser (Flow Chart No. 33). Here the steam and benzol vapors were condensed and flowed from the condenser into a separator (Flow Chart No. 33) where the benzol recovered from the water flowed out of a top outlet to the benzol storage tanks and was reused without any further treatment. Each extractor was steamed out for four hours and this period was ample for complete removal of benzol from the material left in the extractor at the end of the benzol draining period. At the end of the steaming out period, the extractor was immediately unloaded, cleaned out, and reloaded.

Once a day the bottom portions of all benzol storage tanks were drained to the sump tank, and the solvent in these bottoms was reclaimed through the separator used in conjunction with the sump tank. The reason this was done was to eliminate from the system any water which settled from the benzol recovered by fractionation.

Precipitation System. Since the concentrated benzol miscella contained an average of 18 to 22 parts of resins per 100 parts of rubber, it was necessary to reduce this resin content by acetone precipitation. This operation was performed by the use of the precipitation unit, a description of which has already been given (Flow Charts 36 to 42 inclusive). This precipitation procedure was necessary because tensile strength and other properties of goldenrod rubber were adversely affected by resins in excess of 5%.

The resins present in the benzol miscella are quite soluble in acetone or benzol, while the rubber is soluble only in benzol. A small percentage of acetone in the benzol does not materially decrease the solubility of the rubber, but ratios of acetone to benzol between 3 to 1 and 5 to 1 will cause the rubber to precipitate more or less completely. The addition of a trace of NH_4SCN or KSCN in the acetone, added to cause precipitation, was found to produce flocculent precipitation and subsequent coagulation instead of a colloidal suspension of the rubber. Agitation was of considerable benefit in coagulating the rubber.

The pilot plant process of reducing the resins in the concentrated benzol miscella was based on the above considerations and consisted essentially of pumping 40 gallons of acetone to the precipitating tank (Flow Chart No. 36), adding 15 grams of potassium thiocyanide dissolved in acetone, and with the agitator of the precipitating tank in operation, 20 gallons of the concentrated benzol miscella from storage tanks (Flow Chart No. 32) were sprayed into the tank and stirred continuously for ten minutes. After settling for one hour at room temperature, the acetone-benzol-resin solution was decanted through the side connections to the storage tanks (Flow Chart No. 37).

Another batch of rubber of the same size was then precipitated in the same manner as described above, without removing any of the rubber. The rubber from the two batches was then dissolved in enough benzol to obtain a solution containing about 17% rubber. While dissolving the rubber the temperature was maintained at 140° F., and 0.5% Flectol H on the weight of the rubber was added. The warm rubber solution was then drained to the settling tank (Flow Chart No. 41).

The rubber was not washed with acetone after precipitation because the resin content was sufficiently reduced by the above procedure. Purified batches of rubber solution prepared in this way contained approximately 16% to 18% total solids which was a desirable concentration for the precuring operation. The precipitated rubber contained from 2 to 4 parts of the acetone soluble material per 100 parts of rubber.

The precipitating operation, as carried out in the pilot plant,

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produced 40 gallons of concentrated rubber solution per batch with a loss of only 3% of the initial rubber content. The time required to purify 40 gallons of crude benzol miscella was about eight hours. Hence, from the standpoint of the precipitation system, there was ample capacity for handling the quantity of crude benzol miscella produced in the pilot plant extraction system, since, on the average, only 55 gallons of crude benzol miscella were produced during 120 hours of continuous extraction.

The quantity of acetone-benzol-resin mixture obtained from each 40 gallons of benzol miscella purified by the precipitation procedure was 110 to 120 gallons. This mixture was distilled at the rate of 10 to 12 gallons per hour in the still (Flow Chart No. 38) provided for this purpose. The residue was collected from the bottom of the still in the same type of cans used for the acetone extract. The distillate from the still was collected in the distillate storage tank (Flow Chart No. 40). From this storage tank the distilled solvent mixture, which usually contained from 60% to 70% acetone, was transferred to the fractionation unit.

The purified rubber solution was allowed to settle in the settling tank (Flow Chart No. 41), and from this tank was transferred to the precuring unit for the final step in the process.

Pilot Plant Precuring. The general procedure used in precuring the product in the large Loomis mixer was as follows: The amounts of chemicals necessary to precure 18 pounds of resin-free rubber were added to the jacketed tank (Flow Chart No. 44) together with two gallons of benzol. This mixture was brought to the boiling point in order to dissolve these chemicals. The rubber solution, usually at a concentration of about 1.3 pounds per gallon after purification and settling, was then added. The mixture was again brought to the boiling point to ensure homogeneous solution of rubber and chemicals. The steam pressure in the jacket was adjusted so that the solvent evaporated very slowly, usually about three gallons being distilled in this manner during the course of each run. If too much heat was applied at this point, the solution tended to gel and was held up in the mixing vessel, or caused difficulty by plugging of lines leading to the Loomis mixer. By keeping the mixture at the boiling point, settling out of chemicals was prevented.

The contents of the solution compounding tank was then run slowly into the steam heated Loomis mixer, benzol being distilled continuously under vacuum. The maximum rate of distillation for good operation was about six gallons per hour under 14" of vacuum. Care was taken to prevent accumulation of more than about six gallons of concentrate in the mixer at any time in order to avoid excessive foaming. A thermocouple extending into the material working between the blades was used to measure temperature through a potentiometer type recorder. During removal of benzol the temperature was held between 140° F. and 170° F., at which temperature no signs of gel formation were detectable.

As soon as the benzol was completely distilled, the mixer was opened. The temperature of the stock rose, and at about 250° F. the material began to set up or stiffen rapidly. Heating was continued for about 15

minutes during which time the temperature rose to about 280° F., and reaction was practically complete. The steam was then turned off and cold water was run through the apparatus, agitation being intermittent during the cooling stage. This procedure was necessary to ensure uniform cooling of the stock and at the same time undue breakdown of the precured rubber was prevented. As soon as the stock was cooled it could be removed easily by warming the sides and blades slightly and lifting this material out of the top of the mixer.

Operation of the Fractionation Unit. The fractionation unit was operated in conjunction with the other units in the system to fractionate acetone-benzol mixtures transferred from the extraction unit, the precipitation unit, and the precuring unit.

For nine runs (see Tables III and IV) made in the pilot plant system, a total of 556.65 pounds of rubber on a resin-free basis were produced. To process this quantity of rubber from the raw material to a precured form, the following quantities of acetone-benzol mixtures were transferred to the fractionation columns: from the extraction system 15,200 gallons (20% to 30% acetone); from the precipitation unit 1700 gallons (60% to 70% acetone); and from the precuring unit 375 gallons (20% to 25% acetone).

Two columns were designed and constructed, one for fractionating acetone and benzol mixtures, and the other for fractionating acetone-water mixtures. Before pilot plant extractions of goldenrod material were conducted on a large scale, it was considered that the acetone used for acetone extraction would become contaminated with water from the moisture in the ground goldenrod material, and consequently the acetone would have to be periodically fractionated. However, after operating the extraction battery, it was found that the amount of water in the acetone used in the acetone cycle remained at about 4%. One reason for the small percentage of water in the acetone was that the moisture content of the material was only 6% to 8%, and another reason was that every time an acetone extracted cell was taken out of the cycle and a recharged cell placed in the cycle approximately 10 gallons of fractionated acetone were added in the acetone system to make up for the acetone left in the extractor taken out of the cycle. Since eight such additions were made each 24 hours of continuous extraction, and only 80 gallons of acetone were in the whole cycle, these periodical additions of relatively pure acetone kept the water content in the solvent below 4%.

The ten gallons of acetone left in the extracted cell were removed from the benzol system with benzol, and the resulting acetone-benzol mixture was transferred to the storage tanks for fractionation in the acetone-benzol column. During fractionation the small amount of water in this mixture came out in the benzol fraction which was transferred to the benzol storage tanks. Since water and benzol are immiscible, the water settled to the bottom of the benzol storage tanks. By periodically dropping the bottoms to the sump tank, the water was taken out of the system.

The addition of the precipitation procedure to the pilot plant process

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necessitated an increase in the acetone-benzol fractionation capacity. This was accomplished by converting the acetone-water column to an acetone-benzol fractionating column. By increasing the rectification section of the acetone-water column three feet, it was identical in construction to the acetone-benzol column.

During the periods of continuous extraction, these two columns were used jointly to fractionate the mixtures of acetone-benzol transferred from the other units in the system. Since the two columns were identical in every respect, they were operated in the same manner. The total capacity of the two columns was ample for the requirements of pilot plant system. For each column, 10 to 12 gallons per hour of acetone-benzol mixture containing 20% to 30% acetone could be fractionated while for low benzol mixtures (60% to 70% acetone), only 4 to 5 gallons per hour could be fractionated. The purity of the top cut (acetone) varied from 95% to 99% acetone, and the bottom cut (benzol) 96% to 100% benzol containing a small amount of suspended water.

For all composition of feeds relatively high reflux ratios were maintained which varied from 10 to 1 to 20 to 1.

Upon starting, the time required to bring the columns in equilibrium was approximately 45 minutes, and from this point on the columns were operated with very little attention needed since all recorders, controls, and operating valves were conveniently located so that any regulation necessary could be easily made.

The feed temperature, reflux temperature, and the reboiler temperature for each column were recorded once every minute by means of a multipoint potentiometer strip chart recorder. The acetone vapor temperature at the top of the columns was continuously indicated by a vapor pressure type temperature recorder. The required reboiler temperature for each column was automatically controlled by a bellows type regulator. A mercury manometer was used to indicate the internal pressure within the column. Orifice flowmeters were used for each column to measure the feed rate, the acetone cut rate, and reflux rate. During operation of the columns, the following are average temperatures of controlling points: (1) reboiler - 178° F., (2) feed 80° F., (3) - reflux 105° F., (4) acetone vapor 135° F.

Feed to the columns was pumped from one of the four storage tanks (Flow Chart No. 50), and the fractionated acetone (top cut) flowed back by gravity to acetone storage tank (Flow Chart No. 10), while the fractionated benzol (bottom cut) was pumped to the benzol storage tanks (Flow Chart No. 20).

Results. Extraction. Results of extractions performed in the pilot plant system may be divided into three parts according to the nature of the raw material used for processing.

Part 1. Material from general harvest, shipped in bales from Waynesboro, Georgia, reprocessed to remove a large percentage of stems and stalks, and ground in a hammer mill at the Southern Regional Research Laboratory.

Part 2. Material from general harvest, ground at Waynesboro, Georgia, shipped in paper bags, weighing approximately 35 pounds, and screened at the Southern Regional Research Laboratory. The screening process retained approximately 42% by weight of original material enriched in rubber content. This screened fraction was used for extractions, while the rest was discarded.

Part 3. Special lots of material - ensilage, retted material, antioxidant, and temperature drying runs. The procedure and results for these extractions are given in the sections covering these special lots.

For Part 1, a total of 12,150 pounds of this material was extracted in 664 hours of continuous extraction. The concentrated benzol miscella contained 165 pounds of rubber corrected to the resin-free basis. The weighted average analysis of the material charged in the extractors was 1.87%, equivalent to 227 pounds of resin-free rubber in the total of 12,150 pounds, so that the overall efficiency of the extraction operation was 73%. The average resin content of the crude rubber was 18% to 20%. Several batches of precured rubber were made from this rubber, but the resulting vulcanized product was of a very poor grade. The balance of the crude rubber solution was precipitated with acetone, and redissolved in benzol in order to reduce the resin content to a minimum (2% to 4%). The rubber in the benzol extract was compounded and precured in the Loomis mixer. The resulting vulcanized product was of a satisfactory grade.

The material described in Part 1 was extracted in the 8-cell extraction battery, using a 12 hour continuous cycle for both the acetone and benzol extraction of each cell. Several attempts were made to reduce the resin content in the crude benzol miscella by modifications in the extraction process, but for various batches of crude rubber the resin content varied from 13% to 25%.

For Part 2, a total of 28,350 pounds of screened material were extracted in the 8-cell extraction battery, and the resulting crude benzol miscella was acetone precipitated to obtain a purified rubber solution low in resin content (2% to 4%). The purified rubber solution was further processed to a precured form in the Loomis mixer.

The 28,350 pounds of screened material were extracted in a total of nine runs, and the results for the acetone and benzol extractions are given in Tables III and IV respectively.

For the extraction cycles of these runs, a continuous acetone extraction of six hours and a continuous benzol extraction of nine hours were used for each cell. Two extractors were in the acetone cycle, and three extractors in the benzol cycle at all times. The acetone was pumped to the extractors at a rate of 100 gallons per hour, and at a temperature of 140° F., while for benzol the rate was maintained at 50 to 55 gallons per hour for the first seven runs, and at a rate of 75 to 85 gallons per hour for the last two runs. With other factors remaining the same, the increase in rate of flow did not produce any more rubber. For all nine

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runs the benzol, pumped to the extractors, was heated to a temperature of 170° to 175° F.

The results of these pilot plant extraction operations indicate that the average percent of resin-free rubber on a total weight basis extracted from the screened material was 1.985% as compared to 1.36% for the unscreened material on an equal basis. Consequently, from the standpoint of pilot plant extraction, the screening procedure increased the rubber yield 45.5%.

The average density of the screened material was 21.6 pounds per cubic foot, and the average density of resins extracted from this material was 70.5 pounds per cubic foot.

The total amount of goldenrod rubber, on a resin-free basis, extracted from all the material processed in the 8-cell extraction battery was 874 pounds which includes 131 pounds of rubber produced from the special lots; namely, ensilage, retted, drying temperature control, and antioxidant. (See Sections VI, IX, X, and XI of this report for details on these special runs.)

Results. Precipitation Process. The results of pilot plant precipitation of batches of crude benzol extract from the extraction process are tabulated in Tables V and VI. Data on the benzol miscella before precipitation are presented in Table V and similar data on the purified rubber solution after acetone precipitation are shown in Table VI. In these tables are listed the results for 22 runs made in the pilot plant. Runs 1 through 5 were batches of crude benzol miscella extracted from unscreened goldenrod material, while Runs 6 through 19 were made to purify crude benzol miscella obtained from the extraction of screened goldenrod material. Runs 20 through 22 were made to reduce the resin content of special lots of benzol miscella.

III-TABLE III

PILOT PLANT EXTRACTION RESULTS: I. ACETONE EXTRACTION

Run No.	Continuous Extraction Hrs.	Lbs. Extracted	PILOT PLANT RESULTS: Lbs. Resins Extracted	PILOT PLANT RESULTS: % Resins Tot. Wt. Basis	ANALYTICAL EXTRACTION DATA: Raw Material: % Moisture	ANALYTICAL EXTRACTION DATA: Raw Material: % Acetone Ext. Tot. Wt. Basis	ANALYTICAL EXTRACTION DATA: Residue: % Acetone Ext. Tot. Wt. Basis*
1	120	3000	370.0	12.30	6.65	14.06	4.33
2	120	3000	440.4	14.70	8.00	14.45	3.97
3	120	3000	433.0	14.40	7.95	13.95	2.35
4	120	3000	407.0	13.60	8.35	14.70	1.74
5	222	5550	921.0	16.60	8.75	15.00	1.66
6	114	2850	450.0	15.80	7.95	15.90	1.51
7	90	2250	379.0	16.82	7.95	15.00	2.64
8	108	2700	463.0	17.15	9.07	16.10	4.06
9	120	3000	512.0	17.10	9.42	15.45	4.17

* Corrected to original weight.

III-TABLE IV

PILOT PLANT EXTRACTION RESULTS: II. BENZOL EXTRACTION

Run No.	Continuous Extraction Hrs.	Lbs. Extracted	PILOT PLANT RESULTS: Vol. of Extract Gals.	Total Solid in Extract Gms/cc.	Resin Content of Extract %	Lbs. of Resiniferous Rubber	Lbs. of Rubber Resin-free Basis	% Resin-free Rubber Tot. Wt. Basis	ANALYTICAL EXTRACTION DATA: Raw Material % Moist.	Raw Material % Benzol Extract Tot. Wt. Basis	Residue % Benzol Extract Tot. Wt. Basis*	Efficiency of Extraction %**
1	120	3000	54.25	14.4	23.85	65.25	49.75	1.60	6.65	2.465	.774	67.4
2	120	3000	48.25	17.4	22.80	70.10	54.10	1.80	8.00	2.47	.805	73.0
3	120	3000	49.50	17.8	22.30	73.60	57.20	1.90	7.95	2.21	.823	86.0
4	120	3000	54.00	16.6	25.50	74.70	55.60	1.86	8.35	2.16	.797	86.5
5	222	5550	101.50	15.95	22.80	134.75	104.05	1.88	8.75	2.62	.745	72.0
6	114	2850	49.58	17.4	13.85	72.03	62.05	2.18	7.95	2.78	.817	78.5
7	90	2250	45.92	17.8	18.40	68.20	55.66	2.47	7.95	2.75	.918	89.8
8	108	2700	55.03	16.2	22.70	74.20	57.34	2.12	9.07	2.71	.833	78.2
9	120	3000	56.50	16.15	20.10	76.20	60.90	2.02	9.42	2.58	.752	78.3

* Corrected to original weight.

** Efficiency of Extraction = $\frac{\text{\% resin-free rubber, total weight basis}}{\text{Analytical \% benzol extract, total weight basis}} \times 100.$

III-TABLE V
PILOT PLANT PRECIPITATION

	BEFORE PRECIPITATION						
Run No.	% Total Solids	% Resin	Total Crude Rubber Lbs.	Gals. of Solution	Lbs. of Total Solids Per Gal.	Lbs. Rubber In	Lbs. Resin In	Ratio of Acetone to Solution
1	18.7	17.1	12.1	7.75	1.56	10.04	2.06	4.13
2	15.1	17.9	25.6	20.35	1.26	21.1	4.6	3.94
3	16.4	15.2	28.3	20.7	1.37	24.0	4.3	3.87
4	16.4	15.2	24.6	18.0	1.37	20.9	3.7	4.45
5	19.05	13.4	48.7	30.66	1.59	42.2	6.5	4.00
6	14.5	23.4	48.0	39.75	1.21	36.8	11.2	3.02
7	16.9	24.9	51.4	36.5	1.41	38.6	12.8	2.18
8	14.0	5.7	65.5	56.0	1.17	61.7	3.7	0.65
9	20.6	20.4	61.8	36.0	1.72	49.3	12.6	2.22
10	15.9	20.8	48.5	36.5	1.33	38.4	10.1	2.20
11	15.5	30.3	51.7	40.0	1.29	36.1	15.6	2.00
12	15.7	24.8	50.3	38.5	1.31	37.9	12.5	2.00
13	16.3	20.2	49.5	36.5	1.36	39.6	10.0	2.00
14	17.65	12.7	58.1	39.5	1.47	50.7	7.4	2.00
15	20.0	11.5	37.0	22.2	1.67	32.8	4.3	2.00
16	17.6	18.75	57.6	39.75	1.465	46.8	10.8	2.00
17	16.4	23.8	51.8	38.0	1.36	39.5	12.3	2.00
18	15.7	19.8	88.4	67.5	1.31	70.9	17.5	2.00
19	17.65	19.3	33.8	23.0	1.47	27.3	6.5	2.00
20	12.65	17.4	42.2	40.0	1.055	34.8	7.4	2.00
21	11.3	15.5	39.6	42.0	0.942	33.5	6.1	2.00
22	19.75	7.3	72.4	44.0	1.65	67.1	5.3	2.00

III-TABLE VI
PILOT PLANT PRECIPITATION

AFTER PRECIPITATION

Run No.	% Total Solids	% Resin	Gals.	Lbs. of Tot. Solids Per Gal.	Lbs. Rubber Out	Lbs. Resin Out	% Rubber Recovered
1	14.4	3.5	9.5	1.20	11.0	0.4	106
2	13.6	2.9	18.0	1.135	19.8	0.6	94
3	14.8	4.0	19.5	1.235	23.1	1.0	96
4	13.5	3.7	18.7	1.13	20.4	0.8	98
5	15.4	3.9	32.3	1.28	39.7	1.6	94
6	13.3	6.0	34.0	1.11	35.4	2.3	96
7	14.7	6.1	31.4	1.23	36.2	2.4	94
8	12.3	4.9	57.0	1.03	55.5	2.9	90
9	13.8	5.1	28.0	1.15	30.7	1.6	62
10	12.8	4.7	32.0	1.07	32.6	1.6	85
11	12.9	6.2	29.0	1.076	29.3	1.9	81
12	15.5	3.2	28.5	1.29	35.6	1.2	94
13	14.65	3.4	32.5	1.22	38.2	1.4	96
14	19.6	3.3	31.1	1.63	48.9	1.7	96
15	16.9	4.1	24.0	1.41	32.4	1.4	99
16	18.05	3.0	31.4	1.505	45.8	1.4	98
17	15.9	4.4	29.0	1.325	36.7	1.7	93
18	18.15	5.0	49.0	1.51	70.5	3.7	99
19	16.75	5.4	20.0	1.40	26.5	1.5	97
20	15.0	2.7	25.0	1.25	30.4	0.8	-
21	15.2	3.0	26.0	1.267	31.9	1.0	95
22	15.65	3.8	51.0	1.305	64.1	2.5	96

Solvent Loss. For the 28,350 pounds of screened material processed, the average solvent loss per ton was 38.6 gallons of acetone, and 32.7 gallons of benzol. The best solvent loss figures obtained for any one week's operation were 32.6 gallons of acetone and 13.0 gallons of benzol per ton of raw material extracted. These figures include the losses occurring during the operation of the extraction unit, precipitating unit, and fractionating unit. In accounting for these solvent losses, it may be stated:

1. For the extraction of a ton of goldenrod material, approximately 8000 gallons of acetone and 4000 gallons of benzol were recirculated in the extraction system.

The design of the vent condensers could no doubt have been improved to provide more condensing surface and, if necessary, refrigerated water also could have been used. Venting through an absorption system might also have been more effective. It is felt that solvent losses through the vents accounted for a considerable portion of the total, and improvements which were contemplated for future installation would have resulted in lower loss figures.

2. The system contained several hundred valves, and although these valves were carefully maintained, some valve leaks did occur.

3. Gasket leaks are also included in the above solvent losses. The vegetable fiber material (Pac-Oil) used for gasketing the extractors was satisfactory, provided it was either coated with starch glycerine compound or painted with a vegetable oil after each extraction. On an average, one of these gaskets for the extractors lasted for 6 to 8 complete extraction cycles.

4. Ten to twelve gallons of solvent, containing 4% to 7% acetone remained in an extractor at the completion of the benzol draining period. Since the recovery of this solvent was accomplished by directly steaming out an extractor, condensing the vapors and removing the water from the benzol by means of a separator, much of the acetone contained in the benzol was lost in the water routed to the sewer from the separator. For each ton of goldenrod material extracted, 275 to 300 gallons of solvent which contained 10 to 20 gallons of acetone were processed in the above manner. The distribution of the acetone between the water and benzol depended upon the quantity of water separated from the benzol. However, for a ton of goldenrod material processed, it is likely that a great portion of this 10 to 20 gallons was lost in the water coming from the separator.

Improvements in handling that portion of the benzol miscella containing the acetone remaining from the acetone cycle and other improvements in fractionation and in the benzol cycle which might have provided 100% benzol for the final stage of benzol extraction

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were contemplated which would have eliminated much of this acetone loss.

5. The amount of solvent loss in the precipitation process was between 6 and 8 gallons of acetone-benzol for processing the amount of rubber obtained from one ton of goldenrod material.

The precipitation step was carried out in equipment that was on hand, and modified for the purpose. It was not wholly vapor-tight and there was room for considerable improvement in this part of the process for reducing solvent losses.

All of the runs made in the pilot plant should be considered as "warming up" or training operations. The operations were of sufficient duration to produce some rubber and to get some idea as to the workability of the process employed.

This preliminary operating period would normally have been followed by revisions in equipment and procedure, and additional operation until predetermined standards of performance were reached or definitely established as unattainable. This stage of the pilot plant operations was never reached.

Operating Cost. The program for the production of goldenrod rubber in large quantities contemplated the use of existing industrial wood rosin extraction installations. Pilot plant development work carried on at the Southern Regional Research Laboratory was performed with the dual purpose of determining the suitability of the acetone-benzol extraction process, and to obtain experimental data which would be useful in estimating operating cost for a full scale plant.

The estimated costs for industrial production of goldenrod rubber would be approximately $16.40 per ton of goldenrod leaf material, processed by a procedure similar to the one used for pilot plant work. Steam, power, and labor are included in this figure for the precuring step, but not the precuring chemicals. The weight of rubber produced is that of the rubber hydrocarbon on a resin-free basis, and does not include the weight of precuring chemicals. The proposed industrial extraction plant contains an extraction battery of sixteen extractors, each with a working capacity of approximately 425 cubic feet. It was estimated that one ton of goldenrod leaf material would yield approximately 100 pounds of goldenrod rubber and 350 pounds of acetone extract. The estimated cost of $16.40 per ton of goldenrod leaf material represents only the operating cost and does not include the raw material cost, or allowances for original investment, amortization, depreciation, taxes, or maintenance.

A breakdown of the operating cost is given in the following table.

Any value returned from the sale of the acetone extract or materials recovered therefrom can be credited to the extraction cost figures. (See Section XVII.) No such credit was taken in the extraction cost figures here reported.

III-TABLE VII
OPERATING COST FOR PROCESSING THE RUBBER
FROM ONE TON OF GOLDENROD LEAF MATERIAL

		Quantity	Rate	Cost
Electrical power -	Kilowatt Hours	95.0	$0.005	$ 0.48
Process Steam -	1000 Pounds	18.5	0.30	5.55
Cooling Water -	1000 Gallons	63.5	0.02	1.27
Solvent Loss -	Acetone - Gallons	10.0	0.46	4.60
	Benzol - Gallons	10.0	0.15	1.50
Labor				3.00
				$16.40

Check of Possible Health Hazards. During the period of continuous pilot plant operation most of the personnel engaged were examined every two weeks at the Marine Hospital to check possible effects of exposure to vapors of the solvents used. The men were first given the necessary preliminary medical examinations, including blood counts, before being exposed to conditions in the plant. All possible precautions were taken to prevent leaks, to provide ample ventilation, and to maintain a minimum inventory of solvent inside the plant, bulk storage being in the underground tanks. Analyses of air samples taken during typical operating periods showed a very low concentration of solvent vapors locally, and none detectable in most parts of the plant. No ill effects were detected in any case by the medical examinations, and with proper precautions the process should not present any serious industrial health hazard.

IV-VULCANIZATION, TESTING, AND PROCESSING

From the outset of the work on goldenrod rubber it was essential to study the chemical behavior of the material obtained by extraction, particularly with respect to its vulcanization reactions, and to determine physical properties of the raw material and especially of the vulcanizates. The objective of the project being the production from goldenrod leaves of material that would serve as a replacement or extender for hevea rubber, control and direction of all the experimental work in both laboratory and pilot plant were dependent upon vulcanization and physical testing of its suitability for rubber factory processing and utilization. Rubber from goldenrod was known to be chemically at least similar to that of Hevea brasiliensis, and the infrared absorption* and X-ray pattern measurements (Section XVI) soon confirmed the essential structural units to be cis-isomer polymers of isoprene, however, the two rubbers differed markedly in physical properties. The viscosity of goldenrod rubber solutions averaged about 0.7 centipoise contrasted with values of 1.8 to 2.4 centipoises for hevea smoked sheet and pale crepe respectively at the same concentration. Goldenrod rubber is more readily soluble in benzol and other rubber solvents than hevea, and requires larger proportions of non-solvents such as alcohol and acetone for precipitation; a relatively small fraction is obtained on fractional precipitation, which has an intrinsic viscosity approaching the average for hevea, while a wider range of intermediate and low viscosity fractions are present in the goldenrod rubber. These results are discussed in detail in Section XIII, and are indicative of a lower degree of polymerization of the cis-isoprene units in goldenrod rubber. In addition, as shown in Section XVI, X-ray examination of the product from goldenrod revealed a constituent, which may be present in minor amount, which is crystalline in the unstretched state in both the raw and vulcanized rubber; the X-ray crystal spacings of this substance are not those of the trans-isomer, gutta-percha. It may be a non-rubber constituent, or may be a poly-isoprene fraction with a different structural arrangement, such as a mixed cis-and trans-isomer polymer or a "head-to-head" polymerization of isoprene units.

From the practical standpoint the raw product obtained by evaporating the benzol extracts in vacuo resembled raw hevea rubber only slightly. It was a very soft, sticky, greenish black mass, which would stretch slightly but had no appreciable strength or elasticity in this state. It softened almost to fluidity on heating, and stuck to both rolls of a mill where the slightest warming, especially with added chemicals, produced a paint-like mass that could be removed only by use of a doctor blade. The raw material presented almost insuperable difficulties in handling even on a laboratory scale, and the handling of large lots in

*"Differentiation of Rubber and Gutta Type Hydrocarbons in Plant Materials," S. B. Hendricks, E. J. Jones, and S. G. Wildman, manuscript privately communicated to us, pending publication.

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the pilot plant and for shipment evidently would be practically impossible except as a benzol miscella, or "cement." Earlier workers had produced vulcanizates of the rubber purified by the Edison method referred to in Section I, but the highest tensile strength obtained on those samples which could be milled was about 900 pounds per square inch. It was therefore questionable at the beginning whether this rubber could be vulcanized in such a way as to produce vulcanizates of any practical value.

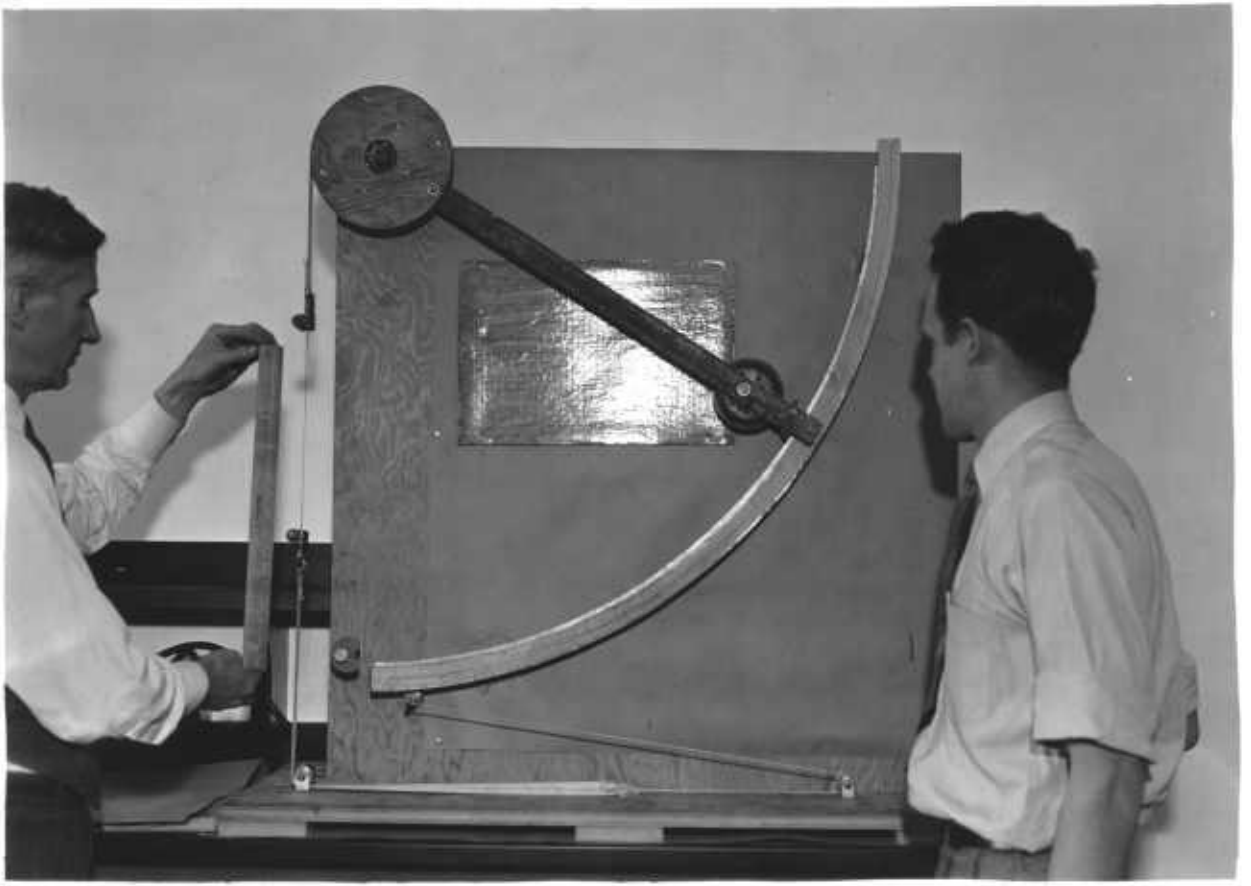
Preliminary Experiments. In the earliest part of the work, samples weighing only a few grams were available. The first experiments consisted of heating this extract, from which benzol had been removed as completely as possible, with sulphur to determine whether the combination had any of the properties of a thermosetting plastic such as rubber. By heating with 10% sulphur in an oven at atmospheric pressure for four hours at 290° F., it was found that the soft, sticky extract could be converted into a hard, non-sticky product which resembled vulcanized rubber. This product possessed some elasticity and much more strength than the untreated extract. Small supplies of commercial accelerators were received, and about 20 g. of mercaptobenzothiazole were synthesized prior to delivery of the commercial grade of Captax, so that it was now possible to study accelerated vulcanization using less sulphur. The following stocks were prepared:

Formula No.	1	2
Rubber - parts	100	100
Stearic Acid - parts	1	3
Zinc Oxide - parts	5	10
D.P.G.*- parts	1.5-3	-
Sulphur - parts	3-7	10
Captax** - parts	-	1

* - Diphenylguanidine
**- Mercaptobenzothiazole (also sold as Thiotax)

It was observed that one and one-half parts of D.P.G. were inadequate for proper vulcanization where the sulphur content was lower than seven parts. Even with the D.P.G. content raised to three parts, curing periods of over one hour were necessary. By using formula No. 2, a well vulcanized product was obtained by heating for thirty minutes at 290° F. Molds of an improvised design were next constructed in the Southern Regional Research Laboratory shops, and a small Carver press with electrically heated 6" square platens was available for vulcanization under pressure. Using Formula No. 2, except with the sulphur content decreased from ten to seven parts, a much better product was obtained by curing at 290° F. and 2000 p.s.i. for thirty minutes.

It was realized that this formulation was far from optimum. As soon as better testing equipment was available a more thorough investigation of low sulphur stocks was begun. Formula No. 3, which follows, and which is recommended by the American Society for Testing Materials for evaluating natural rubbers, was found to be entirely unsatisfactory.



IV. Fig. 1. Improvised tensile testing apparatus used for early work, prior to delivery of Scott Tester.

Formula No.	3	4	5
Rubber - parts	100	100	100
Captax - parts	0.5	0.5	1.0
Stearic Acid - parts	0.5	3.0	5.0
Zinc Oxide - parts	6.0	6.0	6.0
Sulphur - parts	3.5	3.5	3.5
Resin D - parts	-	-	1

Further investigations revealed that by increasing the stearic acid content to three parts, as shown in Formula No. 4, it was possible to vulcanize goldenrod rubber at 260° F. and 2000 p.s.i. in ninety minutes with this lower sulphur content. By raising the vulcanizing temperature or increasing the sulphur content, or by using a booster accelerator such as zinc dimethyl dithiocarbamate, the time of vulcanization could be reduced. Increasing the amounts of both the stearic acid and the Captax, as shown in Formula No. 5, resulted in reasonably good cures in one hour at 260° F., therefore this formulation was used in evaluation of routine samples with the results shown in Table I.

IV-TABLE I

Tests of Various Samples Vulcanized with Formula No. 5 - Tensile Strength and Elongation Determined with Improvised Tester

Curing Temp. °F.	Curing Time Mins.	Max. Tensile Strength p.s.i.	Ult. Elong. %	Remarks
260	60	705	550	Pilot Plant Run #1; acetone precipitated.
260	60	1120	600	" " " #1; " "
260	60	287	325	Shipment No. 1; drying experiments.
260	60	868	600	" " 2; " "
260	60	1175	700	" " 4; " "
260	60	684	550	Pilot Plant Run #1; acetone precipitated.
260	60	947	575	Shipment No. 5; drying experiments.
260	60	379	350	" " 6; " "
260	60	858	575	" " 7; " "
260	60	1260	750	" " 8; " "
260	60	1050	625	" " 9; " "
260	60	1350	675	" " 10; " "
260	60	1270	800	" " 11; " "
260	60	1060	625	" " 12; " "
260	60	1125	700	Pilot Plant Run #3; acetone precipitated.

Improvised Tensile Test Apparatus. Under the existing emergency conditions delivery of a standard Scott testing machine suitable for rubber specimens was delayed, yet it was urgently required to make at least approximate quantitative measurements of tensile strength as a guide and control for the experimental work. Two clamps were made to hold the ends of a dumbbell-shaped rubber specimen, one being attached to a spring balance graduated in pounds and ounces, and the other to a sand bag. Sand was then slowly poured into the bag, the distance between bench marks on the constricted part of the rubber specimen and

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the simultaneous weight in pounds on the balance being recorded at intervals. From these measurements it was possible to calculate rough values of ultimate elongation, tensile strength, tensile product, and modulus at any specified elongation. This apparatus was cumbersome and yielded uncertain results, as difficulty was encountered in pouring in sand at a uniform rate, but it served to indicate the order of magnitude of the strength of some of the early vulcanizates.

Much better results were obtained more conveniently and rapidly with the improvised dead weight pendulum type apparatus shown in Figure 1, which was improvised from parts already available and built at the Southern Regional Research Laboratory. In this apparatus one clamp was attached to a strip of cloth wound over the wheel revolving on ball bearings to reduce friction. A pendulum arm attached rigidly to this wheel carried adjustable weights and was followed on a graduated scale in its upward movement as it was raised by tension on the specimen. The scale was calibrated by use of dead weights. The specimen was pulled by the second clamp attached to a tape which was wound on a motor driven shaft geared to move this clamp at a rate of 20" per minute. The essential requirement met by this apparatus was the uniform rate of extension of the specimen. This apparatus worked very satisfactorily and was found later to give essentially the same results that could be obtained with a standard Scott tester.

Solution Compounding Procedures. With more accurate and reproducible methods of measuring physical properties, the study of vulcanization and the evaluation of samples was facilitated, however, results were still erratic as may be seen in Table I. Tensile strength values varied between 287 and 1350 p.s.i., and ultimate elongations between 300% and 725%. These erratic results were undoubtedly due to the softness of the stock which made proper milling impossible. The consequent poor dispersion of compounding ingredients produced spotty vulcanization, resulting in points of weakness. In addition this soft stock did not have the proper mold flow characteristics which caused air to be trapped in many of the samples as evidenced by the presence of small bubbles in the finished products.

The first experiment to produce better chemical dispersion involved the use of sulphur monochloride. Two parts, based on the rubber content, of sulphur monochloride were added to a benzol solution of rubber and the solution evaporated. This material was stiffened considerably by reaction with the sulphur monochloride. Chemicals were milled in on mixing rolls to give the final compounded stock shown below as Formula #6:

Formula No. 6		
Rubber	100	(Parts)
Sulfur Monochloride	2	"
Flectol H	1	"
Captax	1	"
Stearic Acid	5	"
Zinc Oxide	6	"
Sulphur	2	"

The resulting vulcanizate was free of spots and had a better general appearance than previous vulcanizates. From this promising lead it seemed probable that other chemicals could be dispersed thoroughly in the rubber by dissolving in benzol. In the next experiment stearic acid, sulphur, and Flectol H were dissolved in benzol and added to the rubber solution, and the benzol removed by evaporation. Captax and zinc oxide were milled in on mixing rolls to give the same formulation as No. 5. A still better product was obtained on vulcanization although a few spots could be detected. Since Captax is also soluble in benzol the next logical step was the addition of all the chemicals in a benzol solution, but the zinc oxide, which is insoluble in the solvent, could not be added in this form. As zinc oxide is required as an activator of the accelerator in vulcanization, it was desirable to have at least a part of it effectively dispersed, and this was not possible on the mill. Some zinc oxide could be added in solution as the stoichiometric equivalent of the five parts of stearic acid, by addition in the form of zinc stearate which is soluble in benzol. No stearate was added as the free acid in this procedure. The formula used for this solution compounding method was as follows:

Formula No. 7		
Rubber	100	parts
Sulphur	3.5	"
Zinc Stearate	5.5	"
Thiotax	1.0	"
Flectol H	1.0	"

The resulting vulcanizate was entirely free of spots and was very elastic but extremely weak. To a portion of this material 5.5 parts of zinc oxide were added by milling, in addition to the zinc stearate. The resulting vulcanizate was free of spots and bubbles, and the tensile strength of a sample cured for forty minutes at 260° F. was 2020 p.s.i. at an ultimate elongation of 750%. Stress strain curve determinations showed that this type of stock was flat curing between twenty and sixty minutes at 260° F. By adding 0.5 part of diphenylguanidine (D.P.G.) on the mixing rolls it was possible to make a tighter cure with much higher tensile strength. Using this booster accelerator a sample was cured for thirty minutes at 260° F., which gave a tensile strength of 2870 p.s.i. and an ultimate elongation of 525%.

With this solution method of compounding more consistent physical tests could be obtained on routine samples. An inevitable result of this procedure was that heating of the fully compounded rubber to remove benzol effected some vulcanization or "precure" of the rubber. The mixtures were, in fact, heated for some time after benzol was completely removed to effect precuring to a consistency that would mill satisfactorily, however, the material was found to vary widely in stiffness or firmness from sample to sample, and consequently to behave quite differently on subsequent milling. One of the factors causing this variation in consistency was the acetone soluble resin content of the rubber samples which varied over a wide range, and affected the

over

extent of precure, so that it was impossible to standardize on the length of heating after removal of the benzol.

Purification of the rubber by precipitation with acetone reduced the resin content, and resulted in somewhat more uniform precuring from one sample to the next, and better milling characteristics. Each sample, after vacuum evaporation of the benzol, could be heated in the steam jacketed glass vacuum pot for a sufficient length of time so that the product could be stripped readily from the glass, but the individual samples were not uniformly precured throughout the mass. The portions nearest the glass were over cured, while the top layer was still excessively sticky and had very little cure. This was largely due to the very inefficient transfer of heat in the quiescent, viscous mass, and may also have resulted from the separation from solution and settling of one or more of the chemicals necessary for vulcanization while the benzol was being evaporated. Further improvement of the method was difficult if the precuring temperature was limited to 200° F. or less, as it was in the glass pots heated by atmospheric steam, for precuring at this low temperature required addition of the full amount of sulphur, accelerator, and activating agents. At higher temperatures the extent of precure could be controlled by limiting the amounts of chemicals added, at the same time producing an intermediate product with a composition permitting some latitude in the choice of formulation for processing and final vulcanization. An equally important consideration was the fact that the pot precuring operation did not lend itself to adaptation to pilot plant, or large-scale production; vacuum driers, if obtainable at all, would be expensive and inefficient, and removal of the best precured preparations from metal drier trays would be laborious and uneconomical.

Precuring in Mechanical Mixer (Laboratory Banbury Mixer). A small Banbury internal mixer, with steam heated sides and blades, having a capacity of approximately 300 grams of rubber, was used to provide continual mixing and uniformity of the material being precured. The solution, containing both the rubber and compounding chemicals, was added gradually while benzol was evaporated at atmospheric pressure, after which the temperature was increased and the rubber precured for the required length of time. The general procedure used in carrying out these Banbury precuring experiments was as follows: approximately 1800 ml. of benzol solution, containing 300 grams of rubber and the required proportions of chemicals, were slowly poured into the heated mixer and the benzol vapors allowed to escape with no attempt being made to recover the benzol at this stage. During the first eleven runs the steam pressure in the jacket was kept at 20 to 40 pounds gage while the solution was being fed into the mixer. Temperature at this time was measured by means of a thermometer dipped into the mixture. A thermocouple was later installed just above the blades and a close check on temperature during the entire operation was possible. In runs 12 to 23 the steam pressure in the jacket was held to less than five pounds gage until all of the solution had been added to the mixer, after which it was increased according to the temperature desired.

The preliminary Banbury runs indicated, among other things, that:

(1) less precuring chemicals could be used at the higher precuring temperatures attainable in this apparatus by using steam at higher pressure than atmospheric; (2) carbon black alone did not materially set or dry up the rubber; (3) poor dispersion of zinc oxide and carbon black generally resulted if added before the rubber was properly set up. The graininess resulting from poor carbon and zinc oxide dispersion could not be overcome by milling on the rolls. This graininess was, of course, more pronounced if a compressed carbon black was used; and (4) a good quality of precured rubber could be produced in the laboratory by this means. As it was realized that in order to give this precured goldenrod rubber as much latitude as possible for final compounding, an investigation was begun to determine the minimum amounts of precuring chemicals necessary for the preparation of a stock suitable for milling and easy handling.

These Banbury precuring experiments were all made on rubber extracted from the 1942 crop or similar leaf material which contained but a small amount of non-leafy material such as bloom and stems. By making a number of trials with different combinations of sulfur and accelerators, with the other chemicals as well as the operating conditions remaining constant, the following proportions were found to produce a satisfactory precured stock from goldenrod rubber of low resin content:

Formula No. 8

Rubber	100	Parts
Sulfur	0.6	"
Thiotax	0.75	"
D.P.G.	0.3	"
Zinc Stearate	5.5	"
Zinc Oxide	5.5	"

In most of these runs, all or a part of the carbon black was added in the Banbury mixer at the end of the run after the material had set up. The zinc oxide was likewise added at this time and appeared to disperse well unless the material was quite soft. Table II gives the information on these Banbury precuring runs as to chemicals added in the mixer and on the mill, time and temperature of precuring, combined sulfur, consistency of the stock, and results of physical tests on the vulcanizates. With a few exceptions, the total amounts of chemicals added for final vulcanization are the same with variation only in the portions added in the mixer. Exceptions to this are runs 1-5 in which no D.P.G. was used, and also runs 21 and 23 in which a different accelerator, OXAF, which is the zinc salt of mercaptobenzothiazole, was employed in the hope that the formula could be simplified by omitting the zinc stearate. The stock produced with OXAF, however, did not possess good strength or handling characteristics. Run No. 7, in which all of the chemicals except 2.5 parts of sulfur were added to the benzol solution likewise did not produce a satisfactory product.

The tensile strengths reported are for tread stocks in all but a few cases for which gum stocks were used as shown in the tabulated formulas.

over

Maximum values of 3000 p.s.i. and over were obtained on the better tread stocks while less than 1800 p.s.i. were obtained on the few gum stocks prepared.

The values for combined sulfur varied from 0.20% to 0.67%, and while no definite value could be given as suitable for all stocks, it may be concluded from a consideration of the handling characteristics and physical tests that the combined sulfur for precured low resin rubber should be approximately 0.5%. Other factors being equal, precured rubber with higher combined sulfur, while possessing good milling characteristics, will not develop as high maximum tensile strength. By limiting the amount of sulfur added in the precuring step to 0.6 parts and the accelerators to 0.75 Thiotax, and 0.3 parts D.P.G., it was possible to obtain the desired values of combined sulfur with minimum control in heating.

IV-TABLE II
SUMMARY OF BANBURY PRECURING EXPERIMENTS

Run Number		1		2		3		4		5	
		Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill
Rubber (1 p. Flectol H)	Parts	100.0		100.0		100.0		100.0		100.0	
Flectol H (Additional)	"	1.		1.		1.		1.		1.	
Sulfur	"	3.5		3.5		3.5		3.5		3.5	
Thiotax	"	1.		1.		0.5	0.5	0.5		0.5	0.5
D.P.G.	"										
Zinc Stearate	"	5.5		5.5		5.5		5.5		5.5	
Zinc Oxide	"	5.5		5.5		5.5		5.5			5.5
Carbon Black	"	40.		40.		-		-			40.
Grade of Black		Kosmobile 66		Arrow Black						Kosmobile 66	
Time in Mixer (Total Mins.)		90		185		110		120		97	
Precuring Time (Mins.)		-		-		-		-		57	
Precuring Temp. - °F.		-		208		230		230		225	
S Combined in Precure - %		-		-		-		-		-	
Consistency of Stock		Grainy, soft, and sticky		Grainy, soft, and sticky		Slightly grainy, non-sticky		Non-grainy, non-sticky		Soft and non-sticky	
Opt. Cure @ 260° F.-Mins.		80		80		30		*		80	
Tensile Strength - Lbs./sq. in.		2195		370		1605				2060	
Ultimate Elongation - %		600		250		725				590	
Modulus 500% - Lbs./sq. in.		1645		-		-				1605	
State of Cure, T-50 - °C.		-		-		-				-	

* Sent to U. S. Rubber Company

(Table continued)

IV-TABLE II

SUMMARY OF BANBURY PRECURING EXPERIMENTS

(Continued)

Run Number		6		7		8		9		10	
		Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill
Rubber (1 p. Flectol H)	Parts	100.		100.		100.		100.		100.	
Flectol H (Additional)	"	0.5		0.5		1.0		1.0		1.0	
Sulfur	"	0.4	3.1	1.0	2.5	1.0	2.5	1.0	2.5	1.0	2.5
Thiotax	"	0.5	0.5	1.0		1.0		0.5	0.5	0.5	0.5
D.P.G.	"	0.3		0.3		0.3		0.3		0.3	
Zinc Stearate	"	5.5		**5.5		5.5		5.5		5.5	
Zinc Oxide	"		5.	6.		5.5		5.5		5.5	
Carbon Black	"	15.	25	40.		16.7	33.3	20.	30.	10.	40.
Grade of Black		Micronex		Micronex		Statex		Statex		Statex	
Time in Mixer (Total Mins.)		180		75		60		55		55	
Precuring Time (Mins.)		75		5		15-20		15+5		20	
Precuring Temp. - °F.		226		212		235		252		250	
S Combined in Precure - %		0.45		0.49		0.59		0.27		0.63	
Consistency of Stock		Fluid and very sticky		Grainy and sticky		Very dry, little tack		Soft, tacky, mod. sticky		Good, tacky, not sticky	
Opt. Cure @ 260° F. - Mins.		30				20		30		20	
Tensile Strength - Lbs./sq. in.		1615				3090		3450		3125	
Ultimate Elongation - %		525				500		600		510	
Modulus 500% - Lbs./sq. in.		1385				3090		2775		3085	
State of Cure, T-50 - °C.		-				Overcured		-15		-17	

** Stearic acid replacing zinc stearate

(Table continued)

IV-TABLE II
SUMMARY OF BANBURY PRECURING EXPERIMENTS
(Continued)

Run Number		11		12		13		14		15	
		Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill
Rubber (1 p. Flectol H)	Parts	100.		100.		100.		100.		100.	
Flectol H (Additional)	"	1.		1.		1.		1.		1.	
Sulfur	"	0.75	2.75	0.75	2.75	0.75	2.75	0.75	2.75	0.75	2.75
Thiotax	"	0.3	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
D.P.G.	"	0.2	0.1	0.3		0.3		0.3		0.3	
Zinc Stearate	"	5.5		5.5		5.5		5.5		5.5	
Zinc Oxide	"	5.5		5.5		5.5		5.5		5.5	
Carbon Black	"	30.	20.	30.	20.	50.		50.		50.	
Grade of Black		Statex		Statex		Statex		Statex		Statex	
Time in Mixer (Total Mins.)		75		90		135		110		158	
Precuring Time (Mins.)		40		30		75		50		98	
Precuring Temp.- °F.		255		241		252		248		282	
S Combined in Precure - %		0.34		0.40		0.20		0.32		0.45	
Consistency of Stock		Soft, tacky, and sticky		Grainy, soft, and sticky		Slightly grainy, soft, and sticky		Non-sticky, sticky on rolls		Non-sticky, handled well on rolls	
Opt. Cure @ 260° F. - Mins.		30		40		30		30		40	
Tensile Strength - Lbs./sq. in.		3205		2320		2905		2800		2530	
Ultimate Elongation - %		460		550		525		500		475	
Modulus 500% - Lbs./sq. in.		-		2130		2825		2660		-	
State of Cure, T-50 - °C.		Overcured		-12.2		-16.5					

(Table continued)

IV-TABLE II
SUMMARY OF BANBURY PRECURING EXPERIMENTS
(Continued)

Run Number		16		17	18		19		20	
		Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill
Rubber (1 p. Flectol H)	Parts	100.		100.		100.		100.		100.	
Flectol H (Additional)	"	1.		1.		1.		1.		1.	
Sulfur	"	0.6	2.9	0.6	2.9	0.6	2.9	0.6	2.9	0.6	2.9
Thiotax	"	0.75	0.25	0.75	0.25	0.75	0.25	0.75	0.25	0.75	0.25
D.P.G.	"	0.3		0.3		0.3		0.3		0.3	
Zinc Stearate	"	5.5		5.5		5.5		5.5		5.5	
Zinc Oxide	"	5.5		5.5		5.5		5.5		5.5	
Carbon Black	"	50.		50.				50.			
Grade of Black		Statex		Statex		-		Statex		-	
Time in Mixer (Total Mins.)		158		158		158		158		158	
Precuring Time (Mins.)		98		98		98		98		98	
Precuring Temp.-°F.		262		268		265		248		264	
S Combined in Precure - %		0.43		0.46		0.67		0.40		0.66	
Consistency of Stock		Non-sticky, handled well on rolls		Non-sticky, hardled well on rolls		Non-sticky, handled well on rolls		Sticky and soft		Non-sticky, handled well on rolls	
Opt. Cure @ 260° F. - Mins.		40		40		40		60		30	
Tensile Strength - Lbs./sq. in.		2610		2550		1790		1920		1675	
Ultimate Elongation - %		425		425		650		550		550	
Modulus 500% - Lbs./sq. in.		-		-		550		1485		-	
State of Cure, T-50 - °C.											

(Table continued)

IV-TABLE II

SUMMARY OF BANBURY PRECURING EXPERIMENTS

(Continued)

Run Number	21		22		23	
	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill	Added in Mixer	Added on Mill
Rubber (1 p. Flectol H) Parts	100.		100.		100.	
Flectol H (Additional) "	1.		1.		1.	
Sulfur "	0.6	2.9	0.6	2.9	0.6	2.9
Thiotax "	*1.04	0.15*	0.75	0.25	*0.892	*0.298
D.P.G. "	0.3		0.3		0.3	
Zinc Stearate "		4.0**	5.5		**3.0	
Zinc Oxide "		5.5	5.5		-	5.5
Carbon Black "	50.			50.	50.	
Grade of Black	Cabot No. 6		Cabot No. 6		Statex	
Time in Mixer (Total Mins.)	238		158		200	
Precuring Time (Mins.)	178		98		140	
Precuring Temp. - °F.	253		271		249	
S Combined in Precure - %	0.52		0.57			
Consistency of Stock	Sticky, did not handle well		Slightly sticky			
Opt. Cure @ 260° F. - Mins.	80		60		60	
Tensile Strength - Lbs./sq. in.	1690		2460		1510	
Ultimate Elongation - %	500		550		550	
Modulus 500% - Lbs./sq. in.	1690		2310		1285	
State of Cure, T-50 - °C.						

* OXAF used as accelerator replacing Thiotax

**Stearic acid replacing zinc stearate

Pilot Plant Precuring in Mechanical Mixer (Baker-Perkins Mixer). The Baker-Perkins mixer available was a vacuum, kneading type mixer with a partial steam jacket and having a capacity of approximately eight pounds of rubber. The closed vessel permitted recovery of the benzol and by use of vacuum, it was removed more completely; otherwise its operation was very similar to that of the small Banbury mixer. The blades were not heated. The first Baker-Perkins precuring run was made about nine months prior to the installation of this mixer in the pilot plant for the processing of pilot plant product. This first run was made with acetone precipitated rubber for the purpose of preparing a larger quantity of uniform precured rubber for work to be done by the Firestone Tire & Rubber Company, and the B. F. Goodrich Company (see Section V), as well as for aging tests which were made as described further in this Section under Special Tests.

Following completion of the Banbury precuring experiments, precuring runs were started on the pilot plant extracted rubber, the output of which by this time was greatly increased. The general procedure used in producing precured rubber in these Baker-Perkins runs was to add slowly a benzol solution of rubber and chemicals to the heated mixer, at the same time evaporating the benzol through condensers to an evacuated receiver. After all the benzol was removed, the mixture was heated for a short time at somewhat higher temperature to set it to the required degree. Table III gives proportions of resins in raw rubber, chemicals added in mixer, combined sulfur, consistency of stock, and the final formulation and physical tests on gum or tread stocks for all of the experimental runs made in this apparatus.

The rubber processed was not acetone precipitated and contained considerable and variable amounts of resins, which made it necessary to change the proportions of chemicals in an attempt to secure a more satisfactory product. As no rapid and accurate method of determining the concentration and resin content of the rubber solution was available at this time, the actual formulation varied considerably from the desired proportions, and only limited conclusions are possible from these runs as to optimum precuring conditions. Regardless of the proportions of chemicals used, the product in general was lower in tensile strength and handled with greater difficulty on the rolls than that obtained from raw rubber purified by acetone precipitation. Rubber from runs 2, 3, and 6, which were the best from the standpoint of milling and tensile strength, was blended by milling and shipped to the U. S. Rubber Co. for the preparation of small ash tray tire samples. Tests showed that the abrasion resistance of a composite of runs,2, 3, and 6, was considerably lower than that of the A.S.T.M. abrasion comparison Standard B and of goldenrod rubber stocks previously processed from purer rubber in the Banbury experiments. (See abrasion resistance under Special Tests.)

Approximately 85 pounds of material were produced in these runs. Because of the inferior quality of this precured rubber, as indicated by the lower tensile strength and abrasion resistance, as well as the poor handling characteristics on milling, it was decided that purification of the rubber was necessary in order to prepare a satisfactory product from the current production of the pilot plant from the 1943 crop of goldenrod.

IV-TABLE III

SUMMARY OF BAKER-PERKINS EXPERIMENTS

	1*	2*	3*	4*	5*	6*
Rubber (1 p. Flectol H) Pts.	100.000	100.000	100.000	100.000	100.000	100.000
Resin "				17.800	17.800	17.800
Sulfur "	3.5	0.600	0.783	0.600	0.600	0.735
Thiotax "	0.3	0.750	0.979	0.750	0.750	0.920
D.P.G. "	-	0.300	0.392	0.300	0.300	0.368
Zinc Stearate "	5.5	5.500	7.177	5.500	5.500	6.743
Zinc Oxide "	5.5					
Carbon Black "	-	50.000	50.000	50.000	50.000	50.000
Time in Mixer (Tot.Hrs.)		12	7-3/4	5-3/4	7	6-2/3
Precuring Time (Min.above 250° F.)		15				
Precuring Temp. - °F.						
S Combined in Precure - %	.85	0.72	0.71	0.38	0.63	0.88
Consistency of Stock	O.K.	Dry at first, then slightly sticky. Took chem. well.	Not sticky, lacey, finally handling well.	Sticky and tough. Later soft and hard to handle.	Sticky, tough, and hard to handle.	Dry and lacey.
Gum Stock-Opt.Cure @ 260°F.	30 Mins.		40 Mins.			40 Mins.
" " -Ten.Str.,#/sq.in.	1450		1690			1795
" " -Ult.Elong.-%	700		650			700
" " -Modulus 500%, Lbs./sq. in.	400		620			550
" " -State of Cure, T-50, °C.						
Tread Stock-Opt.Cure @ 260°F.		60 Mins.	80 Mins.	80 Mins.	60 Mins.	60 Mins.
" " -Ten.Str.#/sq.in.		2425	2400	2100	2035	2370
" " -Ult.Elong.-%		500	625	650	550	650
" " -Modulus 500% Lbs./sq.in.		2425	1740	1710	1605	1600
" " State of Cure, T-50, °C.						

* Added in Mixer

(Table continued)

IV-TABLE III

SUMMARY OF BAKER-PERKINS EXPERIMENTS

(Continued)

		7*	8*	9*	10*	11*
Rubber (1 p. Flectol H)	Parts	100.000	100.000	100.000	100.000	100.000
Resin	"	15.350	11.350	21.100	21.100	12.000
Sulfur	"	0.718	0.674	0.660	0.660	0.660
Thiotax	"	0.900	0.843	0.825	0.825	0.825
D.P.G.	"	0.359	0.337	0.330	0.330	0.330
Zinc Stearate	"	6.578	6.183	6.050	6.050	6.050
Zinc Oxide	"					
Carbon Black	"	50.000	50.000	50.000	50.000	
Time in Mixer (Total Hours)		6-1/3	8	9-11/12	16-3/4	11-1/4
Precuring Time (Mins. above 250°F.)						
Precuring Temp.-°F.						
S Combined in Precure - %		0.68	0.53	0.65	0.68	0.41
Consistency of Stock		Slightly sticky, but manageable.	Extremely sticky and gummy.	Very sticky and barely manageable.	Drier than No. 9 and lacey.	Very sticky.
Gum Stock-Opt. Cure @ 260°F., Mins.		40		60	60	
" " -Ten. Str., Lbs./sq. in.		1755		1655	1555	
" " -Ult. Elongation - %		675		650	625	
" " -Modulus 500%, Lbs./sq. in.		560		585	575	
" " -State of Cure, T-50, °C.						
Tread Stock-Opt. Cure @ 260°F., Mins.		40		40	40	
" " -Ten.Str., Lbs./sq. in.		2135		2100	2040	
" " -Ult. Elongation - %		675		650	625	
" " -Modulus 500%,Lbs./sq. in.		1465		1285	1400	
" " -State of Cure, T-50, °C.						

* Added in Mixer

Pilot Plant Production - Precuring in Large Loomis Mixer. In order to produce more uniformly precured goldenrod rubber at full pilot plant capacity, a mixer manufactured by the Evarts G. Loomis Company was used, which was capable of handling about 20 pounds of finished stock in a batch. Details of its construction, and of the pilot plant precuring installations and operation have been given in Section III. The important advantages for the precuring process of this apparatus over the smaller Baker-Perkins machine used for the earlier work were: (1) heating through the mixer blades as well as the jacket with steam under pressure; (2) larger free vapor space above the five gallon working volume occupied by the stock; and (3) a bottom discharge facilitating removal of the product.

Table IV presents a summary of data on the experimental pilot plant precuring of the greater part of the rubber produced. The same formulation for precuring was used in runs 1 - 8. In runs 9 - 11, the proportions of sulphur, Thiotax, and D.P.G. were increased 10%, while in the remaining run, No. 12, these three compounding chemicals were increased only 5% over the proportions used previously. In all cases, additional chemicals were milled in along with carbon black in part of the stock for tread cures, to adjust the final composition to the following vulcanization formula:

		Gum Stock	Tread Stock
Rubber	(Parts)	100.	100.
Sulphur		3.5	3.5
Thiotax		1.0	1.0
D.P.G.		0.8	0.8
Zinc Stearate		5.5	5.5
Zinc Oxide		5.5	5.5
Carbon Black (Statex)		.0	50.

By increasing the percentage of chemicals used in the precompounding steps, it was found that a stock could be prepared which was less sticky and soft, and which would handle satisfactorily on the rolls without any loss in quality. The rubber used in all large Loomis runs after #7 had been additionally purified by settling after acetone precipitation and redissolving in benzol, to remove the small amount of insoluble, suspended, waxy material which had been found to be present in fresh solutions. A considerable quantity of sludge was eliminated in this manner. The effect of this waxy material on the quality of the final vulcanizates was not determined but did not appear to be serious, however, this settling process may have contributed to the production of drier stocks in the last five pilot plant runs.

As will be noted in Table IV, satisfactory weight balances were obtained on the amount of materials charged and of stock obtained. This is of importance if the final vulcanization formula is to be accurately adjusted on the basis of rubber contained. Tensile strength measurements on the tread stocks at optimum cure varied between 2370 p.s.i. and 2920 p.s.i., and ultimate elongation between 450% and 600%. A considerable portion of this processed rubber was shipped to the U. S. Rubber Company for further study in the processing and fabrication tests discussed in Section IV. The total quantity of rubber processed in this pilot plant Loomis mixer was approximately 760 pounds.

over

IV-TABLE IV

SUMMARY OF LARGE LOOMIS EXPERIMENTS

		1*	2*	3*	4*	5*	6*
Rubber (1 p. Flectol H)	Parts	100.00	100.00	100.00	100.00	100.00	100.00
Resin	"	4.40	3.96	3.64	4.00	4.29	5.06
Sulfur	"	0.60	0.60	0.60	0.60	0.60	0.60
Thiotax	"	0.75	0.75	0.75	0.75	0.75	0.75
D.P.G.	"	0.30	0.30	0.30	0.30	0.30	0.30
Zinc Stearate	"	5.50	5.50	5.50	5.50	5.50	5.50
Zinc Oxide	"						
Carbon Black	"	50.00	50.00	50.00	50.00	50.00	50.00
Wt. Chem. & rubber used	Lbs.	26.2	26.1	26.4	22.3	20.9	20.1
Wt. of finished material	"	26.2	24.8	26.3	22.0	20.4	22.0
Time in Mixer (Total Hrs.)			11-1/3	5-1/3	3-5/6	3-2/3	4-1/12
Precuring Time - Min. above 250°F.			20		13	15	12
Precuring Temp. - °F.			250°-258°	250° - 280°	250°-270°	250° - 269°	250° - 270°
S Combined in Precure - %		0.58	0.63	0.56	0.45	0.47	0.40
Consistency of Stock		Very sticky, handled badly on rolls	Not sticky, handled very well on rolls.	Not sticky, milled very well	Slightly sticky, milled fairly well	Slightly sticky, milled fairly well	Quite sticky and soft, milled with difficulty
Gum Stock-Opt. Cure @ 260°F., Min.		20	20	20	20	20	20
" " -Ten. Str., Lbs./sq.in.		2320	2245	2460	2100	2270	2650
" " -Ult. Elongation - %		700	700	700	650	650	700
" " -Mod. 500%, Lbs./sq.in.		630	560	810	875	795	675
" " -State of Cure, T-50, °C.							
Tread Stock-Opt. Cure @ 260°F. Mins.		20	20	20	20	20	40
" " -Ten. Str., Lbs./sq.in.		2435	2410	2485	2400	2370	2920
" " -Ult. Elongation-%		600	600	550	600	600	500
" " -Mod. 500%, Lbs./sq.in.		2000	1900	2240	1935	1970	2920
" " -State of Cure, T-50: °C.							

* Added in Mixer

IV-TABLE IV

SUMMARY OF LARGE LOOMIS EXPERIMENTS

(Continued)

	7*	8*	9*	10*	11*	12*
Rubber (1 p. Flectol H) Parts	100.00	100.00	100.00	100.00	100.00	100.00
Resin "	5.06	5.95	9.28	4.50	6.61	8.33
Sulfur "	0.60	0.60	0.66	0.66	0.66	0.630
Thiotax "	0.75	0.75	0.825	0.825	0.825	0.788
D.P.G. "	0.30	0.30	0.33	0.33	0.33	0.315
Zinc Stearate "	5.50	5.50	5.50	5.50	5.50	5.50
Zinc Oxide "						
Carbon Black "	50.00	50.00	50.00	50.00	50.00	50.00
Wt. of chem. & rubber used-Lbs.	20.1	20.1	20.9	20.0	20.5	20.5
Wt. of finished material "	20.1	20.8	19.2	19.0	20.9	21.1
Time in Mixer (Total Hours)	5-11/12	3-3/4	5-1/4	4-1/2	3-7/12	3-1/3
Precuring Time - Min. above 250°F.	15	20	25	12	15	15
Precuring Temp. - °F.	250-280	250 - 290	250 - 278	250 - 275	250 - 274	250 - 278
S Combined in Precure - %	0.47	0.45	0.57	0.64	0.57	0.45
Consistency of Stock	Same as #6.	Somewhat sticky. Handled with only slight difficulty.	Extremely dry and lacey. Finally worked well.	Too dry and soft. Finally worked well.	Overcured, lacey. Finally handled very well.	Right amount of tack. Milled very easily.
Gum Stock-Opt.Cure @ 260°F., Min.	40	10	20	20	40	20
" " -Ten.Str., Lbs./sq.in.	2230	2040	1570	2290	2000	2170
" " -Ult.Elongation - %	600	650	525	600	550	650
" " -Mod. 500%, Lbs./sq.in.	1330	720	1410	1365	1265	885
" " -State of Cure, T-50, °C.						
Tread Stock-Opt.Cure @ 260° F.						
Mins.	60	20	20	20	20	20
" " -Ten.Str., Lbs./sq.in.	2730	2730	2650	2580	2735	2400
" " -Ult.Elongation - %	450	550	450	500	550	550
" " -Mod., 500%, Lbs./sq.in.	-	2410	-	2580	2370	2170
" " -State of Cure, T-50, °C.						

*Added in Mixer

Precuring in Mechanical Mixer - Laboratory Tests in Small Loomis Mixer. A small laboratory model of the pilot plant Loomis mixer was installed, which was capable of handling 650 to 700 grams of resin-free rubber in a batch. It was similar in design and operation to the large machine, but steam was not applied through the blades. Rubber solution containing precuring chemicals was heated on a steam bath and the hot solution poured into the small mixer. Benzol was removed through a water-cooled condenser leading to an evacuated receiving tank. As a result of slower heat transfer without steam heated blades, about forty minutes were necessary to raise the temperature from 250° F. to 280° F. after removal of all the benzol, whereas in the larger mixer this could be accomplished in fifteen minutes. In all cases the following precuring formula and final completely compounded formula were used:

	Precuring Added in Mixer		Final Formula After Addition of Chemicals on Mill	
Rubber	100.	Parts	100.	Parts
Sulphur	0.6	"	3.5	"
Thiotax	0.75	"	1.0	"
D.P.G.	0.3	"	0.8	"
Zinc Stearate	5.5	"	5.5	"
Zinc Oxide			5.5	"
Carbon Black (Statex)			50.	"

This procedure was used primarily to test samples of special interest which were not available in sufficient quantities to be processed in the larger Loomis mixer. Results of most of the tests made on this scale are given in appropriate special Sections of this report to follow, particularly in Kiln Drying Tests, Section VI, Retting, Section IX, and Ensilage, Section X.

Special Tests on Vulcanizates of Various Samples of Goldenrod Rubber

Effect of Aging or Storing Precured Goldenrod Rubber. The object of this study was to obtain some indication of the aging or keeping quality of goldenrod rubber which had been "precured" or partially cured.

The material used in this study was from Baker-Perkins Run #1 which had been made on acetone precipitated rubber obtained from pilot plant extraction of leaves from the 1942 crop. The precured rubber contained the following compounding ingredients:

Thiotax	0.3	Parts
Flectol H	1.0	"
Sulphur	3.5	"
Zinc Stearate	5.5	"
Zinc Oxide	5.5	"

Portions of this run were tested for tensile strength and analyzed for combined sulfur at 0, 1, 2, 3, 4, and 7 months. The following ingredients were milled into the portions used for tensile strength determinations

at the time of the tests: Thiotax 0.5 parts, and Flectol H 1.0 parts.

As Table V shows, there was no significant change in combined sulfur in seven months. While this data are not conclusive, the experiment indicates that precured goldenrod rubber could be stored at least one month without appreciable loss in maximum tensile strength of the final vulcanizate, and up to four months with only a slight loss.

IV-TABLE V

Time of Aging Months	Max. Ten. Str. p. s. i.	Ult. Elong. %	Mod. @ 500% p. s. i.	Total Sulfur	Combined Sulfur
None	1450	700	400	3.20	0.85
1	1425	760	285	3.11	0.79
2	1210	725	285	3.15	0.83
3	1260	725	195	3.14	0.86
4	1280	675	255	3.12	0.84
7	940	700	315	3.13	0.83

Tear Resistance. Tear resistance tests were made on specimens of goldenrod rubber in accordance with A.S.T.M. Designation D624-41T. A Scott tensile testing machine, equipped with grips having jaws of an approved type, was used. Crescent-shaped specimens made with A.S.T.M. Die A were used throughout.

These tests were made on (1) Banbury Run #16 stock, (2) samples of Banbury Run #20 gum stock, to which had been milled 50 parts of Statex, a special reinforcing furnace black, Kosmobile 77, an easy processing channel black, or Cabot #6, a standard channel black, and (3) stock from small Loomis #1 compounded into tube stock according to the following formulas:

	Red Tube	Black Tube 1	Black Tube 2	Black Tube 3
D.P.G.	0.8	0.5	0.8	0.8
Thiotax	2.5	2.0	2.5	2.5
Zinc Oxide	5.5	5.5	5.5	5.5
Zinc Stearate	5.5	5.5	5.5	5.5
Sulfur	2.5	2.5	2.5	2.5
Carbon	-	40 Statex	40 P-33	40 Statex
$CACO_3$	30	-	-	-
Red Oxide	5	-	-	-

Reference is made to Table II on Banbury experiments, and to the formulation given for the small Loomis runs earlier in this Section for additional information on the processing of these stocks.

In Table VI are given the results of the tear tests. It will be noted that these tear resistances are considerably lower than for similarly compounded hevea rubber. No appreciable difference in tear resistance

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was noted resulting from the use of different types of carbon black milled into the Banbury #20 gum stock. In order to determine whether a higher tear resistance could be obtained with tube stock formulation containing lower quantities of sulfur, several tests were made but no improvement was noted.

IV-TABLE VI

Sample	Tear Lbs/Inch
Banbury #16	438
Banbury #20 with Statex	482
" Kosmobile 77	497
" Cabot #6	487
Small Loomis #1 with Red Tube	67
" Black Tube 1	400
" " " 2	200
" " " 3	250

Permanent Set. The permanent set in this study refers to the percent increase in the distance between one inch benchmarks on a specimen which has been stretched to, and held at, an elongation of 300% for 10 minutes, then released and allowed to recover for 10 minutes. An elongation of 300% was used although this was somewhat less than 3/4 of the ultimate elongation as specified by standard procedure. Due to the type of clamps employed and the low tear resistance, it was impossible to stretch the specimens to the specified length without breaking at the clamp.

Table VII gives the results of permanent set tests on samples of pilot plant extracted rubber from the 1942 and 1943 crops of goldenrod leaves. This rubber was acetone precipitated, processed in the Banbury or the small Loomis mixer, compounded and vulcanized under conditions producing maximum tensile strength. Reference is made to the Table II on Banbury runs and to the discussion of small Loomis runs for additional information. The values of set obtained on these samples, 16% - 25%, appear to be considerably higher than for similarly compounded hevea rubber. The high set for Banbury #12 (52%) should not be considered representative for goldenrod rubber as Run #12 was abnormal in other respects, probably due to the quality of rubber being processed.

The tube stocks which were prepared from small Loomis #1 stock (1943 crop) contained compounding ingredients as given in formulations under the section on Tear Resistance. They contained less sulfur and more accelerator than the above samples which were compounded in the usual manner. While the permanent set values were somewhat lower for the tube samples, the difference is not appreciable.

IV-TABLE VII

Sample	Permanent Set %
Banbury #9	21
" #10	24
" #11	22
" #12	52
" #13	25
Small Loomis #1	
Red Tube	16
Black Tube 1	20
Black Tube 2	20

Abrasion Resistance. Abrasion tests were made in accordance with A.S.T.M. Designation D394-40, Method A, using the duPont abrader. Test specimens were prepared from rubber processed in the Banbury mixer, large Loomis mixer, and from a composite of Baker-Perkins runs 2, 3, and 6. For further information, reference is made to Tables II, III, and IV pertaining to these runs. The samples were cured under conditions which produced maximum tensile strength. Purchased A.S.T.M. comparison standards of Type B, and No. 2/0 emery paper were used throughout these tests. A set of comparison standards was run for every set of specimens tested and it was found that the volume loss per horsepower hour of the standards was 200 cc. plus or minus 5%, except in a few instances where the losses dropped to 183 or increased to 211. Table VIII gives the results of the abrasion tests in terms of cu. cm. loss per horsepower hour, which, of course, is inversely proportional to the resistance to abrasion. An inspection of Table VIII shows the abrasion resistance of samples from Banbury runs 9-13, which were made on acetone precipitated rubber, was equal to or better than that of A.S.T.M. comparison Standard B. Banbury runs 14-17, which were made on rubber which had not been acetone precipitated and consequently was higher in resins, showed lower abrasion resistance than the standard. The large Loomis runs, although made on acetone precipitated rubber, gave lower abrasion resistance for the first four runs made, while the fifth run was equal to or better than the Standard B. The composite of Baker-Perkins runs 2, 3, and 6, which was made with rubber containing about 12% resins, as it was not acetone precipitated, showed much lower resistance to abrasion than the standard. These tests show that it is possible to obtain good abrasion resistance on goldenrod rubber if the content of acetone soluble resins is less than 5% to 6%.

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IV-TABLE VIII

Sample	Cu. Cm. Loss * per H.P. Hour
Banbury #9	185
" #10	180
" #11	178
" #12	210
" #13	174
" #14	255
" #15	248
" #16	235
" #17	251
Large Loomis #1	236
" " #2	244
" " #3	240
" " #4	227
" " #5	189
Composite of Baker-Perkins #2, #3, & #6	374

* The cu. cm. loss/H.P. Hour of A.S.T.M. comparison Standard is 200 plus or minus 5%.

Indentation (Hardness). Tests were made in accordance with A.S.T.M. Designation D531-41, using the Pusey and Jones Plastometer fitted with the 1/8" ball point. The results are reported in terms of Pusey and Jones Number which is the indentation, in hundredths of a millimeter, produced by a 1/8" steel ball under a load of 1 kilogram for one minute. As molds for vulcanizing samples of specified size (3 x 1-1/4 x 1/2 in.) were not available at the time, and these tests were made on abrasion specimens (2 x 2 x 1 cm.) which are considerably smaller in size. These specimens were prepared from acetone precipitated rubber from the 1942 crop and processed in the Banbury mixer. Reference is, therefore, made to Table II on Banbury runs for further information. The test samples were cured under conditions which had yielded the maximum tensile strength.

Table IX gives the results of the indentation tests. These values for indentation, when converted to hardness values by available conversion charts, indicate that the range of hardness of these goldenrod samples is approximately the same as for similarly compounded hevea rubber.

IV-TABLE IX

Sample Banbury Run No.	8	9	10	11	14	15	16	17	22
Pusey & Jones Indentation No.	66	61	67	70	70	64	73	75	98

IV-TABLE X
SUMMARY OF PHYSICAL TESTS OF GOLDENROD RUBBER

Test	Method	Range of Values	Determined by
		TREAD STOCKS	
Tensile	A.S.T.M. (Scott)	2500 - 3200 p.s.i.	Sou.Reg. Res. Lab.
Ult. Elong.	Die D	450 - 600%	" " " "
Modulus 500%	0.125x0.060"	2500 - 3000 p.s.i.	" " " "
T-50		-15° to -20° C.	" " " "
Hardness	Shore	56 - 71	" " " "
Indentation	Pusey-Jones	62 - 107	" " " "
Perm. Set		20 - 25%	" " " "
Abrasion	DuPont	175-240 cc./H.P. Hour	" " " "
Tear	Crescent	440-500 Lbs./in.	" " " "
Aging	O_2(80°C.) 48 Hrs.	Opt. Green 2600-2900 p.s.i. Cure Aged 2040-2220 p.s.i.	" " " " " " " "
"	O_2 48 Hrs.	Green 1600-1700 p.s.i. Aged 1500-1600 p.s.i.	U. S. Rubber Company
Bend Flex.	DeMattia	1st crack 17-53,000 cycles Failure 57-80,000 cycles	Sou.Reg. Res. Lab.
Extens. Fatigue	DeMattia	1st crack 10-30,000 cycles Failure 20-40,000 cycles	" " " "
Flex. Comp.	Goodrich	Comp. set 25% Temp. rise 74-92° F.	" " " "
Resilience	Yerzley	65%-86%	" " " "
Rebound	Firestone	Room t. 32% 212° F. 46-55%	Firestone
Sp. Gr.		1.14-1.15	Sou.Reg. Res. Lab.
Plasticity	Mooney	Uncured 10 (212° F.)	U. S. Rubber Company
"	"	Uncured 19-29 (160° F.)	Sou.Reg. Res. Lab.
		GUM STOCKS	
Tensile	A.S.T.M. (Scott)	2000 - 2600 p. s. i.	Sou. Reg. Res. Lab.
Ult. Elong.	Die D	550 - 700%	" " " "
Hysteresis	Absol.(U.S. Rubber)	Room t. 1.0 Mod. 2.4 280° F. 0.3 Mod. 2.6	U. S. Rubber Company
Hysteresis	Torsional	Room t. 0.07 - 280° F. 0.06 -	U. S. Rubber Company
Plasticity	Mooney	Uncured 10 (160° F.)	Sou. Reg. Res. Lab.
Hardness	Shore	34 - 37	" " " "
Indentation	Pusey-Jones	169 - 184	" " " "
Resilience	Yerzley	93 - 95%	" " " "
		PRECURED RUBBER	
Plasticity	Mooney	20-43 (160° F.)	Sou. Reg. Res. Lab.

V-INDUSTRIAL PROCESSING AND FABRICATING TESTS

As soon as goldenrod rubber was available in two to three pound lots of a quality fairly representative of that obtainable by solvent extraction, samples were submitted to several of the largest rubber manufacturing companies. The first tests undertaken were primarily to check our vulcanization techniques and results against those obtainable by prospective users of the product, and to serve as a guide to further development of the basic process. At this time it was essential to determine the most desirable of several forms in which the rubber might be produced, and to concentrate upon preparation of a product best suited to the probable industrial and emergency uses for the rubber. It had been determined that precuring afforded a means of rendering the rubber tractable to milling, compounding, and vulcanizing in the laboratory, with satisfactory results, but it was of prime importance to determine whether this product could be processed on factory equipment.

In the solvent extraction process the rubber leaves the solvent recovery still as a viscous benzol solution, containing up to 20% of rubber, protected by a small amount of a suitable antioxidant technically termed "cement." To obtain rubber free of solvent, this solution is evaporated to dryness in shallow pot stills under vacuum, producing the material in a sticky form as "raw rubber." An alternative procedure to vacuum drying involves addition to the 20% rubber solution of a benzol solution containing the soluble compounding ingredients, and evaporating the benzol completely while working the resulting mass in a steam jacketed kneading type mixer. The only insoluble ingredient of the vulcanizing formula is the excess zinc oxide, which is added after all of the benzol has distilled off, either in the mixer or subsequently on the mill, and heating is continued at 100° - 105° C. until the rubber is slightly precured, and is dry and firm enough to be readily removed from the mixer. This preparation is designated as "precured rubber." Samples of these three products, amounting in most cases to two pounds or more, were submitted to United States Rubber Company, Firestone Tire & Rubber Company, and the B. F. Goodrich Company by whom tests were begun with the cooperation of members of the technical staff of the Southern Regional Research Laboratory.

Tests Performed by the United States Rubber Company. The 20% benzol solution was considered for use in trying the method of compounding in solution, for use in making dipped articles, and for fabric coating. A test coating on Fruit-of-the-loom cloth was made and vulcanized.

The raw rubber was considered for blending with extremely dry and non-tacky rubbers such as Buna-S. Tests were made on stocks containing 30% and 50% of goldenrod rubber, without added carbon black, and on a stock containing 50 parts of carbon black added to a 50-50 blend of goldenrod and Buna-S rubber. Processing qualities were observed, and determinations made of tensile strength, elongation, permanent set, state of cure, and hysteresis. For this purpose the goldenrod rubber was not regarded

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as simply a tackifier, such as mineral rubber or asphaltic modifiers, but as a blending agent with distinct rubber qualities that might be used in blends up to 40%- 50%.

The precured goldenrod rubber was considered for use as such, and two preparations were submitted for testing; one containing all necessary vulcanizing ingredients except carbon black, and another from which both carbon black and the excess zinc oxide were omitted. Ability to mill, calender, and process these materials with and without added carbon black was investigated, and additional accelerator and antioxidant were incorporated in milling. The gum stocks (without carbon black), and the tread stocks (with carbon black) were vulcanized and determinations were made of tensile strength, elongation, permanent set, state of cure, and aging, on both types of stock. A calendering test was made on one batch of tread stock, and part of a similar batch was used in molding and fabricating a rubber heel of goldenrod rubber. No mixtures of other rubbers with precured goldenrod rubber were considered. Most of the dry, precured stock was used in the milling tests, with added accelerator and antioxidant, and carbon for tread stock.

Milling Test No. 1. This was made with material of Banbury 4B which had the most extensive precuring, and contained initially:

Sulfur	3.5 p.
Accelerator-Thiotax (mercapto-benzothiazole)	0.5 p.
Antioxidant-Flectol H	1.5 p.
Zinc Stearate	5.5 p.
Zinc Oxide (added dry in the Banbury)	5.5 p.

It had been run in the Banbury mixer a total of 115 minutes, including the time for distillation of benzol, and had been brought to a final temperature of 105° C. for at least 45 minutes. This was milled and tested as gum stock.

The sample batch amounting to a total of 221 g. of material (rubber plus vulcanizing ingredients) was put on the rolls, and an extra 0.43 parts of Thiotax and 0.22 parts of Naugatuck antioxidant JZF milled in. With the front roll at 100° F., and back roll at 120° F., the stock milled fairly well for three minutes, after which it broke down rather abruptly, as in our previous experience, and became sticky so that it was removed from the rolls with difficulty. The rolls were cooled to 80°- 85° F., front, and 105° F., back, and the stock was put on and milled more satisfactorily for an additional 1-1/2 minutes. It was the opinion that it would mill much better with fillers such as zinc oxide, or with carbon blacks. The rolls were warmed slightly, and opened to a wider setting, and the stock was sheeted. It did not sheet well enough, and was too tacky to calender, and no attempt was made to run the sheet through the calender rolls. The Mooney plasticity of the sheeted stock was only 10, compared with 80 - 90 for a good milled hevea stock. Half of the sheeted stock was cut into several blanks for

shoddy cures. Results of physical tests as reported by the General Laboratories, United States Rubber Company, are given in Table I, Gum Formula A E A.

Milling Test No. 2. Banbury batch 4A was used for this test. It consisted of part of the same larger batch from which 4B was made, and therefore had the same composition as the material used in Test No. 1, but had been removed from the mixer with 5 minutes less precuring time. The time of heating, including removal of benzol, was 110 minutes, and it had been subjected to the final temperature of 105° C. for about 40 minutes. It was milled and tested as a tread stock.

Precured stock (237 g.) was put on warm rolls, and the extra 0.43 parts of Thiotax and 0.22 parts of JZF milled in within one minute. With the roll temperatures at 110° F., front, and 120° F., back, 58.25 parts of standard channel black were added and milled in within three minutes. As the carbon black was taken up the stock could be worked more satisfactorily, but was described as very "short." It became much smoother after four minutes additional milling and could be sheeted. The total milling time was eight minutes from the time it had been put on the rolls, and the roll temperatures at the end were 105° F., front, and 140° F., back. The sheet was uniform enough, and the stock had good "building tack," but appeared to be just beginning to acquire the gloss or "patent" characteristic of a good dispersion of carbon black. For this reason it was put back and given three minutes additional milling, after which it had a good "patent" gloss, and sheeted readily and uniformly enough to be suitable for calendering. It was calendered on cold calender rolls set at 0.033", and produced a satisfactory, uniform sheet sufficiently dry to handle. Test data on the vulcanizates are in Table I, Tread Formula A E B.

Milling Test No. 3. The material for this test consisted of 100 gs. of the already compounded gum stock made in Test No. 1, from rubber of Banbury batch 4B. The purpose was to determine whether the milling properties of this material, which had been poor as a gum stock, could be improved by addition of carbon black. It was put on the rolls and 58.25 parts of standard channel black added rapidly with rolls at 80° F., front, and back. The stock smoothed considerably, and the black was taken up by the rubber only gradually, on repeated passes through the rolls, requiring three minutes for complete addition of the necessary 58.25 parts. After five minutes total milling the material became somewhat sticky, but could still be cut and stripped from the rolls. Break down was extensive after seven minutes, and the material was now difficult to remove. The front roll had warmed to 90° F. In 7-1/2 minutes the stock was very sticky and had to be cut and dabbed off the rolls. By cooling the rolls it was possible to sheet this soft, sticky stock. Shoddy cures were made and tested with the results shown in Table I, Tread Formula A E C.

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V-TABLE I

Properties of Vulcanized Goldenrod
(Data furnished by General Laboratories, U. S. Rubber Company, Passaic, New Jersey)

Rubber from Southern Regional Research Laboratory

Banbury 4B
Gum Formula - AEA

Min. At 260° F.	Green Tensile	% E	Permanent Set	T-50 500% E	Aged Tensile 48 Hrs. O_2 Bomb
20	792	700	.17	-11.5	1200
30	970	660	.18		
40	725	560	.12	-22.3	578
60	606	550	.09	Broke	158

Banbury 4A
Tread Formula - AEB

Min. At 21#	Green Tensile	% E	Set	T-50 350% E	Aged Tensile 48 Hrs. O_2 Bomb
30	1400	570	.73	+0.6	1500
40	1600	590	.80	-1.8	1600
60	1600	520	.64	-6.6	1600

Banbury 4B
AEC

30	1180	550	.67	+ 2.0	1300
40	1620	540	.78	- 2.5	1300
60	1700	510	.80	- 6.4	1500
80	1600	420	.52	-10.5	1500

Goldenrod-Buna-S Gum and Black Stocks. Gum and black stocks containing raw goldenrod and Buna-S were compounded as follows, the figures representing the weight in grams of each ingredient:

Code	AEU	AEV
Buna-S	50	143
Goldenrod	50	57
Channel Black	50	--
JZF	0.5	1.0
Zn Stearate	5.5	11
Zn Oxide	5.5	11
Thiotax	1.0	1.5
Sulfur	3.5	5.5

During mill mixing, occasion was taken to make certain tentative observations. A 5:2 Buna-goldenrod mixture is satisfactory in its behavior on the mill and is believed to be commercially processable as a skim coat stock at 105° - 110° F. A 1:1:1 Buna-goldenrod-black mixture is also believed commercially processable. A 1:1 Buna-goldenrod mixture is satisfactory on the mill when thick (±50 gauge) but filler would be required to restore good calendering without sticking to the mill roll. All three mixtures; that is, 5:2, 1:1, and 1:1:1, revealed good "building tack" -- a property which Buna-S alone does not possess. The foregoing presupposes no considerable elevation of temperature. The stocks were vulcanized and tested as shown in Table II.

The 2:5 gum stock AEB when vulcanized gave very low tensiles, as does Buna-S alone. The 1:1:1 black stock AEU gave tensiles of 1000-1300 p.s.i.; that is, lower than the 2800 p.s.i. obtainable with Buna-S and black alone, and also lower than the 1600 p.s.i. obtainable with goldenrod and black alone. The difficulty appears to be that with the acceleration, temperature, and time used in the present work, the Buna-S was not vulcanized at all when the goldenrod was well cured, while correspondingly the goldenrod in the mixture was badly overcured by the time Buna-S could be considered well vulcanized. This was true in both the gum and black stocks. The gum slabs showed progressive fall in elongation from 830% (30') to 280% (180'), and the black slabs showed a corresponding fall in elongation from 580% (60') to 200% (180'). It is possible that a compounding study of the vulcanization of Buna-S-goldenrod mixtures might resolve this difficulty, but on the basis of present available data the recommendation would have to be not to mix Buna-S and goldenrod.

A compilation of the hysteresis values of both the goldenrod and Buna-S-goldenrod vulcanizates, in comparison with pale crepe and Buna-S, is presented in Table III. The absolute hysteresis of goldenrod rubber is slightly higher than that of pale crepe, but in general, probably comparable to hevea rubber. Buna-S has higher absolute hysteresis. The absolute hysteresis of the Buna-S-goldenrod vulcanizates, just as would be expected for a mixture, is intermediate between the values observed

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for the component rubbers. Torsional hysteresis of goldenrod is on the high side. Thus, mixing goldenrod with Buna-S: a. increases building tack; b. decreases hysteresis; c. allows processing, (assuming proper proportions); d. decreases tensile and elongation; e. introduces a problem of properly vulcanizing a mixture of rubbers differing widely in rate of cure.

V-TABLE II

Vulcanization of Goldenrod Plus Buna-S
(SRRL Pilot Plant 5)

Min. at 260° F.	Tens.	% E	Set	T-50
		AEV - 30% Goldenrod plus 70% Buna-S		
30	148	830	.37	650% -33.4
60	218	520	.15	500% broke
90	237	400	.10	" "
120	250	320	.02	" "
150	217	310	.04	" "
180	184	280	.09	" "
		AEU - 1:1:1 of Goldenrod, Buna-S, and Channel Black		
60	1300	480	.30	350% -25
90	1300	330	.20	broke
120	1100	240	.10	"
150	1100	210	.07	"
180	945	200	.04	"

V-TABLE III

Hysteresis Values of Goldenrod and Goldenrod Plus Buna-S Compared with Pale Crepe and Buna-S

	Pale Crepe		Buna-S		Goldenrod (AEA)		Buna-S plus Goldenrod *	
			Gum Stocks - Absolute Hysteresis					
	Hys.	Mod.	Hys.	Mod.	Hys.	Mod.	Hys.	Mod.
Room T.	0.5	4.0	3.0	5.1	1.0	2.4	2.3	5.4
280° F.	0.3	5.0	1.1	4.4	0.3	2.6	1.1	5.3
			Tread Stocks - Absolute Hysteresis					
Room T.	7.0	9.5	13.5	13.7	--	--	9.5	10.4
280° F.	3.5	7.6	4.5	8.8	--	--	3.7	7.0
			Gum Stocks - Torsional Hysteresis					
Room T.	--	--	--	--	.07	--	.087	--
280° F.	0.04	--	.048	--	.06	--	.06	--
			Tread Stocks - Torsional Hysteresis					
Room T.	0.38	--	--	--	--	--	.43	--
280° F.	.18-.22	--	.22-.34	--	--	--	.21-.34	--

*Gum stocks: 30% Goldenrod, 70% Buna-S. Code AEV
Tread " : 50% " , 50% " ". Code AEU

Tests Performed by Firestone Tire and Rubber Company. Raw goldenrod rubber was considered primarily for blending with Government Rubber-Styrene type (GR-S); however, a small batch was compounded with considerable difficulty on the mill, adding a large amount of carbon black, and the resulting stock was vulcanized and tested. A series containing 5%, 10%, 20%, and 50% of goldenrod added to GR-S rubber was compounded, and in addition 10 parts of raw goldenrod rubber were milled into a ready compounded master batch of GR-S, containing 100 parts of the latter rubber. Milling was done on a 2-1/2" x 7" laboratory mill in 50 g. batches, so numerous tests could be made, and milling and sheeting properties were observed, but calendering was not actually tried. Plasticity of some of the uncured stock was determined. Tests on the vulcanizates included tensile modulus, tensile strength, elongation, and rebound.

A determination was made by the Williams method of the plasticity of the uncompounded raw goldenrod rubber. A sample of the raw rubber was treated by a method employing stepwise precipitation from toluene solution which is being employed in studying synthetic rubbers. Six fractions were obtained, ranging from very soft and sticky material to a hard residue lacking rubber-like properties. Intermediate fractions could be stripped readily from the glass beakers and were not so sticky and very elastic. A nitrogen determination was made on the raw rubber and the amount found to be 0.09%, which cannot account for the fast curing of this rubber.

Precured rubber was considered for use as such, without blending with other rubbers, and preliminary trials made of the use of p-amino-phenol as an additional antioxidant, and of Santocure (cyclohexylamine-mercaptobenzothiazole) as an additional accelerator, in gum stocks. Tread stocks with 50 parts of carbon black were also prepared, using the added p-amino-phenol and Santocure. An interesting experiment was made on the wetting of the carbon black to aid its dispersion in this soft type of rubber. The same determinations of physical properties were made as in the case of the raw rubber blends. The percentage of combined sulfur and the plasticity of the precured material in the unvulcanized state were also determined.

The precured rubber supplied for the tests had the following initial composition:

Rubber	100 parts
Captax	0.5 parts
Flectol H	1.0 "
Zinc Stearate	5.5 "
Zinc Oxide	5.5 "
Sulfur	3.5 "

Both gum and reinforced (tread) stocks could be made from the precured rubber by using warm mill rolls and taking care that the temperature of the rolls did not vary too much. Although the stocks became coherent and rather sticky on the rolls, they did not smooth out and maintained a "grainy" appearance. Even after considerable milling the black could

be rubbed off the stocks, thus indicating a poor dispersion. Better properties were obtained when a small amount of water was added to the black before mixing although the stock became stickier and more difficult to handle on the mill. It is possible that a better dispersion of the black was obtained by this procedure although the dull appearance of uncured stock was not improved.

The cured stocks possessed good elasticity and elongation although the moduli and tensiles were poor compared to those that may be obtained from crude guayule or cryptostegia (latex) rubbers. Additions to the formulation made during milling, and the results of tests made on the vulcanizates are given in Table IV.

Although the raw rubber was soft and extremely sticky, moderate amounts (up to 30%) could be mixed with GR-S without too much difficulty. The chief characteristics of such stocks compared to GR-S stocks were slightly lowered modulus and tensile properties with a moderate increase in tackiness. The Williams plasticity of the raw rubber (Y_3 @ 185° F.) was 0.50. Tables V and VI present the results of tests made on the various blends of goldenrod rubber with GR-S.

At a later date a special sample of precured goldenrod rubber was submitted at the request of the Firestone Company, which had the same composition as given on page 8, except that the 1.0 part of Flectol H was replaced by an equal amount of p-amino-phenol. This was tested and found in 20-80 mixtures with GR-S to give slightly higher tensile strengths and moduli than the sample containing Flectol H, although milling characteristics and plasticity were unaltered. Results of tests on this sample are compiled in Table VII.

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V-TABLE IV

Data for Physical Tests on Partially Cured Goldenrod Rubber
(Firestone Tire & Rubber Co.)

The following compounds were mixed on the small laboratory mill in batches based on 50 grams of goldenrod rubber.

	R53900	R53901	R53902	R53903	R53904
Partially cured goldenrod rubber	115.3	115.3	115.3	115.3	115.3
p-amino-phenol	0.5	-	-	0.5	0.5
Captax	0.5	0.5	-	1.0	1.0
Santocure	-	-	0.3	-	-
Channel black (Spheron)	-	-	-	50	50
Water (added to black)	-	-	-	-	10
	116.3	115.8	115.6	166.8	(176.8)*

*(including water in black)

Milling Characteristics: All stocks were rough and crumbly. (Similar to reclaim except stickier)

	Cure	R53900	R53901	R53902	R53903	R53904
Modulus @ 400%	10' @ 280° F.	50	150	150	550	1050
	20' " "	250	200	200	800	1000
	30' " "	250	200	200	900	1200
	40' " "	250	200	250	950	1250
	50' " "	150	-	-	850	1250
Tensile Strength	10' @ 280° F.	550	550	550	1200	1800*
	20' " "	600	550	650*	1250	1450
	30' " "	850*	550*	450	1400*	1550
	40' " "	500	250	250	1250	1500
	50' " "	150	150	100	1150	1350
Elongation	10' @ 280° F.	715	720	675	565	550
	20' " "	650	710	655	530	510
	30' " "	670	655	620	520	485
	40' " "	645	505	500	480	440
	50' " "	400	380	305	470	425

*cures used for rebound balls.

Rebound (%)					
at room temp.	39	36	38	32	32
at 212° F.	61	52	58	46	52

V-TABLE V

Study of Goldenrod Rubber--GR-S Mixtures
(Firestone Tire & Rubber Co.)

	R53906	R53907	R53908	R53909	R53910	R53911	R53912
GR-S	95	90	80	50	50	---	---
Guayule	---	---	---	---	50	---	100
Goldenrod rubber	5	10	20	50	---	100	---
Zinc Oxide	5	5	5	5	5	5	5
Santocure	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Stearic Acid	3	3	3	3	3	3	3
Channel Black	50	50	50	65	50	100	100
Bardol	3	3	3	---	1.5	---	1.0
Pine Tar	3	3	3	---	1.5	---	1.0
Sulfur	2	2	2	2.75	2.75	3.5	3.5
	167.2	167.2	167.2	176.95	164.95	212.7	214.7

A stock containing 100 percent GR-S was not tested in this series.

	Cure							
Modulus @ 400%	15' @ 290°F	*	*	*	1100	1400	---	---
	30' " "	1400	1400	*	1650	---	---	---
	50' " "	1700	1700	1450	1800	---	---	---
	70' " "	2050	2050	1550	1950	---	---	---
	90' " "	*	*	1650	*	*	*	*
Tensile Strength	15' " "	*	*	*	2350	1800	950	1450
	30' " "	2900	2200	*	2350	1950	1050	1300
	50' " "	2325	2425	2375	2550	1600	1050	1250
	70' " "	2475	2500	2525	2400	2100	900	1250
	90' " "	*	*	2600	*	*	*	*
Elongation	15' " "	*	*	*	655	490	250	230
	30' " "	600	530	*	495	340	185	180
	50' " "	485	515	525	500	270	200	185
	70' " "	445	480	535	465	310	165	200
	90' " "	*	*	535	*	*	*	*
Rebound (%) @ Room Temp.	50' " "	35	34	33	26	28**	21**	20**
@ 212° F.		43	42	41	37	36	21	20

*This cure of this stock was not tested.

** cured 30' @ 290° F.

V-TABLE VI

Use of Raw Goldenrod Rubber as an Extender in a GR-S Tread Stock
(Firestone Tire & Rubber Co.)

		R53531	R53905
R53531		--	167.2
GR-S		100	--
Zinc Oxide		5	--
Santocure		1.2	--
Pine tar		3	--
Bardol		3	--
Stearic Acid		3	--
Channel Black		50	--
Sulfur		2	--
Goldenrod		--	10
		167.2	177.2
	Cure		
Modulus @ 400%	60' @ 280° F.	1175	850
	80' " "	1425	1025
Tensile strength	60' " "	3100	2600
	80' " "	3150	2950
Elongation	60' " "	610	660
	80' " "	530	700
Rebound	80' " "		
at room temp.		32	33
at 212° F.		43	43

V-TABLE VII

Data on Vulcanizates with p-Aminophenol Antioxidant
(Firestone Tire & Rubber Co.)

	R53940	R53941	R53942	R53943	R53944	R53945
GR-S*	100	80	80	90	80	70
Guayule	-	20	-	-	-	-
Goldenrod Rubber (with 0.5% Flectol H)	-	-	20	-	-	-
Goldenrod Rubber (with 1% para aminophenol)	-	-	-	10	20	30
Pine Tar	2.6	2.6	2.6	2.6	2.6	2.6
Bardol	4.0	4.0	4.0	4.0	4.0	4.0
Channel Black*	50	50	50	50	50	50
Zinc Oxide	5	5	5	5	5	5
Santocure	1.2	1.2	1.2	1.2	1.2	1.2
Stearic Acid	3	3	3	3	3	3
Sulfur	2	2	2	2	2	2
	167.8	167.8	167.8	167.8	167.8	167.8

*Added as a black - GR-S masterbatch.

Physical Testing Data

	Cure						
Modulus @ 400%	20' @ 290° F.	750	800	700	1050	1000	1100
	50' " "	1900	1450	1400	2000	1550	1550
	80' " "	2050	1600	1600	1150	1800	1600
Tensile Strength	20' " "	2150	2050	1800	2350	2250	2150
	50' " "	2450	2300	2300	2450	2400	2150
	80' " "	2400	2500	2300	2650	2500	2400
Elongation	20' " "	730	715	650	615	650	600
	50' " "	465	540	535	440	515	485
	80' " "	430	530	505	450	490	500
Rebound (%)							
Room Temp.	50' " "	41	37	37	41	39	38
At 212° F.	50' " "	50	46	47	51	47	49

Tests Performed by the B. F. Goodrich Company. Both raw and precured goldenrod rubber which were submitted to this Company were considered primarily as blending agents to extend and modify GR-S rubber. Test stocks were prepared on fairly large experimental mills, in approximately 2 pound batches, and in each case carbon black was added to the extent required for a tread stock test. Six batches were milled and compounded, containing on the basis of the rubber used, 10%, 20%, 30% of raw goldenrod in GR-S, and 10%, 20%, 30% of precured goldenrod in GR-S. Their conclusions were that modulus at 300%, tensiles, and elongations favor use of raw rubber blends, while precured blends were better in tear, flexing, and hysteresis, based on test data summarized in Tables IX and X.

The raw rubber was also blended up to 20% with hevea smoked sheet. Three hundred grams of plasticated smoke sheets (2176) were broken down on a mill and then sheeted around the front roll. Goldenrod rubber was added very slowly with time being allowed for each portion to blend in before more was added. With the addition of 75 grams of goldenrod rubber, the batch became quite soft but could still be milled without too much difficulty. However, the addition of a small amount more of the rubber caused the mix to stick to the rolls. The practical limit, therefore, appears to be one part goldenrod rubber to four parts smoked sheets. Based on 100 parts rubber, this gives a 20 parts replacement of the hevea.

The recipes used are as follows:

Recipe	A	B	C
Smoked sheets	80	80	100
Goldenrod	20	20	-
Zinc Oxide	6	6	6
Sulfur	3.5	3.5	3.5
Captax	0.5	0.5	0.5
Stearic Acid	0.8[x]	0.8[x]	0.5
Sodium acetate	-	1.0	-

[x] 2.0 parts stearic acid based on the amount of goldenrod rubber present and 0.5 parts based on the smoked sheets.

V-TABLE VIII

Properties of Vulcanizates with 20 Parts Hevea Smoked Sheet Replaced by Raw Goldenrod Rubber. (Data of B. F. Goodrich Company)

Compound	Time at 260° F.	Tensile	700% Mod.	Elong.	Goodrich Plast. on Uncured Smpl. 30°C.	70°C.
A	20	975	-	1075	46.2	88.0
	40	2300	575	970		
	60	2400	775	900		
	80	2600	950	840		
	100	2700	975	880		
	120	2500	1025	855		
B	20	2400	850	900	36.4	87.4
	40	2725	1600	815		
	60	3075	2000	810		
	80	3000	2125	790		
	100	2875	2375	745		
	120	2975	2425	785		
C	20	2200	650	920	13.6	66.6
	40	3050	1300	875		
	60	3300	1475	845		
	80	3300	1825	815		
	100	3075	1675	805		
	120	3300	1675	820		

Although the addition of goldenrod rubber to hevea rubber in the A.C.S. test recipe produces a slow curing rubber with poor physical properties, it has been found that by proper compounding, 20 parts of the 100 parts smoked sheets can be replaced by goldenrod rubber without any decrease in tensile and modulus properties. If more than a one-fifth replacement is attempted, the mix becomes too soft and tacky for easy handling on the mill.

A small sample of the precured rubber alone was tried on a very small laboratory mill, and as it softened rapidly 50 parts of carbon black were added at once. Additional precured rubber was put in the batch to reduce the carbon black to 25 parts, and to more nearly fill the small mill. It was held for subsequent remilling to incorporate additional accelerator. Microscopic examinations were made of both raw and precured goldenrod rubber as submitted, and of a milled and compounded blend of 30% goldenrod in GR-S stock.

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V-TABLE IX

Compounded and Uncompounded Goldenrod Rubber for Extenders for Styrene Synthetic Rubber

(Data of B. F. Goodrich Co.)

Compound No.	57DS126			57DS127			57DS128			58DS200		
Recipe												
Styrene Synthetic Rbr.	90.0			80.0			70.0			100.0		
Raw Goldenrod Rubber	10			20.0			30.0			Blank		
Channel Black	45.0											
Zinc Oxide	5.0											
Sulfur	1.75											
Santocure Accelerator	1.50											
	153.25			153.25			153.25			153.25		
Cure at 280° F.	300%	T	E	300%	T	E	300%	T	E	300%	T	E
15 Min.	600	1600	575	400	1100	540	800	2200	600	Break	only	600
30 "	1600	2000	350	1100	2000	450	1350	2400	460	1300	2500	510
45 "	1800	2000	315	1400	2100	400	1500	2150	400	1600	2400	400
75 "	2000	2100	305	1400	2100	380	1500	1900	380	1800	2250	350
150 "	-	1800	280	1500	2200	370	1600	2100	370	2000	2100	315
Special Tests	17x280		32x280	17x280		32x280	17x280		32x280	17x280		32x280
Durometer Hardness	53		62	47		60	56		66	62		65
% Schopper Rebound	36		40	30		39	29		34	38		40
Goodrich Plasticity 5x35°	6.92			10.8			21.9			7.5		
85°	26.1			57.7			73.1			16.5		
100°	27.2			62.8			66.3			14.0		
Tear at Room Temperature	10.5		34.15	6.15		36.35	14.4		34.7	28		27
Tear at 212° F.	3.4		17.4	0.7		19.1	6.1		19.5	18		18
Cycles, 30x280° F.	60,000			140,000			60,000					
Hysteresis at 212° F.	*I.C.%	ΔT	% P.S.	I.C.%	ΔT	%P.S.	I.C.%	ΔT	% P.S.	I.C.%	ΔT	% P.S.
25x280	30.7	106	B.019	21.3	64	26.8	22.9	94	36.5	21	53	18
40x280	23.4	76	27.7	20	49	14.6	20.7	77	Bo?	20	47	13

* I.C.%, Initial Compression %

Δ T Temperature Rise

% P.S., % Permanent Set

V-TABLE X

Compounded and Uncompounded Goldenrod Rubber for Extenders for Styrene Synthetic Rubber

(Data of B. F. Goodrich Co.)

Compound No.	57DS129			57DS130			57DS131			58DS200		
Recipe												
Styrene Synthetic Rbr.	90.0			80.0			70.0			100		
Precured Goldenrod Rbr.	10.0			20.0			30.0			Blank		
Channel Black	45.0											
Zinc Oxide	5.0											
Sulfur	1.75											
Santocure Accelerator	1.50											
	153.25			153.25			153.25			153.25		
Cure at 280° F.	300%	T	E	300%	T	E	300%	T	E	300%	T	E
15 Min.	1100	2100	440	1100	2200	460	1800	2000	310	Break	only	600
30 "	2000	2200	320	1800	2000	310	-	1700	240	1300	2500	510
45 "	1900	1900	300	-	1800	260	-	1700	230	1600	2400	400
75 "	-	1900	260	-	1700	250	-	1600	200	1800	2250	350
150 "	-	1900	250	-	1700	250	-	1600	200	2000	2100	315
Special Tests	17x280		32x280	17x280		32x280	17x280		32x280	17x280		32x280
Durometer Hardness	57		66	59		64	65		70	62		65
% Schopper Rebound	38		44	40		45	40		41	38		40
Goodrich Plasticity 5x35°	4.71			3.78			5.02			7.5		
85°	20.5			22.4			48.1			16.5		
100°	15.6			32.8			43.3			14.0		
Tear at Room Temperature	23.05		27.4	25.5		28.65	38.65		31.2	28		27
Tear at 212° F.	11.4		13.8	17.4		15.7	16.8		17.1	18		18
Cycles, 15x280° F.	180,000			210,000			70,000					
" 30x280° F.	40,000			25,000			45,000					
Hysteresis at 212° F.	*I.C.%	△T	%P.S.	I.C.%	△T	% P.S.	I.C.%	△T	% P.S.	I.C.%	△T	% P.S.
25x280	21.4	54	21	19.6	46	21.2	16.2	47	15.3	21	52	18
40x280	18.2	41	11.2	18.4	37	11.3	13.9	38	9.9	20	47	13

* I.C.%, Initial Compression %
△ T Temperature Rise
% P.S., % Permanent Set

Summary of Tests by Rubber Manufacturers
Raw Goldenrod Rubber

Milling and Fabricating Properties. Raw goldenrod rubber as produced at present is too sticky and soft to be milled, and handling the material even with a large excess of added carbon black was extremely difficult and unsatisfactory, although a stock was finally produced which gave a maximum tensile strength of 1050 pounds per square inch. In blends with GR-S type synthetic rubbers, the raw goldenrod rubber can be milled satisfactorily up to substantial percentages in the mixture. Amounts below 10% in fact have little or no effect on the milling properties of the synthetic; from 10% to 30% the stock is softened and building tack is definitely increased; and a stock containing 50% is excessively softened and becomes sticky without gaining much more in tack. In blends up to 30% the material is amenable to usual milling, compounding, sheeting, and calendering practices, and its properties for tubing should be improved.

Vulcanizing (Curing). These experiments bring to the fore the problem of compatibility of goldenrod and synthetic rubbers as to their vulcanizing characteristics, which must differ rather widely. Fractionation confirms the observation that the polymer chain lengths of both types vary over wide ranges, but that the average chain length of goldenrod is small while that of the synthetic rubber is large. Goldenrod rubber is fast curing; as produced its acidic resin content is very low and it requires added stearic acid; and its optimum curing temperature is low. Synthetic rubber is slow curing; it contains fatty acid due to soap used in the emulsion polymerization so no addition is required, and its optimum curing temperature is high. It is significant that one company cured the blended stocks at the low temperature of 260° F. suitable for goldenrod, one chose an intermediate temperature of 290° F., and one proposed to cure the blends at the high temperature of 310° F. best suited to the synthetic rubber.

Tensile Properties. When cured at 260° F. the addition of goldenrod to synthetic rubber resulted in lower ultimate tensile strengths and elongations than are obtained with either rubber alone. Similar blends cured at 290° F. gave ultimate tensile strengths approaching that of synthetic rubber alone, ranging from 2900 pounds per square inch for the 5% goldenrod blend, to 2550 pounds per square inch for the 50% goldenrod blend, appreciably above the value obtained for goldenrod rubber alone. A parallel blend of 50% guayule in the same synthetic stock gave only 2100 pounds per square inch maximum tensile strength at a somewhat longer curing time. The modulus, or tensile strength at 400% elongation, of all blends was decreased, but was relatively higher in respect to the ultimate strength for the 50% blend in which it was 1800 pounds per square inch. Elongation at break of the blended stocks was considerably improved by even the lower percentages of goldenrod, and reached values of 500%--600%. This effect appeared to be disproportionate to the amount of goldenrod rubber incorporated. In a test on a vulcanizate containing but 10 parts of goldenrod to 100 parts of GR-S synthetic as its rubber constituents, and cured for 80

minutes at 280° F., elongation was increased from 530% to 700%. The modulus at 400% elongation was decreased from 1425 to 1025 pounds per square inch, and the ultimate tensile strength from 3150 to 2950 pounds per square inch. In view of the contradictory results obtained by curing at a temperature as low as 260° F., further checks on the optimum curing conditions for the blended rubbers will be necessary.

Hysteresis and Rebound. In a gum stock, prepared in this case from precured goldenrod rubber, the hysteresis value of goldenrod alone approaches that of pale crepe rubber, and is generally comparable to hevea rubber. Hysteresis of straight GR-S gum stock is higher, which is undesirable because of the increased tendency to heat in flexing. The values for tread stocks are of greater practical significance; in these stocks containing carbon black hevea (pale crepe) has an absolute hysteresis of 7.0 (room temp.), and 3.5 (280° F.), while GR-S alone gave values of 13.5 (room temp.), and 4.5 (280° F.). A blended stock of 50 - 50 goldenrod-GR-S rubber tread stock had absolute hysteresis values of 9.5 (room temp.), and 3.7 (280° F.), near those of hevea rubber.

Rebound tests as made by the Firestone Company are an index of fatigue and elastic properties, and a measure of the "efficiency" of the rubber. In this test, blending of up to 20% goldenrod in GR-S synthetic rubber had a negligible effect on the rebound efficiency, in spite of a decreased tensile modulus and greatly increased elongation. A blend containing 50% goldenrod showed a decreased rebound efficiency. This property of conferring greater extensibility in GR-S blends containing goldenrod rubber should be correlated with the reduction of hysteresis in similar blends.

Precured Goldenrod Rubber

Milling and Fabricating Properties. Precured goldenrod rubber can be handled on a mill without addition of carbon black if the temperature of the rolls is kept below 140° F., and a certain amount of additional compounding ingredients can be worked in, but it is doubtful if the operation would be practical. Milling time is limited because of the readiness with which this rubber breaks down, and because of the "nerve" and softness of the stock, dispersion of added solids is difficult. Gum stocks were prepared and sheeted satisfactorily for testing purposes, but these stocks could not be calendered.

As over ninety-eight per cent of all manufactured rubber goods contains fillers, principally carbon blacks, the processing properties of tread stocks containing carbon black are of greatest importance. Addition of 50 parts or more of carbon black to the precured rubber on the mill resulted in a stock that could be handled satisfactorily, and milled for a much longer time. Working of the stock was continued until a good dispersion of black was obtained as indicated by a glossy sheen. The stock could be sheeted to a uniform, smooth sheet, and a sheet of one batch of tread stock was calendered satisfactorily on cold

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calender rolls set at 0.033". These stocks had good building tack. Opinions varied on the effect of the stickiness and softness of the stock in fabricating operations, but it was believed that the material could be handled. It was also evident that these goldenrod rubber tread stocks could be extruded in the "tubing" process for making tire treads. The stickiness of the material in the form prepared in these tests made it doubtful that inner tubes could be molded successfully from extruded forms of this stock.

Vulcanizing (Curing). Because of the partial curing to which the rubber had been subjected in its preparation, some adjustment is probably necessary in the final vulcanizing conditions. That these conditions are not extremely critical is evident from the concordant results on both gum and tread stocks of this rubber, cured in one laboratory at 260° F. for periods ranging from 20 - 60 minutes, and in another at 280° F. for 10 - 50 minutes. A test for the state of cure (T-50) indicated that at the lower temperature the gum stocks were somewhat overcured, while the tread stocks were in most cases undercured. This test was not run on vulcanizates made at the higher temperature; nevertheless in most of the tests at both temperatures maximum points were obtained in the time of cure-tensile strength curves, indicating that an optimum cure for the conditions used was reached.

A determination of the chemically combined sulfur in one lot of the precured goldenrod rubber gave 0.96%, of a total sulfur content of 3.09%. This was considered to be too high, and further work was urged to determine the very minimum extent of precuring which will permit handling and milling of the material. Work toward this objective was undertaken at the Southern Regional Research Laboratory, as described in Section IV. It was suggested that the extent of precuring might be controlled more effectively by limiting the amount of sulfur used, rather than by reducing the amount of accelerator as was done in some of the preparations made for use in these tests. Opinions differed as to the use of special accelerators rather than Captax (mercaptobenzothiazole) which is the most widely used accelerator in rubber manufacturing practice. Introduction of rapid, or "booster" accelerators, and types that work only at high temperatures may be objectionable in the precured rubber because of the complication of the subsequent final vulcanization process. Captax is best understood, and its action is easily controlled, but in combination with stearic acid it has a softening effect on hevea rubber, and goldenrod rubber is inherently soft. The suggestion was made that further work be done on addition of fillers and carbon black to the rubber solution in an attempt to prepare raw rubber in a form that can be handled without any precuring, but preliminary trials previously made along this line had not been very promising.

Tensile Properties. When cured at 260° F. and 280° F. the highest ultimate tensile strengths obtained for gum stocks were 970 pounds per square inch, and 850 pounds per square inch, respectively. These are very much lower than gum stock tensiles obtainable with hevea

rubber, but are appreciably higher than the gum stock tensiles of GR-S type rubbers. Even at 260° F. the indication of the T-50 test for state of cure, and the decrease of elongations with increased curing times, indicated that these gum stocks may have been overcured. The tensile modulus at 400% elongation of goldenrod gum stocks was low, in line with its very high ultimate elongations reaching over 700%. The importance of tests on gum stocks is for the evaluation of the quality of the rubber itself, rather than determination of its properties for use in manufactured rubber goods.

The highest ultimate tensile strengths obtained on regular tread stocks containing 50 and 58 parts of carbon black were 1400 pounds per square inch at 280° F., and 1700 pounds per square inch at 260° F. The tensile modulus at 400% elongation was considerably higher than that of the gum stocks, while the ultimate elongation was lower, but still over 500%. The effect of wetting the carbon black in one special tread stock was of particular interest. The black was first uniformly wetted with 20% of its weight of water, and added to the batch in the usual manner on the mill. The cooling effect increased the breakdown and stickiness of the stock, but it was satisfactorily milled and sheeted. This stock, cured at 280° F., gave an ultimate tensile strength of 1800 pounds per square inch, 50% higher than the same cure with unwetted carbon black, with 10 minutes curing time; the tensile modulus at 400% elongation was almost double that of the comparable control, and the ultimate elongation was 550% compared to 565% for the control. With a longer cure for 30 minutes the stock made without wetting gave higher values than it did for only 10 minutes curing, but not equal to this wetted stock at any curing time.

Hysteresis, Rebound, and Aging. As stated above in connection with hysteresis tests of goldenrod-GR-S blends, the absolute hysteresis of straight goldenrod rubber approaches that of hevea rubber when tested as gum stock. Rebound values on the gum stocks were 36% - 39% at room temperature, and 52% - 61% at 212° F., about three-fourths of the values obtainable with hevea rubber gum stocks. The tread stocks gave values of 32% at room temperature, and 46% - 52% at 212° F. The higher value of 52% was given by the stock in which the wetted carbon black had been used. The values are somewhat higher for straight goldenrod tread stocks than for the blends with GR-S synthetic rubber. Aging tests were made on a few samples, and indicated that the aging characteristics of both gum and tread stocks of goldenrod rubber are good, and there is no inherent tendency to deterioration in this type of rubber when vulcanized.

Both preparations - raw and precured - were of definite interest, and improvements in methods of preparation and quality of the products were indicated for further development. Results of these preliminary processing tests had shown that:

1. Raw goldenrod rubber can be blended with GR-S synthetic rubber up to at least 30% with desirable results, and has the desirable

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properties of increasing building tack, reducing absolute hysteresis, and increasing elongation of the product, and can replace up to 20% of hevea with satisfactory results.

2. If goldenrod rubber is used for blending with GR-S, solution compounding and precuring of the rubber seems to be unnecessary and would be undesirable; a method of handling and shipping the sticky raw rubber must be devised.

3. Precured goldenrod rubber has desirable properties and can be satisfactorily processed by milling, calendering, and extruding in the form of tread stocks with carbon black filler. Improvement of the quality of this product for the best possible processing to develop its maximum properties can be made by limiting the extent of precuring to a minimum.

4. If milling and compounding procedures are completely worked out for goldenrod rubber, either precured or in blends with GR-S, the quality of the stocks produced will permit subsequent manufacturing operations without any difficulties.

The results summarized served to establish the most imperative lines of work on perfection of a practical process for producing goldenrod rubber, and to indicate experimental studies which were of importance in developing its optimum properties for industrial application. The most important advance was the change in the direction of the development of the precuring procedure toward the use of less sulfur as a means of limiting the extent of precure. The accelerator was held at the same or higher levels, still below the final amount required for complete vulcanization, so that more latitude remained in the possibilities of final compounding on the mill. Later the use of a combination of D.P.G. with Captax resulted in a considerable uniform increase of tensile strength, particularly of gum stocks, and permitted more effective adjustment and control of the conditions and extent of precure applied.

At the time that substantial quantities of precured rubber, in 8-10 pound lots of somewhat more satisfactory consistency and degree of precure, became available, advantage was taken of the offer of the U. S. Rubber Company to mold a number of small advertising model tires such as are used on ash trays, as a demonstration and test of the suitability of a tread stock for extrusion and molding. At an earlier date this Company had carried out laboratory vulcanizations and physical tests on a half pound sample of fully compounded stock, to determine the correlation of results obtainable by their test procedures and those of the Laboratory. This sample was a composite of material precured in the small Banbury mixer using reduced amounts of sulfur and accelerators, the final additions of these chemicals being made during milling.

STOCK FOR CORRELATION OF TEST DATA

	Parts Added		
	In Mixer	In Milling	Total
Rubber	100	-	100
Sulfur	0.6 - 1.0	2.9-2.5	3.5
Thiotax	0.5 - 0.75	0.5-0.25	1.0
D.P.G.	0.2 - 0.3	0.1-0	0.3
Flectol H	1.0	-	1.0
Zinc Stearate	5.5	-	5.5
Zinc Oxide	5.5	-	5.5
Carbon (Statex)	50.0	-	50.0

The same curing temperature and times were used both at the U. S. Rubber Company and the Southern Regional Research Laboratory, but the former made the cures in Chelsea molds approximately 0.1" thick, instead of 0.06" thick standard molds as used by the Laboratory. The results were as follows:

CORRELATION OF TEST DATA

Time of Cure At 260° F.	Tensile Strength p.s.i.		Ultimate Elong. %		T-50 °C.
	U.S.R.	S.R.R.L.	U.S.R.	S.R.R.L.	U.S.R.
20	2800	3085	560	500	-13.4
30	2650	3015	510	475	-31.0
40	2650	3080	440	450	-25.6

This indicates that there is around 300 to 400 p.s.i. difference in the tensile, attributable to the difference in thickness of the test specimens. This is not an uncommon result and is generally known to be true. The results indicated a flat curing stock of good quality. A single abrasion test, on which too much value cannot be placed, showed not much difference between this stock and the abrasion standard used by the U. S. Rubber Company. The correlation of results was sufficiently close that tests on precured or compounded stocks made at the Southern Regional Research Laboratory would adequately measure the suitability of the stock for use in further testing and processing by the rubber manufacturer.

For the purpose of molding the small ash tray sample tires, approximately 26 pounds of fully compounded stock was prepared. This larger supply was a composite of three batches precured in the Baker-Perkins mixer, in which about 9-10 pounds of material could be handled in a batch. After extensilve milling and vulcanizing tests on the first dozen runs of rubber prepared in this mixer, the three batches were selected as having the most desirable properties in regard to both processing and vulcanizate quality. The rubber used up to this time had

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not been purified by reprecipitation in large quantities, therefore the composite batch selected for this test contained somewhat more acetone soluble material, 11.9% of the crude rubber, than is desirable when maximum tensile strength is required. The small model tires did not require material of the highest tensile strength for their fabrication. Several variations of the formula and curing conditions were tried, to obtain the best possible results with the given quality of the precured goldenrod rubber available.

The composition of the precured rubber, the additional chemicals and carbon black added in milling, and the final formulation are shown in Table XI. After blending proportional amounts of the three lots of precured material to make a mill batch of about 500 g. (maximum capacity of the laboratory mill) and smoothing out the rubber, the accelerators, sulfur, and zinc oxide were milled in and dispersed to prepare gum stock on the following typical schedule:

Rolls: 4" diameter, 7" wide (between guards).
12 r.p.m. front roll, 16 r.p.m. back roll.
Water cooled to 63°F.-65°F.

Additions	Spacing		Time
None-Smoothing	0.033"		2 min.
Accelerators	0.033"		1½ "
Sulfur	0.043"		2 "
Zinc Oxide	0.043"		2 "
None-dispersing	0.050"		2½ "
		Total	10 min.

The gum stock was sheeted five times, and was not too sticky to be handled and cut from the chilled rolls by regular milling technique. All of the material was milled into gum stock, requiring the milling of eighteen batches on the small mill.

This gum stock was next returned to the mill in batches of about 350 g., allowing for the addition of 50 parts carbon to make a 450 g. (approximately 1 pound) finished batch within the mill capacity. Carbon dispersion was best accomplished by milling on warm rolls, with 120° F. front roll, and 100° F. back roll, spaced 0.035" initially until enough carbon was taken up to prevent sticking; most of the carbon was then added in 5-6 minutes with the rolls opened to 0.067-0.070", and final dispersion accomplished by 4-5 minutes milling at a roll spacing of 0.060". At the end of the milling the rolls were rapidly cooled, and as soon as the temperature of the stock was lowered it could be cut from the rolls and sheeted five or six times. Twenty-seven such tread stock batches were milled to produce the amount required. Table XI gives the results of vulcanization and test data obtained on this stock at the Southern Regional Research Laboratory.

V-TABLE XI

Fully Compounded Tread Stock for
U. S. Rubber Co. Molding of Ash Tray Tires

	Parts Added		
	In Precure	In Milling	Final Parts
Rubber (resin-free)	100	-	100
Resins (acetone soluble)	13.5	-	13.5
Sulfur	1.0	2.85	3.85
Thiotax	0.95	0.15	1.10
D.P.G.	0.43	0.45	0.88
Zinc Stearate	5.63	-	5.63
Zinc Oxide	-	5.63	5.63
Flectol H	1.12	-	1.12
Carbon Black (Statex)	-	50.0	50.0

Vulcanization and Test Data

Composite Gum Stock Sample:

Cure	Modulus p.s.i.		Maximum Tensile	Ult. Elong.
@ 260° F.	300%	500%.	p. s. i.	%
20 Min.	173	655	1655	650
40 "	240	1000	2000	600
60 "	235	950	1455	550
@ 276° F.				
30 Min.	240	915	1730	600
45 "	270	850	1490	600

Random Samples of Individual Mill Batches-Tread Stocks

Cure	Modulus p.s.i.		Maximum Tensile	Ult. Elong.
@ 260° F.	300%	500%	p. s. i.	%
40 Min.	710	1900	2200	575
40 "	765	1900	2270	550
40 "	785	1935	2170	550
40 "	800	1965	2300	575
- Averg.	765	1925	2235	562

Curing Time-Tensile Data on Sample of One Representative Batch-Tread Stock

Cure				Ult.	T-50
@ 260° F.				Elong.	°C.
20 Min.	590	1540	2205	625	-
30 "	690	1840	2265	600	-14.2,-14.6
40 "	740	1840	2230	575	-16.8,-17.2
50 "	755	2000	2265	550	-17.2,-17.4
60 "	820	1935	2230	550	-19.7,-20.4
70 "	785	2000	2165	550	-
@ 276° F.					
15 Min.	655	1605	2230	600	-13.6,-14.0
30 "	785	1900	2330	625	-18.3,-19.6
45 "	785	1935	2265	550	-20.4,-21.4

The stock was formed for molding by extrusion in a factory type tubing machine, and was molded without any difficulty in a nine place gang mold to produce about 30 of the advertising sample tires. These "tires" are, of course, a single piece molding from a simple blank of homogeneous stock, with no ply construction involved. This test indicated the possibility of handling properly compounded precured goldenrod rubber in factory operations and of proceeding to the fabrication of a built-up tire involving ply construction.

Bicycle Tire Manufacturing Test

In order to test the practical value of goldenrod rubber on a larger scale and to determine conclusively the possibility of handling large amounts in regular factory operations, it was decided with the cooperation of the U. S. Rubber Company, to manufacture a factory production run of bicycle tires. The fabrication of bicycle tires involves all of the operations of automotive tire manufacture, but could be carried out with a smaller amount of rubber to produce a sufficient number of tires for a fairly representative production test. Although the completed standard 26x2.125" bicycle casings are made from a little over two pounds each of vulcanized rubber stock containing about a pound and a quarter of crude rubber, a minimum of one hundred pounds of rubber was necessary to prepare sufficient stock to load factory processing mills and calenders. Small samples for laboratory examination were first submitted to the Development Department of the Indianapolis plant of the U. S. Rubber Company, and later approximately 170 pounds of precured rubber was supplied for the purpose of making the tires.

The precured rubber was produced in full pilot plant-scale production from general harvest material of the 1943 crop. For this production the precuring operation was carried out in the large jacketed Loomis mixer, the batch capacity of which was 20-22 pounds of product, and the shipment was made up of ten individual batches of rubber. As the conditions and control of precuring were still in the development stage at this time, the different batches varied in plasticity and milling properties, although their composition was essentially the same. All of the rubber used had been purified by reprecipitation with acetone to reduce the resin content to an average of approximately 5%, and the amounts of precuring chemicals added were very nearly the same for all batches. Three of the batches were made employing a 10% increase in the amount of sulfur and accelerators, to produce firmer and drier material that would stand longer milling. Before milling the entire 170 pounds of material, a 50 pound test batch was milled blending equal weights of each batch, and a final laboratory study was made to determine the best compounding formula applicable to this homogeneous composite batch of rubber.

The results of the formulation study are given in Table XII. Choice of the formula was restricted by two essential conditions: the additions of carbon black and zinc oxide should be such as to reduce the excessive softness and stickiness of the stock and give satisfactory milling characteristics, and at the same time the best possible physical properties should be obtained with the restriction of final vulcanization

conditions to 10 minutes cure at 330° F., the regular operating conditions in the factory molds, where the goldenrod tires were interspersed with the regular production. In the laboratory platen molds for test strips, curing 8-10 minutes at 307° F. gives results equivalent to those obtained at 330° F. in the watch case tire molds in the factory. The final formulation given in Table XII is in error by about 1% because of the slightly higher resin content of the composite base stock, 5.24 parts, instead of the value 3.8% applicable to a preliminary sample composed of the first two only of the ten batches finally used. The correction has not been made because the effect of this slight variation upon the results obtained was negligible. The use of a combination of half channel and half furnace black was especially advantageous in improving milling properties. The use of a much larger amount of zinc oxide in the best stock, No. 10, is noteworthy; in previous experience at the Southern Regional Research Laboratory even 5.5 parts of zinc oxide had a marked effect in making the stock softer and stickier, but addition of the zinc oxide simultaneously with the combination of carbon blacks permitted satisfactory handling, and the increase to at least 17.5 parts improved the tensile strength considerably. The tensile-time curing data at the bottom of Table XII show a reasonably safe, flat curing curve, with a maximum at 10 minutes, the required factory vulcanization time schedule.

For the manufacturing operations, four mill batches were made of the predetermined composition and following weights:

	Lbs.	Ozs.	Parts
Base stock	30	8	111.45 (98.7 rubber)
Sulfur		13	3.00
Captax		1	0.23
D.P.G.		2	0.46
Zinc Oxide	4	12	17.60
Carbon black EPC (Wyex)	6	14	25.5
" " HMF (Gastex)	6	14	25.5
	50	0	

The mill was one of the standard 40" by 15" diameter machines, operating at a front roll surface speed of 22 yards per minute (16.8 r.p.m.) and back roll speed of 30 yards per minute (22.9 r.p.m.). No particular difficulty was encountered during milling by regular factory operators. Sulfur and accelerators were first put in together, followed by the mixture of zinc oxide and carbon blacks, the total milling time being 30 minutes. Toward the finish the stock softened but did not become excessively sticky, and was readily rolled off in a manageable sheet. The speed of the mill used was the slower of two standard mill speeds in use, as it was felt that a high speed mill would almost certainly effect too much heating and softening of the stock. The rolls were water-cooled, but the stock after milling was at a temperature of 130°F.-140° F.

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V-TABLE XII

FORMULATION & TEST DATA ON BICYCLE TIRE STOCK

(Data of U. S. Rubber Co.)

Base Stock	Prelim. Samp. 2 Batches	Composite 10 Batches
Goldenrod rubber (resin-free basis)	100.00	100.00
Resins (acetone soluble)	3.80	5.24
Sulphur	0.60	0.62
Thiotax	0.75	0.77
D.P.G.	0.30	0.31
Zinc Stearate	5.50	5.50
Flectol H	0.50	0.50
	111.45	112.94

In this discussion, the term "base stock" will apply to the above.

Laboratory Work

To eliminate the excessive softness and stickiness of the stock to obtain good processing and physical properties, the following batches were mixed and cured:

	1	2	3	4	5	6	7	8	9	10
Base Stock	111.45	111.45	111.45	111.45	111.45	111.45	111.45	111.45	111.45	111.45
Sulphur	2.90	2.90	2.90	2.90	2.90	2.90	2.90	2.90	2.90	2.90
Thiotax	.25	.25	.25	.25	.25	.25	.25	.25	.25	.25
D.P.G.	.50	.50	.50	.50	.50	.50	.50	.50	.50	.50
Zinc Oxide	5.50	5.50	5.50	10.00	17.50	25.00	10.00	10.00	10.00	17.50
HMF Black(Kosmos 40)	50.00	100.00	150.00	50.00	50.00	50.00	50.00	50.00	50.00	*25.00
EPC Black (Wyex)	-	-	-	-	-	-	-	-	-	25.00
**Magnesium Oxide	-	-	-	-	-	-	5.00	10.00	15.00	-
Shore Hardness	65	85	94	64	66	65	62	64	65	66
Tensile/in.^{2}	1970	1320	1090	1200	1960	1960	1690	1810	1710	1950
Elongation in %	540	160	70	320	460	440	460	510	500	470
Comments on milling	Sticky	O.K.	Dry & Leathery	O.K.	O.K.	O.K.	Sticky	Sticky	V. Sticky	O.K.

*SRF (Gastex)

**Very difficult to disperse

Cure time - 8 min. @ 307° F.

Laboratory Batch #10 was chosen for factory trial. The base stock used in factory work was a blend of equal portions of 10 batches received.

Continued

V-TABLE XII
(continued)

Physical data on factory mixed stock follows:

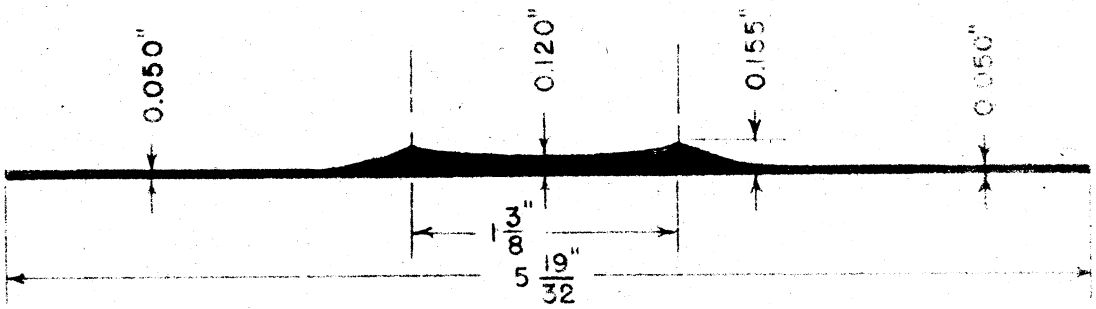
Cure in minutes @ 307° F.	3	5	8	10	15
Tensile - Lbs./in.^{2}	2000	2030	1950	2160	1870
Elongation in %	650	550	470	510	470
Modulus @ 200%	400	525	605	730	535
300%	725	895	1050	1215	1010
500%	1490	1860	-	2190	-
Shore Hardness	60	62	66	65	64
Tear - Lbs./inch thickness *	9.6	9.6	5.5	4.9	4.2
Specific Gravity - 1.207					

* Tongue-shear tear test, modified method of Wright, I.E.C.(Anal. Ed.) Vol. 1, 17-20 (1929).

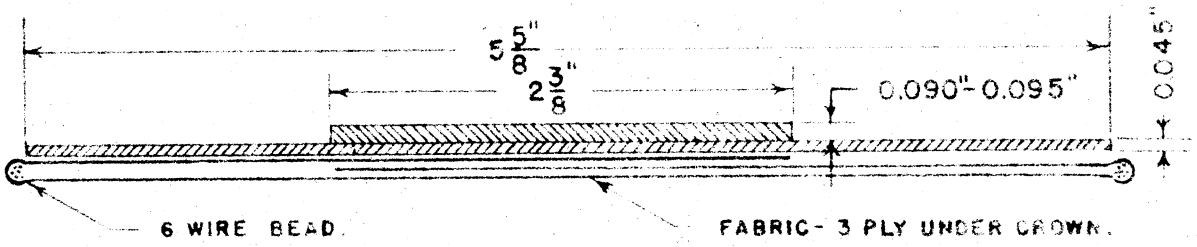
The construction of the standard 26x2.125 U. S. No. 500 chain tread casings is illustrated in Figure 1. Attempts to extrude, or "tube," the cover of the casing in one piece (Figure 1,A) including tread and sidewalls, were unsuccessful, as the stock heated and became too sticky to handle upon extrusion. As an alternative procedure the stock was calendered to gage, and rolls of stock were prepared in two strip sizes: 5-5/8" wide by 0.045" thick, and 2-3/8" wide by 0.090"-0.095" thick. By laying these strips one upon the other as in Figure 1,B, in building each hoop cover, an amount and distribution of rubber stock approximately equivalent to section A could be obtained, and this procedure was adopted. A standard cotton cord fabric, coated by frictioning with the same stock of goldenrod rubber, was built into a center lap construction with two plys around each bead and three plys under the center crown, as shown in Figure 1,B. Cord angle was 48°, determined as explained below by the cutting of the coated fabric. The hoops were preformed and vulcanized in the requisite molds to the shape and cross-sectional structure approximately illustrated in Figure 1,C.

Calendering of all the requisite parts of the tire was a continuous operation, on a standard three-roll factory calender. Rolls were cooled to 70°-80° F., and the machine was kept loaded manually by addition of successive charges of the milled stock. The 45 gage 5-5/8" strip was cut off first and the strip rolled in a varnished cambric liner (Textolin), after which the gage was increased to 90-95 and a 2-3/8" strip cut off and rolled in a similar liner. These operations were carried out by the regular calender crew. Considerable difficulty was encountered due to stickiness of the stock, but was largely overcome by soaping the rolls to assist separation of the strip of stock. The soft stock strip broke occasionally. On the basis of these observations, it was evident that a skim coated fabric could not be prepared from this soft material, however, the goldenrod stock lent itself ideally to skim coat application. The bottom speed of the bottom calender roll was increased with respect to the other two, and the rubber was frictioned onto standard 40" wide fabric, first on one side and then on the other. This operation proceeded very well, and about 50 yards of coated fabric were rolled in a wide Textolin liner. This fabric was later cut into strips at a 48° angle to the cord direction, by regular operators using a Spadone fabric cutting machine. There was occasional tendency for the material to stick to the knife blade, but not too much difficulty was encountered. Cloth liners were used to roll the cut fabric.

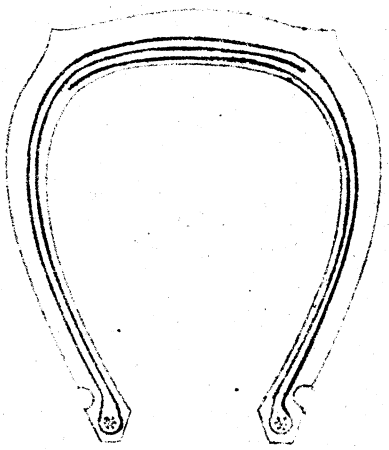
Building of the tire hoops was carried out during half of one regular shift by an operator on one of the semi-automatic center lap tire building machines. This machine is relatively simple and its mechanical operations greatly facilitate the manual operations involved in plying the material. Standard wire beads, coated with a very small amount of hevea reclaim stock, were employed. In this job two beads are first looped in grooves on the powered rollers of the machine. The fabric strip is fed from its spool behind the machine (as faced by the operator), the feed being controlled by foot pedal, and the required length of fabric is ripped off and joined in a hoop. It is deftly rolled



A. TUBED BICYCLE TIRE COVER SECTION.



B. EQUIVALENT SECTION OF CALENDERED STOCK SHOWING APPLICATION TO CENTERLAP FABRIC PLY.



C. APPROXIMATE MOLDED SECTION OF FINISHED TIRE.

V FIG. 1

over each bead and lapped by running twice around over the rollers. Next the wide sidewall cover strip is drawn from one spool at the operator's left and run on over the fabric, cut to length, and joined. Scissors are used for cutting the strip, and a hot knife is employed to remove excess rubber at the joining point and ensure a smooth, continuous, bond of rubber. The tread strip was similarly applied, being manually centered, and the completed hoop was released and taken off the machine. No difficulty whatever was experienced in joining ends and holding the various parts in position, the stock having excessive tack. The operator was assisted in speeding the job by two men who helped remove the rubber strips from the varnished cambric and fed it smoothly to the machine, as the stock tended to adhere to this liner. It was believed that cloth liners would be more satisfactory, and part of the tread strip was rerolled in cloth from which it was readily handled.

Fifty-five hoops were built from the available stock and fabric. As they were completed in groups of six they were placed on a chain conveyor with regular production tires and carried through the soapstone blower to coat them for handling. The regular operators took these hoops in turn and had no difficulty in inserting the steam bags and preforming in vacuum boxes to approximate tire casing form. From this operation they proceeded along with standard tires to vulcanization in the appropriate watch-case molds on the same 10 minute curing cycle at 330° F. as the victory grade all-reclaim bicycle tires in regular production at the time. Trimming, buffing, waxing, and inspection were carried out in the regular production line. Twelve tires were rejected for various defects, such as blow holes, mashed beads, inaccurate construction, etc., but in only a few cases were the defects attributable to improper flow, the stock being somewhat too soft to drive out trapped air in these instances.

The finished tires occasioned much favorable comment by the technical staff and the plant workmen of the U. S. Rubber Company who carried on or observed the work. They had a livelier and "snappier" feel, and far greater pliability than casings made of reclaimed hevea rubber currently being manufactured. It was noted that while the treads of flash could easily be pulled off the reclaim tires, the flash threads of the goldenrod tires had a far higher tensile strength, sufficient to support more than the weight of the casing on a single thread. Comments quoted from the report of the Development Department, Indianapolis Plant, U. S. Rubber Company are: "The results, considering that it was the initial attempt at factory-scale processing, were considered good.

Disadvantages:
1. Special precaution needed to process.
2. Becomes too soft and stickywith prolonged working.
3. Could not be extruded.
4. Non-uniformity of pre-cured batches.

Advantages:
1. Excellent tack.
2. Good molding properties.
3. Good tensile and elongation.
4. Fast curing - still safe processing.
5. Takes compound readily.

over

As the work was not exhaustive, it is probable that some of the disadvantages could be overcome either by compounding or in process of manufacture of rubber." In view of the impossibility of extruding or "tubing" of the tread and sidewall cover, no attempt could be made to produce inner tubes for these tires of goldenrod rubber.

A mileage test on three of the tires was subsequently made employing the test wheel at the Indianapolis Plant. Table XIII gives the results of this test as reported by the Company. The relatively high tensile strength, low hysteresis, and good flex resistance, and excellent bonding of fabric of the goldenrod rubber are reflected in the mileage indicated, which is not only three times that of the all-reclaim casings being produced under war conditions, but is nearly double that of pre-war crude rubber casings.

V-TABLE XIII

WHEEL TEST OF GOLDENROD BICYCLE TIRE CASINGS

Tire	Brand	Size	Tread Stock	Fabric	Beads	Special Features	Mileage	Avg. Mileage	Failure
#1	#500 chain	26x2.125	65109	1433-28f^{2}65109	25C14	Blistered tread & high bead	1577		Fabric broken at flexing line
#2	" "	"	"	"	"	Mashed bead	1447		" " " "
#3	" "	"	"	"	"	Mashed bead	1062		" " " "
								1362	

Note: No indication of failure at any of the tire defects; i.e. blistered tread, high and mashed beads.

Conclusion: This test shows "goldenrod" rubber tires to be better than "Reclaim" or "Pre-war crude rubber" construction of the same line class. (Based on mileage.)

Reclaim	- approx.	450 miles
Pre-war	- "	700 "
Goldenrod	- "	1362 "

VI - DRYING OF GOLDENROD FOR RUBBER EXTRACTION

Drying of the leaf or leaf-containing plant material is essential for storage and grinding, and is a major step in the processing of goldenrod for rubber. Besides the cost of the operation, factors to consider were the suitability of different types of drying for handling material of this nature, and the effect of temperature upon the quality of the rubber subsequently extracted. All information initially available from limited past experience seemed to indicate the necessity for low temperatures not exceeding 145° F., with consequently long drying time cycles. This would practically preclude the use of continuous type driers, and would require a relatively costly operation, both as to fuel and labor requirements. Experiments were conducted with available pilot plant driers of both the tray type for batch drying and the rotary continuous type. Limitations of construction materials and time dictated the adoption of a kiln type tray drier for handling the crop produced in 1943. Employing trucks carrying stacks of trays, this kiln drier could be operated economically and was of inexpensive construction. Its design, developed by the Forest Products Laboratory, was partly based on preliminary experiments on drying temperatures and rates reported in this section.

Batch Tray Drier Experiments. Drying tests were carried out on 10 pound lots of fresh goldenrod leaves harvested and shipped by express at one day intervals, in every case on the day received. In most cases material arrived in 48 hours, but some batches were delayed in transit and were received 72 hours after shipment. These leaves were in good condition after 72 hours, but a single lot which was delayed for 96 hours was spoiled by heating and fermentation, and the leaves were badly discolored. This lot of fermented leaves was run through a test, nevertheless, but a duplicate run at the same temperature was later run on an unspoiled lot.

Twelve samples were dried, two being reruns because of the spoiled leaves in one case, and because of failure of the drier control in another case. Temperatures employed were, approximately: 110°; 125°; 145°; 165°; 185° F. Control of most temperatures was held to plus or minus 2° F. except at the lowest temperature which was held to plus or minus 5° F. One satisfactory test at each temperature was made with gas heating, and one at each temperature with steam, as a check. There should be no difference due to the source of heat, as the arrangement for gas heating introduces only traces of combustion products and does not measurably reduce the oxygen concentration, even though products of combustion enter the drier.

The drier used was a 20 tray mechanical convection type, with a total tray area of 166 square feet. The 10 pound lots of leaves placed only a very light load on the capacity of the drier, which is designed to evaporate 200 pounds of water per hour. Four 30" x 40" trays only, or 20% of the tray area, were required to spread the leaves evenly at an average depth of 1-1/4". This is approximately 2.9 pounds per cubic foot of leaves spread for drying. Moderate cross circulation of air was used, with a minimum of venting and fresh air intake. A positive exhaust is maintained at all times on this drier by a small auxiliary fan.

over

The quart sample sealed at time of shipment was analyzed for moisture only. In nearly every case the moisture as shipped was 1 to 3% less than in the material as received, because of precautions taken to add and maintain moisture in packing. Moisture was determined on a sample obtained by quartering immediately on opening the package, and moisture in the dried material was determined on a sample uniformly taken from the four trays while still at the drying temperature at the end of the run, and sealed at that time. The trays were separately removed at one hour intervals and rapidly weighed, to determine rate of drying, and complete drying was assumed when the loss in weight per tray was less than .03 pounds on approximately 2.5 pounds of fresh leaves, or a little over 1%.

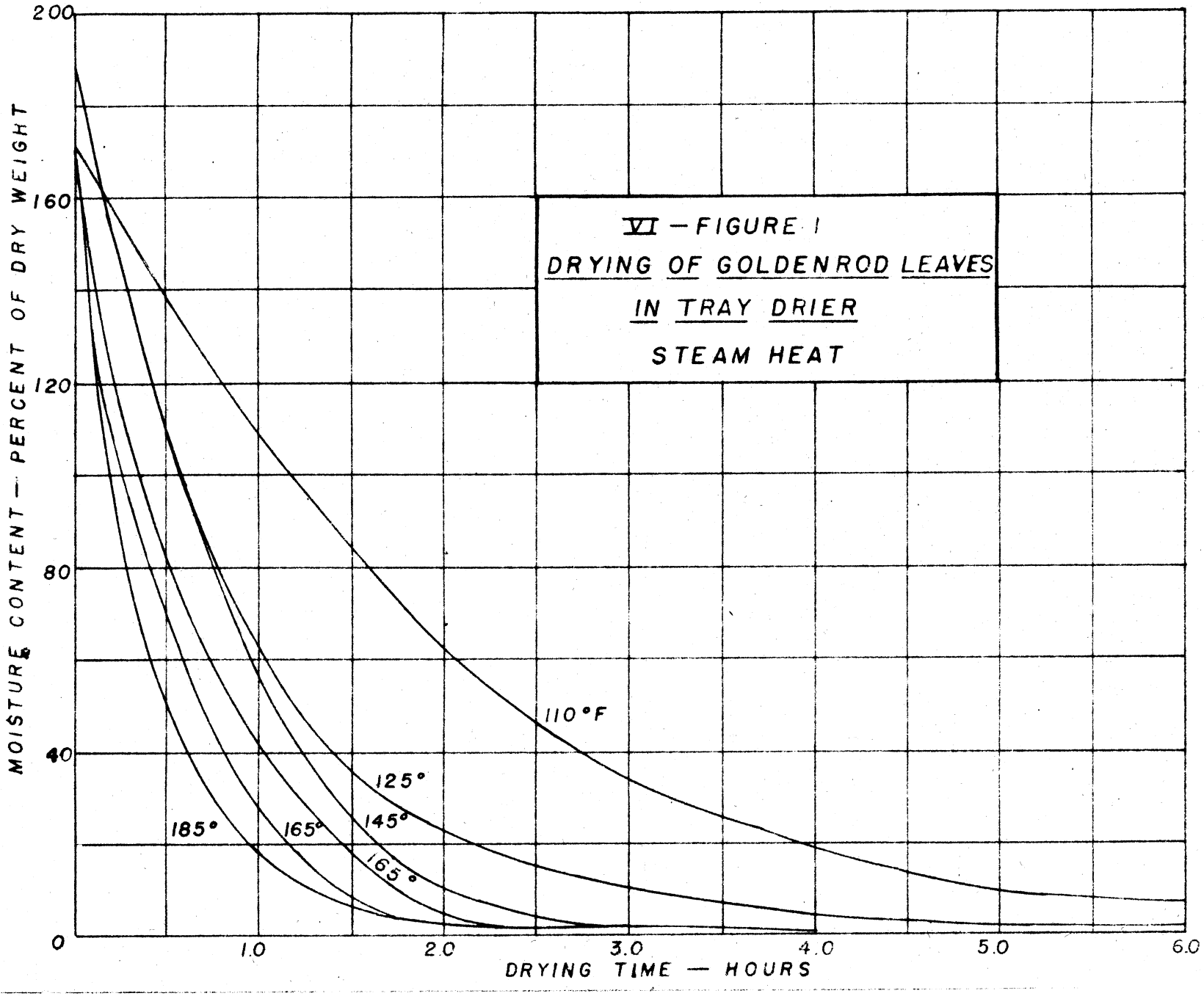
Drying rates of the two sets of determinations are shown by the curves of Figures 1 and 2. At the lowest temperature approximately 110 plus or minus 5° F., initial humidity on charging the drier rose to approximately 50%, and decreased to approximately 40% when drying was complete, the material being dried to about 6% moisture content. At the highest temperature, approximately 185° plus or minus 2° F., initial humidity was 18%, and final humidity 12%, with the material at 2% average moisture content. At 145° plus or minus 2° F. initial humidity was 24% and final humidity 18%, with the material in this case at about 7% final moisture content. Humidities were not significantly different with gas or steam heating.

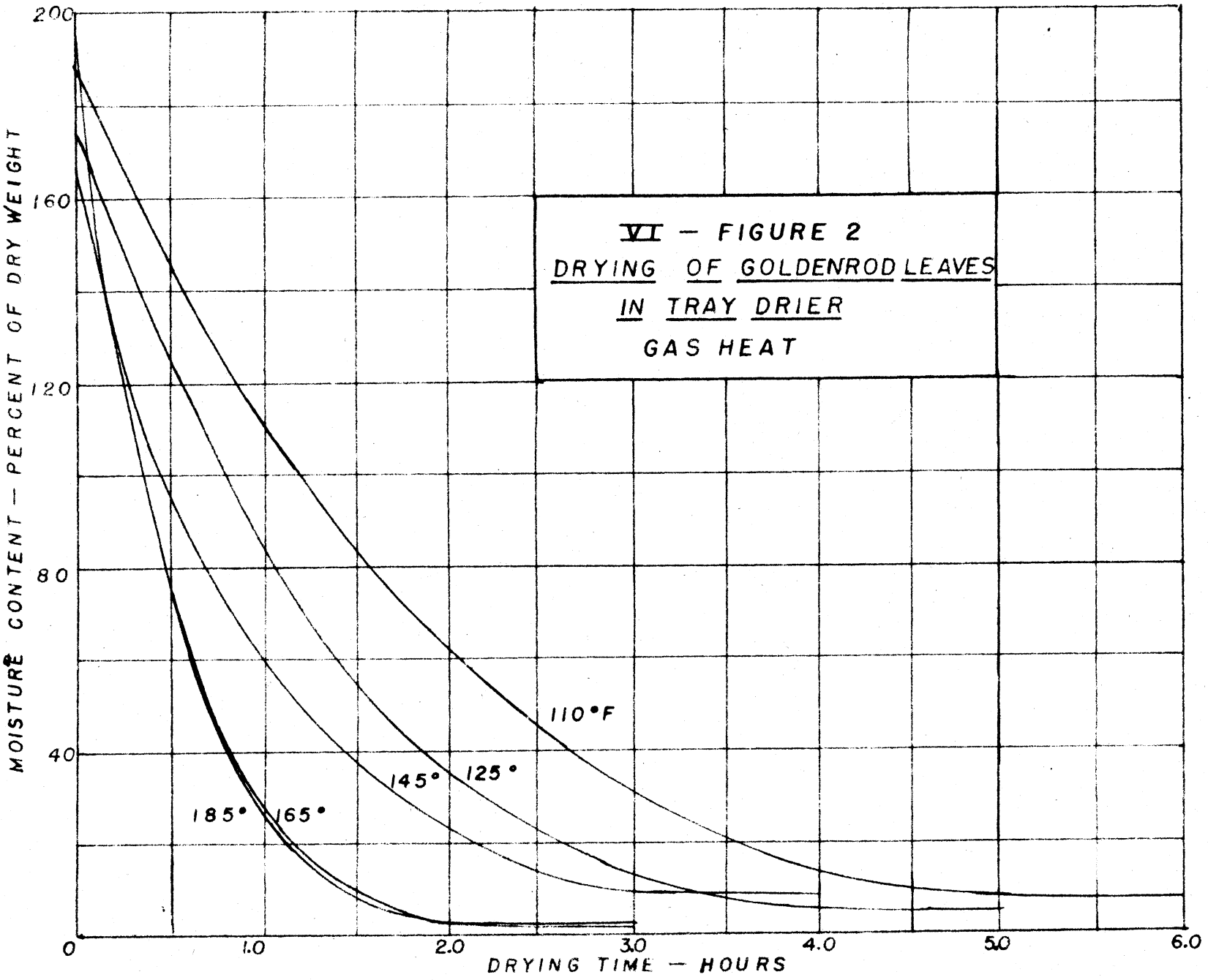
Each lot was analyzed as received for both rubber and resin (acetone soluble) content. The dried lots were analyzed for both rubber and resin to determine any change in these quantities, calculated on a moisture-free basis. In addition 100 g. of each lot was ground and subjected to acetone and benzol extraction to establish the probable yield of rubber and resin by the extraction process.

The bulk of each dried lot was processed by cooking with alkali and acid, followed by acetone and benzol extraction, to check the yields by this procedure. Details of this alkali-acid cooking are given in Section VIII. From the larger amount of rubber obtained in these treatments of the bulk of each lot, a vulcanizate was made, to indicate the quality of the rubber as affected by temperature of drying. Results are collected in Table I, showing drying conditions, rubber analyses before and after drying, and tensile tests on vulcanizates.

Conclusions. Within the limits of accuracy of the extraction method of analysis, there is no loss of extractable rubber at any temperature tested. Occasional determinations show an apparent increase in percent rubber after drying, balancing the slight decreases, and all within the probable error of the method. The yields from the 100 g. lots check the analyses, and show uniformly high results equalling the available percent rubber before drying. The material in all these lots contained approximately 7% rubber on a moisture-free basis. Yields of rubber by the cooking procedure are higher than by direct extraction, reaching 7.6 to 7.8%.

No facilities were available at the time these experiments were made for uniform curing and quantitative tests of rubber quality. The product from material dried at 145° F. appeared to be as good as that from batches dried at lower temperatures. Vulcanizates of material dried at 165° F.


VI — FIGURE 1
DRYING OF GOLDENROD LEAVES
IN TRAY DRIER
STEAM HEAT
MOISTURE CONTENT — PERCENT OF DRY WEIGHT
200
160
120
80
40
0
1.0
2.0
3.0
4.0
5.0
6.0
DRYING TIME — HOURS
110°F
125°
145°
165°
185°
165°


VI — FIGURE 2
DRYING OF GOLDENROD LEAVES
IN TRAY DRIER
GAS HEAT
MOISTURE CONTENT — PERCENT OF DRY WEIGHT
200
160
120
80
40
0
1.0
2.0
3.0
4.0
5.0
6.0
DRYING TIME — HOURS
110°F
125°
145°
165°
185°

and 185° F. showed some tendency to bloom and appeared to be slightly inferior to those dried at lower temperatures, but tests of tensile strength showed no decrease in this property. At the time these experiments were completed the importance of acetone soluble resin content in affecting vulcanization, and the solution compounding method had not been worked out, nor had the best compounding formula been developed. No Scott tester, nor even a substitute machine for uniform rate of elongation of test specimens was available, and the tensile values are at best estimates obtained by a crude arrangement of loading the sample by sand weight and reading the tension applied on a spring balance. Only 60 min. cures of the vulcanizates at 260° were made in each case, as the amount of material was limited. Under these circumstances it is obvious that the tensile strength values have little quantitative significance, but it is interesting that even these crude procedures yielded fairly high results on samples of rubber from leaves dried at temperatures up to 165° F. The decrease in each series when drying temperature was increased to 185° F. is not very significant, in view of the extraordinarily low results obtained on material exposed to the lowest temperatures. No explanation can be offered for this unexpected anomaly, other than the extreme crudity of the only test procedures available at the time.

The drying curves show that drying at 145° F. required about 2 to 2-1/2 hours to reach 10% residual moisture. Increasing the temperature to 185°F. only reduced the time by about one hour. This decrease in drying time does not justify the risk of damage to the rubber obtained and it was therefore recommended that drying be done at air temperatures not exceeding 145° F. All drying was done in a substantially light-proof drier and this precaution was also recommended.

At a later date, when the decision had been reached to use through circulation instead of cross circulation in the large kiln to be built at Waynesboro with tray loading up to 4" deep, two experiments were carried out under these conditions. The same drier was used with baffles to provide the through circulation of steam heated air, through two trays only. Wild goldenrod harvested near the laboratory was stripped by hand, and 17.28 pounds of leaves used in each test, equally divided between the two trays. The effectiveness of this system of drying is evident from the rate of drying curves at 145° F. and 165° F. shown in Figure 3, drying to 10% being accomplished in 63 minutes and 38 minutes, respectively. Had all 20 trays been loaded, the charge would have been about 175 pounds; with through circulation passing single layers of trays, only the capacity of the small pilot drier, allowing time for loading and unloading, could have been maintained at approximately 200 pounds per hour operating at 165° F.

over

VI-TABLE I

TRAY DRYING OF 10 POUND BATCHES OF GOLDENROD

Batch No.	MOISTURE PER CENT: As Ship'd.	As Rec'd.	After Drying	DRYING: Heat Source	Temp. °F.	Humidity Init.	Humidity Final	Time to 10% Hrs.	RUBBER PER CENT (Moisture-free Basis): As Rec'd.	Dried	Yield (100g)	Ten.Str. p.s.i.
8	62.4	59.8	5.7	Steam	102-6 (100-118)*	51	38	4.90	7.1	3.3(1)	7.0	1260
1	65.9	65.3	2.6	"	124-9	-	-	3.00	7.5	8.1	7.3	287
2	62.8	64.8	0.9	"	140-4	33	25	2.00	6.9	6.9	6.7	913
4	60.3	63.7	1.1	"	164-6	19	15	1.43	5.2(1)	5.9(1)	7.0	1175
12	62.7	64.0	7.6	"	163-6	-	-	1.75	6.7	6.6	7.4	1060
5	59.6	62.2	1.3	"	182-6	17	11	1.25	6.9	6.5	7.0	947
6	64.4	65.8	6.0	Gas	108-18	49	42	4.35	6.3	6.8	6.4	379
9	62.5	64.2	4.1	"	124-6	30	24	3.20	6.9	7.8	7.9	1050
10	60.2	63.2	7.5	"	144-6	24	18	2.80	7.2	7.9	7.3	1350
11	63.9	64.8	1.6	"	163-5	20	14	1.42	7.1	6.7	7.8	1270
7	62.0	65.3	2.6	"	183-5	19	14	1.40	5.5(1)	7.2	7.9	858

* Extreme temperatures reached for short intervals.

(1) Results doubtful because of large possible error in 5 g. sample used.

Continuous Rotary Drier Experiments. Preliminary experiments on continuous drying of leaves in a rotary type drier were carried out in equipment available at the Southern Regional Research Laboratory. The primary purpose of the tests was to ascertain the suitability of a drier of this type for handling fresh leaves, and its capacity. It was realized that higher drying temperatures would be required to dry the material to the requisite 10% moisture content in a continuous drier. The time of exposure of the leaves to the drying temperatures would necessarily be short for two reasons - to minimize the possible effect of high temperatures on the quality of the rubber, and to reach as high a capacity as possible through the drier.

The equipment used was a stainless steel pilot plant rotary drier with 2' x 12' shell, equipped with flights. Shell speed was variable from 0 to over 20 r.p.m., as was the pitch from a negative incline of 0.16" per foot to as much as 0.5" per foot positive incline. Heat was supplied by direct combustion gases from a gas furnace with rated capacity of approximately 200,000 B.t.u. per hour. Although arranged for "intermediate feed" and counter-current operation, these methods were not expected to be applicable to light, bulky material such as fresh goldenrod leaves. A short trial demonstrated the correctness of the expectations; the leaves matted and choked the rotary air lock of the intermediate feed cyclone, and were too light to be carried by the flights against the high gas velocity in counter-current drying. The leaves also choked and would not pass through the mechanical screw feeder. After trying out these features with locally harvested wild goldenrod leaves, the experiments were made employing direct hand feeding of material to the shell with concurrent heating gas flow.

The drier was equipped with automatic controls to maintain gas inlet and outlet temperatures, but as it was not insulated at the time these experiments were performed little importance can be attached to the figures on gas consumption, although they were recorded. The essential data of seven test runs made with approximately constant conditions during each run are given in Table II. These tests were sufficient to establish the capacity of the rotary type drier for handling goldenrod leaves. Practically complete drying could be attained only by rerunning the leaves in a separate second pass, in runs 2 and 7, and over all feed capacities in these runs in conjunction with runs 1 and 6 for predrying were only 15 pounds per hour and 10 pounds per hour, respectively. Only the conditions of run 4, with inlet gas at 368° F. and outlet gas at 219° F., resulted in drying on a single pass to a suitably low moisture content, 10.9% (dry basis). The wet feed capacity was 30 pounds per hour with average retention time of material in the drier 15 minutes. The tray drier of same rated heat capacity used in the experiments described in the previous section has 20 trays. As cross circulation was used in the tray drier, loading all 20 trays would have had little effect on the drying time, as compared to only 4 loaded trays used in the tests. At only 165° F. air temperature, its minimum capacity would be 50 pounds per hour; if the trays were loaded to a depth of 2-1/2", instead of only 1-1/4" as used in the temperature experiments, it could handle 100 pounds per hour employing temperatures not over 200° F. Using 4" tray loading and through circulation,

over

tray drier capacity as shown in Fig. 3, would approach 200 pounds per hour, with air temperature of only 165° F., nearly seven times the capacity of the rotary drier operating at 220° F. outlet temperature.

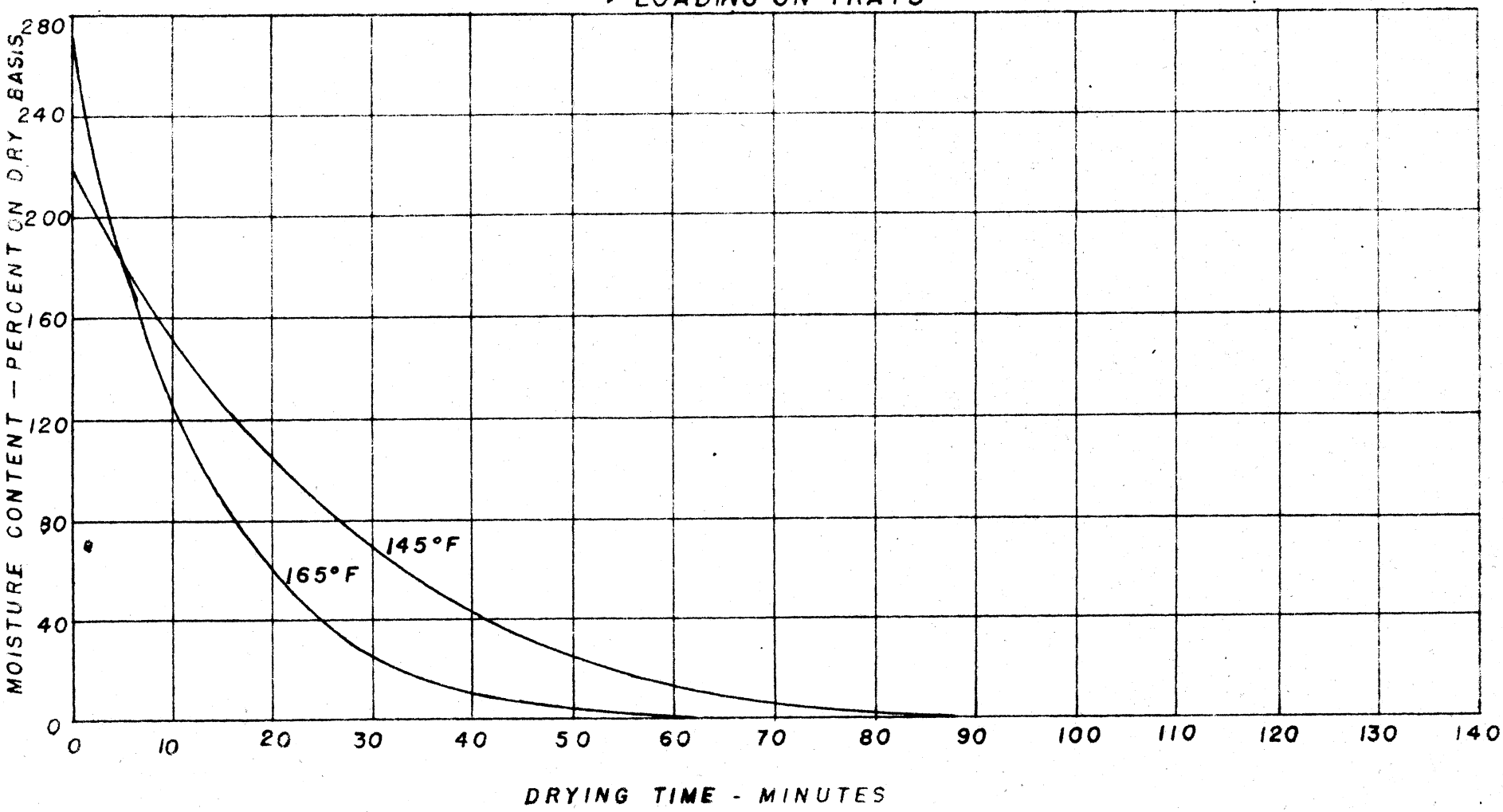
Determinations of resins and rubber were made on a number of the samples, as well as on control samples dried at 145° F., with the results shown in Table II. While there is considerable variation in the results due to the difficulty of sampling material from such a series of tests, there is no indication of any loss of rubber due to drying at the temperatures employed. The amount of rubber is the percentage of benzol soluble material extractable after thorough acetone extraction. The amount of uniform test material obtained in each case was not sufficient to permit extraction of enough rubber for vulcanization and testing. Even if the quality of the rubber were not impaired by exposure of the leaves to high drying temperatures, the requirements of steel and structural materials, and of motor drives and power, under war conditions ruled out the rotary type drier unless a much greater capacity than tray drying could be attained. At the capacity indicated by these tests, construction of a rotary drier or driers large enough to handle the crop planted at Waynesboro, Georgia, was out of the question.

VI - FIGURE 3

DRYING OF GOLDENROD IN TRAY DRIER

STEAM HEAT THROUGH CIRCULATION

4" LOADING ON TRAYS



VI-TABLE II
ROTARY DRIER TESTS ON GOLDENROD LEAVES

Run No.		1	2	3	4	5	6	7
Feed rate #/hr.		30.	30.	18.	30.	60.	15.	30.
Moisture in feed %		61.8	36.7	63.0	57.4	57.4	57.4	20.3
" " dischg. %		34.2	1.9	16.3	10.9	20.7	13.7	1.0
Feed-solids #/hr.		11.44	18.96	6.66	12.78	25.60	6.39	23.90
Discharge-solids #/hr.		11.48	19.50	3.82	12.87	24.90	6.55	20.91
Water Evaporated #/hr.		12.54	10.12	9.85	15.55	28.61	7.41	8.87
Gas consumption c.f./hr.		128.	108.	106.	175.	-*	102.	107.
Inlet gas temp. °F.		244.	310.	320.	368.	375.	307.	303.
Outlet gas temp. °F.		172.	180.	181.	219.	211.	179.	184.
" wet bulb °F.		99.	108.	104.	115.	117.	102.	102.
" rel. hum. %		9.5	12.0	9.0	6.0	8.0	9.0	8.0
Holding time, avg. min.		44.$\overline{7}$	29.$\overline{6}$	9.$\overline{7}$	15.$\overline{0}$	18.$\overline{0}$	17.$\overline{6}$	9.$\overline{1}$
Shell speed, r.p.m.		0.6	3.0	3.0	3.0	3.0	3.0	3.0
" pitch, in./ft.		+0.191	-0.147	-0.147	-0.147	-0.147	-0.147	-0.147
			Run 1 redried			*Over 200		Run 5 redried
% M. F. B.	Controls							
Resins	11.6 / 18.4	16.5	14.4	15.1	20.3	-	-	15.3
Rubber	5.0 / 3.6	4.0	5.6	4.6	5.8	-	-	4.9

High Temperature Flash Drying Experiments. The purpose of these experiments was to study flash drying of goldenrod leaves over a wide range of high temperatures, and to ascertain by analytical and physical laboratory evaluation tests the effect of different drying temperatures up to 1000° F. upon the quantity and the quality of the rubber. Only moderately high temperatures were used in the tests with the rotary drier at the Southern Regional Research Laboratory, and the object of these further tests with a continuous rotary drier was to determine the possibility of using even higher temperatures if the time of exposure of the material was very short.

Approximately 500 pounds of goldenrod leaf material of variety 3-S-79 was harvested at Waynesboro, Georgia, on the morning of September 28,1943. Immediately after harvesting the plants were stripped on the small model leaf stripper. Four hundred pounds were packed in cartons with dry ice refrigeration and hauled by truck to Atlanta, Georgia, for shipment by airplane on the same evening to the Louisville Drying Machinery Company plant at Louisville, Kentucky, where the pilot plant test drying runs were conducted. One hundred pounds was similarly packed with dry ice and held at Waynesboro as a control. After 24 hours these cartons were opened and the leaves dried at 145° - 165° F. in tray driers. All of the drier runs were completed with as little delay as possible in order that the time-degradation factor for the undried material would be reduced to a minimum.

The shipment of leaves was inspected promptly on delivery at Louisville and some portions were found to be considerably damaged due to insufficient refrigeration over the period of transit. The same condition was found for the control sample at Waynesboro. Each of the 32 cartons (total weight 430 pounds) contained a warm (125° F.) damaged zone of blackened leaves at the approximate center of the loosened packed mass. All damaged leaves, amounting to approximately 120 pounds, had to be carefully removed and discarded before spreading out the material for aeration and cooling. The undamaged leaves were scattered in a thin layer over a concrete floor and a ceiling fan turned on for a few minutes until cool. The leaves were then shoveled into large open-weave oat sacks and hauled to a nearby cold storage warehouse and stored at 36° F. for withdrawal when and as needed.

The material doubtless degraded progressively to some extent during shipping, storage, handling, etc. between harvesting and the time of completion of the last drier run, and allowance for this had to be made in evaluation of the results as it was not possible to process the entire lot within a shorter period. The refrigerated leaves appeared fresh and green up to and including the last day of storage, and showed little or no deterioration with the exception of some heat damage to two of the last sacks, resulting from slight wetting while in the warehouse, and some black leaves had to be removed. The undamaged material was used as a feed for drier runs 8 and 10 as stated in the data sheets. The dried product amounting to 10-15 pounds from each of the drier runs was packed separately and shipped to the Southern Regional Research Laboratory for laboratory comparison with the control.

Several types of small size rotary driers were made available at the

pilot plant of the Louisville Drying Machinery Company for this experimental work, but only one was recommended as being by far the most practical and economical rotary type machine for use with goldenrod. This recommendation was made after discussing the matter at great length with the Company's drying engineers and others who had extensive experience in experimental as well as successful commercial drying of a wide variety of materials using rotary type machines of the Company's manufacture.

The particular drier recommended was the direct heat, gas fired, parallel current (or concurrent) type and all of the goldenrod runs were made using this 1' diameter by 6' long, variable pitch, variable speed pilot unit. It was stated emphatically that results obtained on all of these experimental size driers were closely translatable to factory size equipment and that several installations had been made recently in university engineering laboratories.

After carefully inspecting and servicing all rotating parts of the drier, calibrating thermometers, etc., several short preliminary test runs were made using the discarded material for determining and coordinating feed rates, shell speeds, shell pitch, capacities, processibility, and general behavior and appearance of the material at the various drying temperatures contemplated along with other information which would be useful in conducting the experimental tests.

It was necessary at the outset to install a separate centrifugal type premix gas burner on the drier in place of the existing one, in order to reach the higher temperatures required for the runs. This done, the shell speed and pitch of the drier were adjusted so as to allow the drying material to remain in the shell not over 3-4 minutes. The feed rate was regulated at each temperature for discharging dried material at approximately 5-10% moisture content and particular care was taken not to overdry the material during any run, and whenever possible to keep the moisture content just under 10%.

Preliminary testing on the first day indicated that the material as received contained a considerable proportion of stems 4" to 10" in length which had to be sorted out and chopped into smaller pieces (1-2") as these had a tendency to stick between and under the shell flights and thus prevent satisfactory showering of the material. In addition, the larger stems balled up, bird-nest like in the shell and hindered the flow of material and gases.

The undamaged material (300 pounds) was sufficient for conducting seven separate drying experiments, each at a different temperature for obtaining a suitable quantity (10-15 pounds bone dry basis) of product of each run for making the necessary tests at the Southern Regional Research Laboratory. Approximately 40 pounds of the leaf material were dried at each of the following furnace gas inlet temperatures: 350, 500, 600, 700, 800, 900, and 1000° F. The low temperature run was made first for the purpose of establishing as nearly as possible a basis or reference for comparing the content and quality of the rubber contained

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VI-TABLE III
PILOT PLANT FLASH DRYING OF GOLDENROD

Run #	Date	Av.Temp. °F.Inlet Furnace & Gases	Av.Temp. °F.Drier Exhaust Gases	Av.Temp. °F.Discharged Material	Total Wt.(#) of Feed	Total Wt. (#) of Dischgd. Material	Feed Rate #/Hr.	Moist. Cont. of Feed	Moist. Cont.of Dischgd. Material	Speed of Shell r.p.m.	Pitch of Shell Inches
	1943										
1*	9/29	4-600								3-10	0 to -1
2	9/30	345	180		22.5	16-1/4	8	66.0	13.4	7	Neg.3/4
3**	10/1	350	182		7.8		8	56.8	6.0	7	" 1
2,3**	10/1	350	184		10.5		8	56.8	6.0	7	" 1
4	10/1	600	255	135	27.5	22-1/4	28	56.4	5.3	7	" 1
5	10/2	600	258		15.0		28	54.6	4.5	7	0
6	10/2	500	235	120	40.5	10-3/4	18	54.8	8.9	7	0
7***	10/4	700	275	135	41.5	17-1/2	28	58.6	8.4	7	0
8x	10/4	800	290	138	39.0	17-3/4	30	56.0	4.2	7	0
9	10/4	900	280	142	40.5	20.0	32	54.0	8.2	7	0
10x	10/5	1000	275	160	39.0	18.5	34	56.4	6.3	7	0

*Preliminary determination of approximate operating conditions for main drier runs to follow.

**Most of drier discharge ran 14-18% moisture at this feed rate and was redried at 250° F. (high feed rate used) to reduce moisture content to under 10%.

***Material discharging seemed wet and approximately one-half of this was redried at 250° F.

xFeed for runs 8 and 10 was slightly heat damaged in one spot due to wetting and was re-sorted to remove black leaves.

Notes - Drier used for all runs was direct, gas-fired, concurrent, cylindrical shell, 1' diameter x 6' long.
Moisture tests determined overnight in oven at 220° F.
Temperatures shown have been corrected.
Material discharging from drier was spread out to cool as discharged.
Dried material from each run was collected and packed separately for shipment to New Orleans.

in the material at this stage of the run with that at the high temperatures and with that in the leaves which were to be dried at 145°-165° F. as a control. Complete data including feed rates, temperatures, etc. were recorded and are given in Table III. The same fan speed or approximately the same volume of air per minute was employed for all runs. The warm discharging material in all cases was cooled as it discharged by spreading out thinly over the floor in order to reduce further degradation. Incidentally, it was observed that the leaves showed a reduction in moisture content due to handling, etc. from 65% as received to approximately 57% average as fed into the drier.

Because of the importance of reducing the time-degradation effect on the rubber contained, all of the drier tests were run with as little delay as possible. Runs were made in order of ascending temperature with the exception of the one at 500° F. At this point trouble was encountered with the air adjustment of the furnace blower and the 600° run was made while the blower was being repaired.

It may be noted that in two of the runs, Nos. 3 and 7, repassing of the drier discharge was necessary due to the feed rate being too high. Redrying, in this instance, was at a low temperature (250° F.) with the feed rate doubled. Only half of the No. 7 run had to be redried to give an average moisture content below 10%. The relatively high temperature of the exhaust gases was obviously due in part to the short shell length of this small machine and to imperfect showering off the flights.

After the principal runs were completed, some of the leftover damaged leaves (57% moisture) were passed through a small hammer mill with 1/2" screen openings to observe the effect of size reduction. The material did not gum up in the mill, and did not mill into a soupy consistency as was expected. However, it was slightly sticky and the general prediction was that the latter condition would cause objectionable sticking of the feed to the drier shell, but 15-20 pounds were dried and no difficulty was encountered. The comminuted material handled well and also showered well off the flights and lowered exhaust gas temperature considerably, as shown in data for run No. 11. A sample of this dried material was taken but no regular run was made as the supply of fresh leaves was exhausted. Some of the fresh green leaves were passed through the hammer mill on the first day, and as this 66% moisture material showed excessive stickiness we advised at the time against trying it in the drier.

In discussing the drying of different material types in various type driers, it was brought out that the rotary type drier is usually considered not the best answer to drying leafy material, and this includes rotary units such as the steam-tube type, with or without mechanical draft; L-type (see operating principle described in their catalog); indirect fuel-fired, concurrent or countercurrent, and also the countercurrent direct heat types. The direct heat, fuel-fired, parallel current rotary drier was recommended as the most practical and economical rotary type machine for goldenrod. Use of the latter type is indicated whenever the material is not injured by high temperature when wet and where it is not required that the final moisture content be very low. It was pointed

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out that the gases in a parallel current direct heat drier rise in humidity and decrease in temperature, while the material reacts in exactly the opposite manner and because of this it is necessary to have a longer shell in order to get evaporative results comparable to that obtained in a countercurrent drier.

Among the many advantages claimed for the parallel current direct heat drier is the rapid reduction in gas temperature at the inlet end which results directly in a reduction of radiation losses in the shell and for this reason among others, this type can, if operated properly, be fairly efficient in fuel consumption. Also, this type of machine is considered better for handling air-sensitive material. It is obvious that this type drier must be so designed and operated as to avoid possibility of the dry material reabsorbing moisture from the cooled humid exhaust gases at the discharge end. The main shortcoming of the concurrent type lies in the tendency of material to case-harden and in the fact that dry, dusty material cannot be handled satisfactorily. The thermal efficiency of driers used under conditions which permit the employment of high temperature gases is usually higher than for lower temperatures. The drying time is shorter, the capacity greater, and if the drier is designed and operated properly, the temperature of the exhaust gases will be lower and there will also be less total heat lost in the exhaust gases per pound of material dried because of the shorter drying time.

Due to the small surface area exposed by leafy material per unit weight, the rate of drying is relatively low, and a correctly designed rotary type unit would require a fairly long shell of suitably large diameter and would have to operate with a high differential temperature between the hot gases and the drying material. It is obvious that leafy material should always be size-reduced, if possible, and that flights perpendicular to the circumference of the shell would be desirable for obtaining maximum material showering and minimum fouling of the flights.

The control and each of the seven batches of dried leaves was ground at the Southern Regional Research Laboratory through a 1/32" screen using a Ball and Jewell mill. Extractions of 1 kg. batches of the control sample and of each of the seven test lots of leaves dried at 350° F., 500° F., 600° F., 700° F., 800° F., 900° F., and 1000° F. were conducted by extracting for 32 hours with acetone to remove the resins, followed by 32 hours extraction with benzol to obtain the rubber. It will be noted that the resin content of the benzol extracts from the high temperature batches is considerably higher than that obtained for the control sample (see Tables IV and V). The standard solution method was used to precompound all benzol extracts, including the control, in glass still pots.

Additional chemicals were milled into the dried precured samples. The rubber from the flash dried leaves was too dry for satisfactory milling and the vulcanizates gave low tensile strength values much below the control (see Table VI). Attempts were made to evaluate the tensile strength of the vulcanizates after 0.5 parts of D.P.G. was milled into the gum stocks before vulcanization. In most cases milling was extremely difficult due to dry and crumbly samples which would not follow

VI-TABLE IV
FLASH DRIED GOLDENROD

Sample Dried At	Laboratory Extraction: Acetone Extract: Resins %	Acetone Extract: Avg. Resins %	Benzol Extract: Crude Rubber %	Benzol Extract: Avg. Crude Rubber %	Benzol Extract: Rubber Resin-free %	Analytical Results: Benzol Extract: Resins %	Benzol Extract: Titra. Value	Benzol Extract: Vis-cosity	Raw Material: Moisture %	Raw Material: Rubber Resin-free %
Control 145° F	14.7 17.9	16.3	4.49 4.68	4.58	4.20	8.2	4.65	0.675	6.17	4.27
350° F	12.6	12.6	5.51	5.51	4.47	18.7	4.50	0.678	6.75	4.46
500° F	16.0 13.8	14.9	5.02 4.73	4.87	4.32	11.5	4.60	0.678	6.71	4.05
600° F	13.7 14.2	13.9	4.96 4.73	4.84	4.03	16.8	4.45	0.676	6.18	3.93
700° F	15.2 13.8	14.5	5.12 4.93	5.02	4.23	15.5	4.50	0.674	6.26	3.86
800° F	15.3 11.9	13.6	5.17 5.24	5.20	4.40	15.1	4.55	0.672	6.31	4.10
900° F	13.4 13.4	13.4	5.28 5.55	5.41	4.61	14.8	4.50	0.674	6.43	3.99
1000° F	13.6 17.0	15.3	5.27 5.03	5.15	4.18	18.7	4.55	0.670	6.29	4.12

VI-TABLE V

COMPOUNDING AND FORMULA CALCULATED TO RESIN-FREE BASIS

Sample Flash Dried At

	Control	350° F.	500° F.	600° F.	700° F.	800 F.	900° F.	1000° F.
Rubber, Resin-free-parts	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Resins, incl. with rubber - parts	8.9	23.0	13.0	20.2	18.4	17.8	17.4	23.0
Added in solution for precure: - parts								
Sulphur	3.82	4.30	3.96	4.20	4.14	4.12	4.11	4.30
Thiotax	1.09	1.23	1.13	1.20	1.18	1.18	1.17	1.23
Zinc Stearate	5.98	6.77	6.23	6.62	6.50	6.48	6.47	6.75
Flectol H	1.09	1.23	1.13	1.20	1.18	1.18	1.17	1.23
Added in Milling:								
Zinc Oxide (to entire stock)	5.98	6.77	6.23	6.62	6.50	6.48	6.47	6.76
D.P.G. (to part of stock only)	0.54	0.61	0.56	0	0	0.59	0	0

VI-TABLE VI
VULCANIZATION & TENSILE STRENGTH
GUM STOCKS WITH FORMULA GIVEN IN TABLE V

Sample Dried @	Cure Minutes @ 260°F.	Modulus @ 300%	Modulus @ 500%	Maximum Ten.Str. p.s.i.	Ult. Elongation %	Remarks
Control						
145° F.	20	125	390	1230	650	Fair but dry milling.
	40	155	430	1300	650	
	60	135	330	1010	650	
350° F.	15	95	290	450	600	
	30	105	345	655	600	
	45	155	510	510	500	Fair milling.
	60	150	-	300	425	
500° F.	15	120	455	820	600	
	30	165	460	920	600	Much too dry milling.
	45	155	430	905	600	Material would not
	60	195	485	1095	650	follow rolls.
600° F.	15	230	690	690	500	Extremely dry and
	30	235	705	705	500	crumbly. Material
	45	230	795	905	525	would not follow rolls.
700° F.	15	190	-	225	350	Extremely dry and
	30	190	605	680	525	crumbly. Material
	45	185	-	520	450	would not follow rolls.
800° F.	15	180	565	655	550	Poor milling due to
	30	160	550	870	600	shorter precuring.
	45	150	450	870	600	
	60	185	490	830	600	
900° F.	15	105	-	105	300	Extremely dry and
	30	150	-	220	325	crumbly. Material did
	45	150	-	220	350	not follow rolls.
1000° F.	15	188	605	605	500	Extremely dry and
	30	188	605	680	525	crumbly - shorter pre-
	45	225	605	830	550	cure.
GUM STOCKS WITH D.P.G.-0.5 PARTS ADDED						
Control						
145° F.	15	180	520	1650	625	Fair but dry milling.
	30	230	640	1690	650	
	45	260	700	1690	650	
350° F.	15	155	510	825	575	
	30	195	510	980	600	Fair but dry milling.
	45	195	630	855	600	
500° F.	15	190	690	1385	625	Very dry milling.
	30	235	665	1350	600	Material would not
	45	240	680	1280	600	follow rolls.
800° F.	15	190	655	1115	600	Poor milling due to
	30	230	730	1115	600	shorter precuring.
	45	190	615	1115	600	

Note: Samples dried at 600°, 700°, 900°, and 1000° F. milled too poorly for addition of accelerator.

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the rolls or stick to them.

The flash dried leaves were extracted and the benzol extracts compounded, vulcanized, and tested before experimental data was obtained indicating that acetone precipitation of the benzol extract was necessary to remove the excess resins in the rubber in order to secure proper milling and vulcanization. The resin content of the benzol extract for the control sample was 8.2%, whereas the resin values for the flash dried benzol extract varied from 11.5% to 18.7%.

Resins contained in the benzol extracts were considerably higher than for the control. This indicates that goldenrod leaves when subjected to high temperature drying are, comparatively speaking, poorly and incompletely extracted with acetone, thereby leaving a high percentage of resins which will be removed for the most part with the rubber during the subsequent benzol extraction.

The titration values and viscosities of the benzol extracts indicate that the rubber quality has not been very seriously impaired by subjecting the goldenrod leaves to a fairly wide temperature range of drying, however, the tensile strength values of the vulcanizates are below the control.

The precured rubber from the flash dried leaves milled unsatisfactorily with additional chemicals required before vulcanization. All samples were very dry and crumbly, in fact, it was impossible to mill in properly the requisite amount of zinc oxide and D.P.G.

In the Laboratory all extractions, precompounding, milling, vulcanization and testing, etc. have been carried out on the 1943 harvests with the apparatus and equipment used on the goldenrod leaf material for the 1942 crop. However, all of the goldenrod harvested from the 1943 crop, including the general harvests, special batches such as ensilage and retting experiments, kiln dried, sun dried, and flash dried material contained stems and blossoms in addition to leaves, and the last date of harvest samples contained an appreciable quantity of dead leaves and some blossom. Since there is little or no rubber in the stems and blossoms, and the rubber from dead leaves is of exceptionally poor quality, the percentage of benzol extract reduced in most cases to a very low value of approximately 1-1/2 to 2%. For this reason the bulk of the material to be extracted must be large in order to obtain enough benzol extract for determining gum and tread stock vulcanizates necessary in satisfactorily evaluating the quality of the rubber contained. Furthermore, the ratio of the resin content of the material to be extracted to its rubber content was 3 to 4 times higher than that obtained on the leaf material from the 1942 crop. A long extraction time with acetone was required to remove the resins, in fact, the usual extraction time of 24 to 32 hours applied to 1943 material still left an appreciable quantity of resins for removal along with the rubber during the benzol extraction. Resin content of the benzol extract of 9-10% or more usually accounts for low tensile strength values. Many of the special batches of goldenrod material have been insufficient in quantity to obtain enough benzol extract for satisfactory

quality evaluation of the rubber contained. This is especially true with the date of harvest samples and some others such as sun dried, flash dried, controls on ensilage, and retting experiments, etc. Larger quantities of benzol extracts are required when removing the excess resins present by means of acetone precipitation of the rubber. Significant conclusions cannot therefore be drawn from these experiments since the scale is entirely too small for proper evaluation.

The results noted in these experiments show the fallacy of conducting projected work on the relatively small lots of dried goldenrod, especially when they contain appreciable quantities of stems and blossoms in addition to the leaf material. In the event subsequent studies should be contemplated on the recovery of natural rubber from goldenrod, use of at least 1/2 ton lots of flash dried material is recommended for proper evaluation tests. Large rubber companies generally require a minimum of two pounds of **hevea** rubber (smoke sheet) for processing any preliminary testing. At least 10 pounds of goldenrod rubber are suggested for obtaining satisfactory evaluation.

No significance can be attached to results of tests on rubber obtained from the laboratory extractions because of the variable, and in most cases exceedingly high resin content of the extract prepared from the material dried at the various temperatures. For this reason, and because laboratory pot cures of rubber extracted and tested without purification to remove the appreciable quantities of resins are also of questionable value, no particular significance can be attached to the fact that vulcanizates for the different temperatures show tensile strengths below that of the control.

Over the drying temperature range 350-1000° F., analytical and laboratory extraction tests as well as viscosity and titration values indicate no conclusive evidence of any deleterious effect upon the quantity or the quality of the rubber extractable from the dried product.

It is recommended that in order to properly evaluate flash drying of goldenrod, lots of the order of 1/2 ton of dried leaf material should be furnished, depending on the rubber content, for providing at least 10 pounds of resin-free rubber for adequate evaluation.

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KILN DRYING TESTS

These tests were made in order to determine the optimum temperature for large-scale kiln drying of goldenrod, by ascertaining the effect of temperatures up to 205° F. under actual kiln conditions upon the quality and quantity of the rubber obtainable.

Material. The goldenrod material used was selection 3-S-79, all harvested from Manley field October 6-7. Four separate lots were received, dried under full load kiln conditions at Waynesboro, Georgia, at 145° F. (Bags 358-367), 165° F. (Bags 334-345), 185° F. (Bags 323-333), and 205° F. (Bags 346-356). The material had been air-separated but was not ground. At the Southern Regional Research Laboratory each lot was thoroughly mixed and ground separately in the 15" x 8" Jeffrey hammer mill through a 1/16" screen, reducing the entire amount to such fineness that 75-80% passed through 40 mesh.

Laboratory Extraction and Tests. Approximately 1 kg. portions of each batch were extracted in large soxhlet laboratory extractors, small control samples being taken in each case for analytical determination of moisture, resins, and rubber. Extraction in the large soxhlets was carried out with acetone for 24 hours, followed by benzol extraction for 24 hours to obtain the rubber. Results of these experiments are given in Table VII. Recovery of rubber under the extraction conditions used for the kilogram lots differs from the rubber content determined analytically, even when allowance is made for the amount of acetone soluble material included with the benzol extract. The results are somewhat higher in two cases and lower in one, while agreeing almost exactly in another; these erratic differences are due to the difficulty of effecting complete extraction or clean separation of substances such as rubber and resinous or tarry contaminants by practical, arbitrary extraction procedures with comparatively large batches of material. Extraction of small analytical samples is exhaustive and thorough in the case of each solvent, and the percentages of rubber by analysis are more consistent and undoubtedly more accurate. The purpose of the large laboratory extractions was the rapid production of a uantity of rubber sufficient for vulcanization and testing. The extraction yields and particularly the rubber analyses of the four samples show no change in rubber content due to drying at temperatures between 145° F. and 205° F.

The concentrated benzol extracts were analyzed to determine the resin content as well as the rubber concentration in each case, but no purification, or separation of the acetone soluble resins included with the rubber was carried out. The vulcanizates were made with the material containing the percentages of resin shown in Table VII. Precuring was carried out by adding sulfur and chemicals in solution, evaporating and heating in laboratory vacuum pots by the standard procedure. The precured rubber milled satisfactorily, but the vulcanizates had a spongy appearance, possibly due to high contents of acetone soluble resins in the raw rubber, and the determinations of ultimate tensile strength are of doubtful significance in this series of tests. The values, shown in Table VIII, are unusually low, and are not much increased by addition of D.P.G. to the standard Captax accelerator formula. There was not sufficient material for preparation of carbon black reinforced test specimens from these laboratory extracts.

Pilot Plant Extraction and Tests. For pilot-scale tests three extraction cell charges of 75-80 pounds were extracted of each lot of goldenrod material.

VI-KILN DRYING TESTS, TABLE VII

LABORATORY EXTRACTION DATA

Kiln Drier Run & Sample No.	Moisture %	ANALYSIS Res. Acet. Ext. % M.F.B.	ANALYSIS Rub. Benz. Ext. % M.F.B.	SOXHLET EXT. YIELDS Acetone Extr. % M. F. B. Indiv. Ext'ns.	Acetone Extr. % M. F. B. Aver.	Benzol Extr. % M. F. B. Indiv. Ext'ns.	Benzol Extr. % M. F. B. Aver.	Resins (Acet. Sol.) in Benzol Ext. %	Rubber Res.-free Yield % M.F.B.	Titration Value ml.	Viscosity c. p.
#9 - 145°F.	7.00	18.4	2.70	13.44	13.87	3.77	3.52	18.1	2.88	4.85	0.685
Bags 358-367				14.30		3.27					
#7 -165°F.	7.20	16.6	2.69	15.34	15.66	2.94	2.85	16.5	2.38	4.65	0.687
Bags 334-345				15.98		2.76					
#6 -185°F.	6.88	17.1	2.58	12.72	13.13	2.98	3.06	10.4	2.74	4.60	0.682
Bags 323-333				13.54		3.14					
#8 -205°F.	6.24	18.1	2.73	13.80	13.54	3.53	3.46	20.8	2.74	4.50	0.679
Bags 346-356				13.29		3.39					

VI-KILN DRYING TESTS, TABLE VIII

VULCANIZATION AND TEST DATA
LABORATORY EXTRACTION SAMPLES

Compounding Formula
Calculated to Resin-free Rubber Basis

Sample dried at:		145° F.	165° F.	185° F.	205° F.
Added in Solution for Precure:					
Rubber, resin-free (g.)		81.9	83.5	89.6	79.2
Rubber, resin-free	Parts	100.	100	100	100
Resins, incl. with rubber	"	22.1	19.8	11.6	26.3
Sulfur	"	4.27	4.19	3.90	4.42
Thiotax	"	1.22	1.20	1.12	1.26
Zinc Stearate	"	6.71	6.58	6.13	6.94
Flectol H	"	1.22	1.20	1.12	1.26
Added on Mill:					
Zinc Oxide (to entire stock)	"	6.71	6.58	6.13	6.94
D.P.G. (to part of stock only)	"	0.61	0.60	0.56	0.63

Vulcanization & Tensile Strength

Sample Dried at	Cure @ 260° F. Mins.	MODULUS 300 % p.s.i.	MODULUS 500% p.s.i.	Tensile Strength p.s.i.	Elongation %	Remarks on Milling and Vulcanizate	Vulc. No.
145° F.	20	195	390	675	600		
	40	235	430	750	600	Milled well.	445
	60	235	430	660	575	No D.P.G. added.	
165° F.	20	75	280	800	700		
	40	120	390	850	650	No D.P.G. added	443
	60	125	440	860	600		
185° F.	10	<40	165	365	625		
	20	35	195	470	650		
	40	80	240	720	700	Milled well. No.	444
	60	75	275	665	700	D.P.G. added.	
205° F.	20	-	-	100	250	No. D.P.G. added.	
	40	225	415	430	500	Spongy vulc.	446
	60	230	385	385	500	doubtful value.	
145° F.	15	120	315	520	575		
	30	195	430	785	600	D.P.G. added.	
	45	235	470	810	600		
165° F.	40	195	550	1100	600	D.P.G. added.	
185° F.	45	160	400	1040	700	D.P.G. added.	
	60	155	390	940	675		
205° F.	15	115	310	380	575	D.P.G. added.	
	30	190	310	500	575		

Care was exercised to keep both the acetone and benzol extracts of each lot separate, qualitatively as well as quantitatively. Acetone extraction of the three cells of one lot was not begun until acetone extraction of the preceding lot had been completed, and similar precautions were taken for benzol extraction. In addition all rubber miscella tanks and evaporators were thoroughly rinsed with benzol between extractions of different samples. Acetone extraction was continued for 14 hours, circulating 115 gallons per hour at 140° F., after which the rubber was obtained by 14 hours extraction with benzol at 75 gallons per hour and 175° F., rates of flow and temperatures of solvents being averages for the duration of the run.

Results of these pilot plant extractions are given in Table IX. Yields were calculated from the volumes, concentrations, and analyses for resins of the concentrated benzol solutions of rubber produced.

As information on safe kiln drying temperatures was urgently required, a rapid preliminary evaluation of the rubber quality of these pilot plant samples was made without further purification. Sufficient volumes of each solution were taken to provide 100 g. of total solids, and after concentration to a convenient volume in the laboratory vacuum pots the standard amounts of sulfur, accelerator and other chemicals were added for complete solution compounding. The rest of the benzol was removed under vacuum, and the rubber precured at 80° - 90° C. for 2 hours. These vulcanizates contained the 8-13% of resins shown in Table IX, and amounts of rubber consequently varied from 87 g. to 92 g. in the different samples. Compounding in every case was based on an estimated 94 g. resin-free rubber as shown in Table X, in which milling, vulcanization, and test data are summarized. For the gum stocks only zinc oxide was milled into the precured composition, after which a portion of the stock was vulcanized and the remainder milled with D.P.G. as a booster accelerator and carbon black to prepare tread stocks. Preparation of separate gum stocks was possible only in the case of samples from goldenrod dried at 165° and 205° F.; the gum stocks of samples from material dried at 145° and 185° F. were so sticky that molding was impossible, and only the carbon black reinforced tread stocks could be handled satisfactorily for vulcanization. These results, as well as the tensile strengths of the tread stock vulcanizates, are erratic and do not show a consistent trend with drying temperatures employed. Resin percentages were not determined until after these preliminary vulcanizations were completed, and it may be significant that the two preparations containing over 12% resin were the ones that could not be milled as gum stocks. A high resin content may account for the relatively low tensile strength of the 185° F. sample, although the 145° F. sample has a fairly high tensile strength despite its high resin content. As only 60 minutes cure were made on each case, these results can have only limited significance.

In order to determine the quality of the rubber more accurately it was necessary to eliminate the effect of resin content as completely as possible, and to carry out the precuring operation under more uniformly controlled conditions. For this purpose a sufficient volume of solution of each sample was taken to obtain about 750-800 g. of rubber, and purified by addition to three volumes of acetone to precipitate the rubber and remove most of the acetone soluble resins. The purified rubber was redissolved in benzol and in most cases about 700 g. compounded in solution. Only about 560 g. of the 185° F. sample was available. The benzol was evaporated and precure applied in a small Loomis jacketed mixer of 1/4 gallon capacity. With these larger,

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VI-KILN DRYING TESTS, TABLE IX

PILOT PLANT EXTRACTION DATA

Kiln Drier Run and Sample No.	Material Extracted Tot. Wt. Lbs.	Anal. Rubber % on Tot.Wt.	RUBBER SOL. Volume (l.) (Conc.fract. (Dil. "	RUBBER SOL. Total Solids g./l.	Resin in Total Solids %	Rubber Yield Total Crude Lbs.	Rubber Yield Resin-free Lbs.	Rubber Yield % on Total Weight	Ext. Eff. %
#9-145° F.	240	2.51	(18.03	89.6)	12.5	4.79	4.18	1.74	69.4
358 - 367			(17.03	32.8)					
#7-165° F.	236	2.49	(16.88	112)	10.5	5.33	4.76	2.02	81.1
334- 345			(13.88	38)					
#6-185° F.	240	2.40	(19.09	63)	12.9	3.56	3.10	1.29	53.9
323 - 333			(13.79	30)					
#8-205° F.	226	2.55	(18.01	88)	8.4	4.89	4.47	1.98	77.6
346 - 357			(17.01	37)					

VI-KILN DRYING TESTS, TABLE X

VULCANIZATION AND TEST DATA
PILOT PLANT EXTRACTIONS
VACUUM POT PRECURING OF UNPURIFIED RUBBER

Compounding Formula
Calculated to Resin-Free Rubber Basis

Sample dried at:		145°	165°	185°	205°
Added in Solution for Precure:					
Rubber-crude, incl. resins, g.		100	100	100	100
Resins in crude rubber, %		12.5	10.5	12.9	8.4
Rubber, resin-free, g.		87.5	89.5	87.1	91.6
Rubber, resin-free	Parts	100	100	100	100
Resins, incl. with rubber	"	14.3	11.7	14.8	9.2
Sulfur	"	3.76	3.68	3.78	3.59
Thiotax	"	1.07	1.05	1.08	1.03
Zinc Stearate	"	5.91	5.78	5.94	5.65
Flectol H	"	1.07	1.05	1.08	1.03
Added on Mill:					
Zinc Oxide (for all stocks)	"	5.91	5.78	5.94	5.65
D.P.G. (for tread stocks only)	"	0.57	0.56	0.57	0.55
Carbon (Statex) (for tread stocks only)	Parts	57.1	55.9	57.4	54.6

Tensile Strengths
60 Min. Cures Only @ 260° F.

Sample Dried At	Stock	MODULUS 300% p.s.i.	MODULUS 500% p.s.i.	Tensile p.s.i.	Elongation %
145° F.	Tread	340	950	1900	700
165° F.	"	425	1180	1775	625
185° F.	"	265	735	1600	700
205° F.	"	460	1310	2230	700
165° F.	Gum	-	-	500	775
205° F.	"	-	-	655	825

over

purified samples it was possible to make a more complete series of both gum and tread stock vulcanizates to determine maximum tensile strengths in each case. Compounding, milling, and vulcanization data, and tensile tests are recorded in Table XI. Milling was satisfactory in every case and both gum and tread tensile strengths are much higher than in the case of laboratory pot precures of the unpurified rubber. No more consistent trend is evident in these results than in the series obtained on unpurified rubber given in Table X. In both series the rubber prepared from goldenrod dried at 205° F. is somewhat better than any of the lower temperature test samples, and the results indicate no deleterious effect on the product due to increased drying temperatures over the range 145° F. to 205° F.

Conclusions. 1. No significance can be attached to results of tests on rubber obtained from the laboratory extractions, because of the variable and, in most cases, excessively high resin contents of the preparations. The determinations of viscosity and titration values on these samples show no significant variation in quality of the rubber due to drying at any of the temperatures used.

2. Laboratory pot precures of rubber extracted in the pilot plant and tested without purification to remove the appreciable quantities of included resins are also of questionable significance, although carbon reinforced tread stock vulcanizates gave fair tensile strength values indicating no adverse effect on quality of drying temperatures up to 205° F.

3. Pilot plant extracted rubber, purified to contain uniformly less than 2% resins, and precured in larger batches under as uniform and carefully controlled conditions as possible, gave maximum tensile strengths on vulcanization which show no significant trend with change in drying temperature. Up to 205° F. there is no evidence of any deleterious effect upon the quality of the product.

4. Analytical determinations made upon samples of the various batches of kiln dried goldenrod material after mixing and grinding show no significant difference in rubber content as a result of the differences in drying temperatures.

VI-KILN DRYING TESTS, TABLE XI

VULCANIZATION AND TEST DATA
PILOT PLANT EXTRACTION-PURIFIED RUBBER - PRECURED IN SMALL LOOMIS MIXER

Compounding Formula for all Samples Calculated to Resin-free Rubber Basis

		Added in Solution for Precure	Added in Milling
Rubber, resin-free	Parts	100.0	-
Resins, incl. with rubber	"	1.6 - 1.9	-
Sulfur	"	0.60	2.90
Thiotax	"	0.75	0.25
D.P.G.	"	0.30	0.50
Zinc Stearate	"	5.50	-
Flectol H	"	0.50	-
Zinc Oxide	"	-	5.50
Carbon (Statex) for tread	"	-	50.0

Sample Dried At	Cure @ 260° F. Mins.	MODULUS 300% p.s.i.	MODULUS 500% p.s.i.	Maximum Ten. Str. p. s. i.	Ult. Elong. %	Remarks
145°F.	10	165	625	785	525	
	20	200	-	435	400	Gum stock with DPG added.
	40	265	-	1100	475	Milled very well.
165° F.	10	100	400	2000	725	Gum stock with DPG added.
	20	200	865	2470	650	Milled very well at first,
	40	200	1200	1530	550	later sticky.
185°F.	10	100	300	1300	650	Gum stock with DPG added.
	20	170	830	2000	625	Milled very well.
	40	235	-	400	375	
205°F.	10	135	565	1670	650	Gum stock with DPG added.
	20	205	965	2350	625	Handled extremely well.
	40	300	1600	1770	525	

TREAD STOCK-50 PARTS STATEX ADDED

145°F.	10	735	1635	2135	600	
	20	1230	2535	2535	500	Milled well.
	40	1540	-	2330	425	
165°F.	10	620	1900	2350	600	
	20	1180	2430	2430	500	Did not mill so well.
	40	1485	-	2320	425	
185°F.	10	575	1625	2170	600	
	20	1200	2270	2270	500	Milled well.
	40	1530	-	2535	425	
205°F.	10	735	1905	2600	650	
	20	1255	2540	2850	550	Sheeted on cold rolls.
	40	1535	-	2375	400	

over

Tests on Effect of Sun Drying and Heating in Storage. The goldenrod material for these experiments was harvested October 5, machine stripped, and the coarse stems picked out by hand in Waynesboro. For the sun drying tests the material was spread on trays with paper covered bottoms and exposed to the sun for 24 hours on three 8-hour days. For the test on heating in storage, material was packed in cartons and sealed, and allowed to heat for 66 hours. Upon removal it was dried in a tray drier for 5-1/2 hours at 145° F. Green leaves for the control on these tests were dried for 7 hours at 145° F. in the tray driers.

The dried samples were ground through the 1/32" screen of the Ball and Jewell mill at the Southern Regional Research Laboratory. Large-scale laboratory extraction data and analytical results are summarized in Table XII. Vulcanization and testing data are given in Table XIII.

The titration values of the benzol extracts, obtained from the control and leaves heated before drying, indicate the presence of rubber of slightly higher molecular weight than that obtained from the benzol extracts from the sun dry extractions, but significance of titration values is doubtful as a measure of quality of the entire sample. It will be noted that the acetone extract is lower and the benzol extract is slightly higher from the control and heated leaves, also that the resin content of the benzol extracts is higher in these cases. The yield of resin-free rubber has not been decreased by exposure to sunlight in sun drying.

The precured samples of rubber, from the control and sun-dried tests, milled very well with the additional chemicals required before vulcanization, whereas the precured rubber from the leaves heated in storage appeared to be too dry for satisfactory milling. While the accuracy of evaluation is probably not sufficiently great to determine differences in quality of the rubber on these samples, however, these data do indicate that the quality of the rubber has not been impaired by subjecting the leaves to sun drying or by heating in storage before final drying.

VI-TABLE XII
EFFECT OF HEATING & SUN DRYING ON YIELD

Sample	% Moisture As Rec'd.	% Resins Acetone Ext. M.F.B.	% Rubber Benzol Ext. M.F.B.	% Resins in Benzol Extract	% Rubber Resins-free M.F.B.	Titrn. Value Benzol Ext.	Visc. Benzol Ex-tract	% Rubber Analytical M.F.B.
Sun Dry (24 hours)	9.70	19.08-19.75	3.80-3.87	8.40	3.52	4.60	0.691	3.54
Heated leaves before drying.	7.72	12.18-12.93	4.30-4.19	14.40	3.62	4.50	0.680	3.72
Control	7.05	15.78-15.57	4.20-4.06	13.60	3.57	4.50	0.673	3.66

VI-TABLE XIII
EFFECT OF HEATING & SUN DRYING ON QUALITY

	Sun Dry 24 Hrs.	Heated Leaves Before Drying	Control
Rubber, crude, incl. resins, g.	49.2	56.1	45.1
Resins in crude rubber, - %	8.4	14.4	13.6
Rubber, resin-free, g.	45.1	48.0	39.0
Rubber, resin-free Parts	100.00	100.00	100.00
Resins, incl. with rubber "	9.2	16.8	15.7
Sulfur "	3.82	4.09	4.05
Thiotax "	1.09	1.17	1.16
Zinc Stearate "	6.00	6.43	6.36
Flectol H "	1.09	1.17	1.16
Added on Mill:			
Zinc Oxide "	6.00	6.43	6.36
D.P.G. "	.55	.58	.58

Sample	Cure @ 260° F. Mins.	MODULUS @ 300%	MODULUS @ 500%	Maximum Ten. Str. p. s. i.	Ult. Elong. %	Remarks
Sun dry, 24 hours.	20	60	185	1230	750	
	40	145	400	1440	700	Sample milled satisfactorily.
	60	185	470	1590	675	
	80	160	520	960	600	
	15	140	370	1660	750	
	30	220	690	1880	700	0.5 part D.P.G. added.
	45	275	925	1720	625	
Heated leaves before drying	20	140	420	930	600	
	40	180	460	1010	600	Too dry for satisfactory milling. Probably too much precure.
	60	180	520	1050	575	
	80	190	500	770	575	
	15	165	540	1050	550	
	30	260	660	1250	550	0.5 part D.P.G. added.
	45	260	690	1130	550	
Control	20	130	290	785	675	
	40	155	360	890	650	Good milling.
	60	180	425	890	575	
	15	120	330	990	700	
	30	190	500	1290	650	0.5 part D.P.G. added.
	45	200	590	1280	625	

VII-RAW MATERIAL, GRINDING, AIR-SEPARATION, AND SCREENING

The purpose of this work was twofold; first, to determine the suitability of a hammer mill for large-scale grinding of dried goldenrod harvest material and, second, to determine whether a screening method could be developed for effectively separating or fractionating the dried mixture of ground goldenrod leaves, stems, and bloom received from Waynesboro, Georgia. The first part of this section covers the grinding experiments which were made to check the final decision to use a hammer mill for grinding the entire goldenrod crop at Waynesboro. The second part of the section is devoted to the experiments conducted on screen-fractionation of the ground material and also includes a brief account of the experimental work done on air-separation of the ensilage-cut whole plant material after drying, which was abandoned in favor of air-separating of the ensilage-cut freshly harvested material before drying.

GRINDING

The hammer mill used for grinding the goldenrod material was a standard 8" x 15" Jeffrey machine, with 10 horsepower driving motor fitted with standard rectangular construction swing hammers. The mill was not equipped with any auxiliary pneumatic system for discharging, recycling, or segregating the ground product. The pulverized material was merely collected in a suitable cloth-enclosed receiving can placed under the discharge outlet. A series of eight runs (tabulated below) was made, in which the following operating factors were varied: feed rate, mill speed, hammer size or thickness, and size of screen opening.

Run No.	Mill Speed r. p. m.	Hammer Size (Thickness)	Screen Size (Openings)
1	1730	1/4"	1/32"
2	1730	1/8"	1/32"
3	2440	1/8"	1/32"
4	2440	1/8"	1/16"
5	2440	1"	1/16"
6	2440	1"	1/16"
7	2440	1/2"	1/16"
8	2440	1/4"	1/16"

The exact arrangement of the hammers for each run is shown in Figure 1. Careful observations were made throuhout of the general function and behavior of the machine in regard to factors found to be critical in this operation; i.e., overheating of the material, horsepower consumption, and clogging of the screen openings at the high feed rates. Complete results of these runs are given in Table I. Power readings, taken over only short-time intervals, were merely indicative and did not necessarily represent actual average power requirements at equilibrium conditions over long periods of operation. Two runs were also made using a Ball and Jewell mill for the purpose of comparing the screen analysis of the pulverized material using corresponding size

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screens in the hammer mill experiments, but no feed or capacity rates or power readings were taken.

The material used for the runs was taken from various lots of the 1942 goldenrod crop which had been hand-stripped and contained practically no stems and blooms. One lot of material was used for the Ball and Jewell mill run, another for hammer mill run No. 1, another for runs 3, 4, 5, and still a different lot for runs 6, 7, and 8. Run No. 2 was made using a mixture of coarsely ground leaves, partly ground leaves, and whole leaves. All of the leafstock averaged 8-10% moisture. The dried stock was of a brownish green color and was of good general appearance with the exception of that used in run No. 2 which appeared to be of inferior grade.

In run No. 1 the material was fed steadily up to and at the maximum rate at which the mill was able to handle the feed. Bridging of the leaves above the hammers occurred several times in the course of this run. This was believed due partly to the feed material being matted and compressed, and partly because of the method of feeding used. The heterogeneous mixture of stock used in run No. 2 was fed too fast into the mill and the consequence was that the material heated excessively (185° F.) and clogged the screen. Run No. 3 was the first run conducted at the high speed and was made for comparison with the results obtained at the lower speed. The capacity of the mill was considerably reduced at the higher speed but the pulverized product was very much finer. Runs 4 to 8 inclusive were all made at 2440 r.p.m. using the 1/16" screen throughout. The only difference was the variation in the size of the hammers used. It was observed that the maximum rate of feed up to the power capacity of the driving motor was limited in these runs only by bridging of the material over the hammers, which condition persisted and served to complicate the operation. In runs 7 and 8 there was a tendency for bridging of the leaves upon any slight increase in the feed rate.

Separate pilot plant extraction of the goldenrod leaves ground through the Ball and Jewell mill using 1/16" and 1/32" screens indicated that the screen with the 1/16" openings did not produce a product fine enough and of correct particle size distribution for extracting over 70% of the available rubber in the leafstock, whereas a relatively high extraction efficiency approaching almost complete extraction was obtained when the 1/32" screen was employed. Extraction results reasonably paralleling those obtained with the Ball and Jewell mill were obtained with the material from runs 1 to 3 inclusive, which had been ground in the Jeffrey hammer mill using the 1/32" screen. This is entirely predictable on a basis of the respective screen analyses for the two screen sizes shown in Table II, regardless of the size of the hammers used. As evidenced by the results shown, the size of the hammers has only a minor effect on the fineness of the ground product and also on the capacity of the mill. Data are given for 1/8", 1/4", 1/2", and 1" thick hammers used against a 1/16" screen, but only 1/8" and 1/4" thick hammers were used against the 1/32" screen. As far as fineness of grind and particle size distribution using the 1/16" screen

is concerned, best results were obtained where either the 1/2" or 1" hammers were used. It was not possible to conduct a systematic study comparing screen sizes from a standpoint of rate of material throughput or capacity at the maximum rated motor horsepower at any one speed or over a range of speeds. Observations made during these tests indicate that considerations other than power consumption are the limiting factors of capacities attainable for continuous operation of the hammer mill, such as overheating of the material and plugging of the screen openings. It was also observed that holdup above the hammers consistently preceded overheating of the ground material, lowered capacity, and eventual clogging of the screen resulting in frequent stoppage of operation.

In all of the runs made, the feed rates shown are close to the maximum that could be handled by the mill for preventing overheating of the material holdup above the hammers in the case of the 1/32" screen and because of bridging of the material in the other cases as stated. This bridging effect was due largely to the condition of the leaves and to the method of feeding. The leaves were considerably matted and tended to bridge above the hammers unless they had been well separated before delivering into the mill. It was obvious that elimination of bridging would not be a difficult procedure and would result directly in considerably increasing the grinding capacity of the hammer mill.

As all of the power data listed in this report cover at best only short time intervals, and also because of the complicating factors stated above, little significance can be placed on, and conclusions drawn from these results for indicating what the power requirements would be for continuous operation of the mill at different loads. For the same reason and also due to the overheating of the material at high feed rates, especially for the small screen openings, it would be impossible to predict accurate capacities for any set of conditions over a comparatively long period of sustained mill operation. Although a throughput of approximately 15 pounds per minute was obtained for run 5-e with the 1/16" screen, at top mill capacity (2 minutes duration), it may be safely stated, after taking all of the above factors into consideration, that a conservative estimate of the mill capacity for sustained operation would be not more than 10 pounds per minute at 2440 r.p.m. using a 1/16" screen with 1/2" or 1" hammers, and not more than 5 pounds per minute using a 3/64" screen for assuring adequate material fineness necessary for complete extraction of the rubber, together with minimum clogging of the hammer mill screen. Use of a 1/32" screen is definitely not recommended because of the reduced capacity of the mill and also inasmuch as the ground product is finer than is necessary for extraction.

The exact wearing effect that a material of the goldenrod leaf type would have on the various parts of the hammer mill can only be determined by conducting runs over a long period of time. The 1/32" screen was badly dented at the end of run No. 3 but this was attributed to the presence of several large pieces of stem material which kept recirculating in the throat of the machine just above the hammers. The 1/16"

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screen had three small dents after completion of runs 4 to 8 inclusive, but otherwise was in a very good condition.

Results of the studies reported indicated that a standard hammer mill similar to the Jeffrey type is a suitable machine for grinding goldenrod leaf material. Under the right conditions, that is, with the proper size of screen and hammers, this mill can very effectively grind this type of material to a fineness suitable for complete pilot plant extraction of the rubber contained. On the basis of these findings, a hammer mill was used for grinding the bulk of the dried crop at Waynesboro, Georgia. This material had been ensilage-cut on harvesting and then air-separated before drying and consisted roughly of only 20% leaves and the balance bloom and stems, but the mixture ground satisfactorily in the mill. The ground product, however, contained very little rubber and further purification by screening or air-separation methods was necessary in order to increase the rubber content for pilot plant processing.

VII-TABLE I

GOLDENROD GRINDING AND SCREENING TESTS

Run No.	Speed R.P.M.	Screen Openings Inches	Hammer Thickness Inches	Lbs. Ground	Time Mins.	Feed Rate #s/Hr.	Watt-hour Meter *Rev. Total	Watt-hour Meter K.W.H. Used	K.W.H. per 100 #	Avg. H.P.	Temp. °F Avg.	Density #/cu. ft.
1	1730	1/32	1/4	36	33	64.5	125.5	2.26	6.25	5.37	125	-
2a	1730	1/32	1/8	26	11	140.5	-	-	-	-	-	37
2b	1730	1/32	1/8	45.3	59	46.1	-	-	-	-	-	37
2c	1730	1/32	1/8	75.5	41	110.5	-	-	-	-	185	37
3	2440	1/32	1/8	109	128	50.8	225	4.05	3.72	2.71	115	33.7
4	2440	1/16	1/8	66	13.75	288.	26.75	0.48	.73	2.83	100	29.4
5a	2440	1/16	1	47	7.66	368.	26.00	0.47	1.00	4.81	115	32.6
5b	2440	1/16	1	10	1.05	554.	-	-	-	-	-	32.6
5c	2440	1/16	1	-	-	-	-	-	-	-	-	32.6
5d	2440	1/16	1	30	2.33	775	13.5	0.24	.81	8.43	115	32.6
5e	2440	1/16	1	27	1.88	860	12.	0.21	.80	9.23	115	32.6
5f	2440	1/16	1	45	2.28	1182	22.	0.40	.89	13.9	115	32.6
6a	2440	1/16	1	30	3.16	570	13.75	0.25	.82	6.25	109	-
6b	2440	1/16	1	40	4.75	510	19.75	0.36	.89	6.05	109	-
7a	2440	1/16	1/2	10	1.66	362	5.5	0.10	.99	4.76	110	30.4
7b	2440	1/16	1/2	10	1.58	380	5.5	0.10	.99	4.87	110	30.4
7c	2440	1/16	1/2	30	4.78	378	17.	0.31	1.02	5.15	110	30.4
8a	2440	1/16	1/4	39	8.25	284	22.75	0.41	1.05	4.00	110	29.
8b	2440	1/16	1/4	34	7.30	280	19.75	0.36	1.05	3.92	110	29.

*Meter factor: 18 watt-hours per revolution.

VII-TABLE II
SCREEN ANALYSES

	Jeffrey Hammer Mill							Ball & Jewell Mill	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 7	No. 8	No. 1	No. 2
				Hammers					
	1/4"	1/8"	1/8"	1/8"	1"	1/2"	1/4"		
				Screen				Screen	
	1/32"	1/32"	1/32"	1/16"	1/16"	1/16"	1/16"	1/16"	1/32"
				Speed (r.p.m.)				Speed (r.p.m.	
	1730	1730	2440	2440	2440	2440	2440	1000	1000
Mesh:	% Passed Through							% Passed Through	
20	100.	99.8	100	99.2	99.8	99.9	99.4	95.2	100
30	99.8	99.6	99.9	87.2	95.4	95.5	89.6	71.2	100
40	95.9	96.1	98.8	53.	72.7	72.7	58.6	39.8	94.5
50	49.3	56.7	77.2	22.3	35.1	35.8	27.6	18.9	28.7
60	46.6	54.2	72.8	18.7	30.7	31.2	23.4	14.12	28.5
70	28.9	19.1	50.2	13.2	21.9	21.6	16.6	8.61	23.2
80	24.3	18.7	47.5	11.6	19.4	19.0	14.8	7.06	20.0
100	18.1	17.7	40.7	9.0	15.7	15.1	12.2	5.15	14.7

AIR-SEPARATION

A complete air-separation unit with a handling capacity of 150-200 pounds of material per hour was designed and constructed at the Southern Regional Research Laboratory for pneumatically purifying the 1" ensilage-cut, dried, whole goldenrod plant stock shipped from Waynesboro, Georgia. The assembly consisted essentially of a large wooden air-box with adjustable swing and slide type baffles, a fan of adequate capacity and suction pressure, and a cyclone collector. After making the necessary preliminary adjustments for optimum operation of the unit, effective two-way separation was obtained on a single pass, which yielded a fairly concentrated fraction of impure leaf material by removing a stem fraction amounting to approximately one-half of the weight of the original material. However, the machine did not successfully remove any appreciable quantity of the light bloom and chaff, the bulk of which remained included with the leaves. The following table lists the various fractions obtained with their respective percentages by weight for a typical set of runs aggregating approximately 1900 pounds of raw material processed.

Run No.	Raw Material #	Stems #	Leaves #	Bloom #
1	155	75	67	2.5
2	338	158	166	10.0
3	401	202	191	13.5
4	678	338	318	16.0
5	361	149	196	14.0
Total Weights	1933	922	938	56.0
Fraction %		47.7	48.5	2.9

The enriched leaf fraction was concentrated to about 48.5% of the original raw material before separating and assayed 1.85% crude rubber content. Approximately 10,000 pounds of enriched material was produced from the baled stock shipped from Waynesboro. The entire production was later extracted in the pilot plant without any further separation or enrichment.

Around this time, installation of air-separation equipment of adequate capacity had been completed at Waynesboro and the above procedure was abandoned in favor of air-separation of the freshly harvested ensilage-cut whole plant stock for removal of the stem portion prior to drying and grinding. This procedure was permanently adopted at Waynesboro. Further final separation by screening was carried out at the Southern Regional Research Laboratory and is described in the following part of this section.

SCREENING

The material processed through the screening machinery was the general harvest goldenrod which had been cut in an ensilage cutter,

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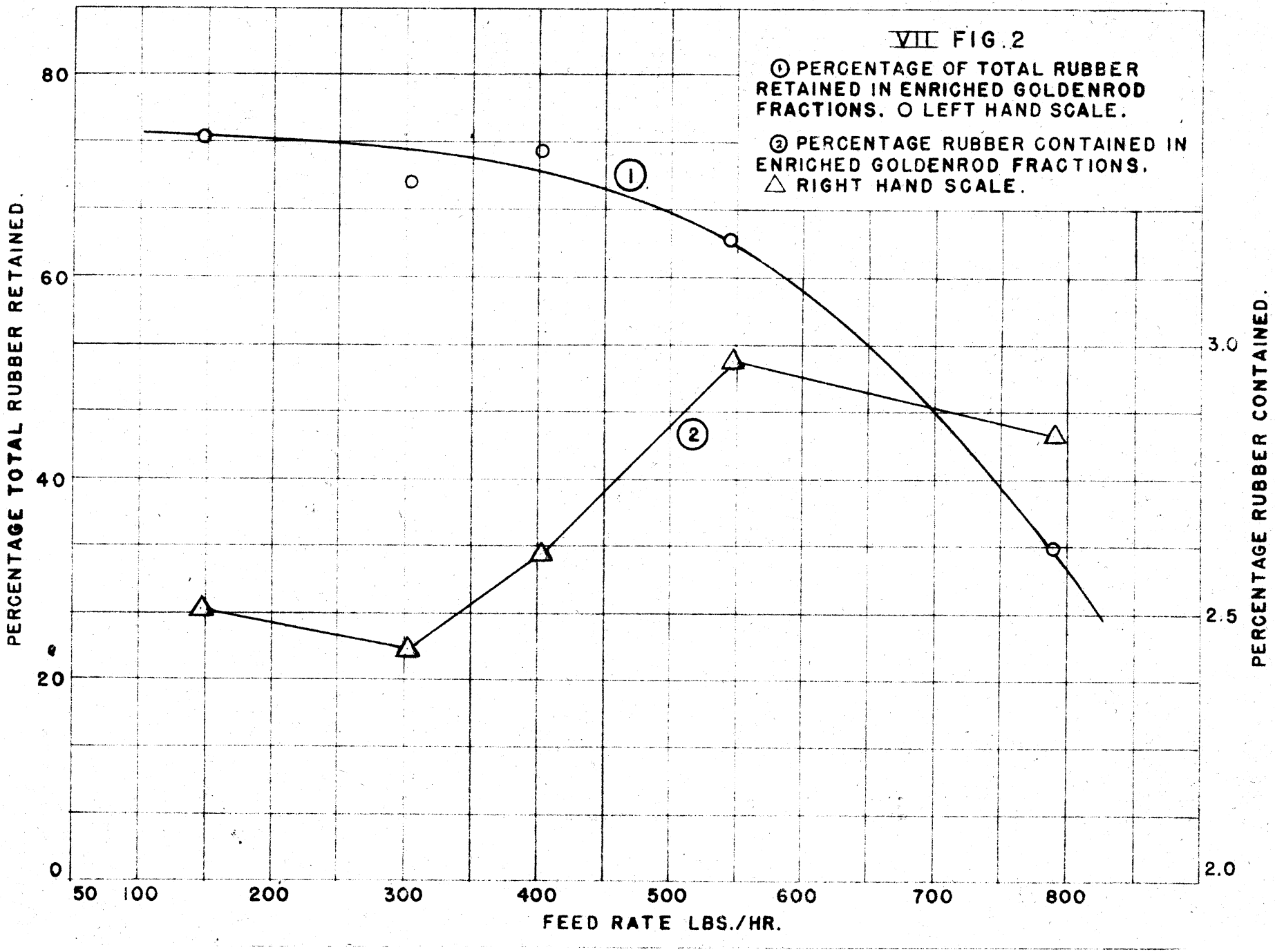
air-separated to remove large stems, kiln-dried, and finally ground in a hammer mill with 1/32" or 1/16" screen. The ground product which had a composition of approximately 20% leaves, 30% stems, and 50% bloom (flower, seed, chaff) was shipped to New Orleans from Waynesboro, Georgia, in paper bags each containing 30 to 40 pounds of goldenrod. A total of 3153 bags or 116,489 pounds was received.

A standard 18" wide, three-tray cottonseed meats purifier operating at a shaker speed of 300 cycles per minute was used to separate this material. This machine was equipped with high pitched shakers specially suited for processing relatively large particles of cottonseed or peanut meats and hulls through corrugated perforated metal plates but performed satisfactorily with this finely divided goldenrod material using flat wire screen, and gave a fairly good separation at a handling rate of approximately 550 pounds per hour. Dusting was reduced to a minimum by means of cloth enclosures fitted closely around the purifier trays and other openings maintained under a slight suction, the dust-laden air before final venting being delivered to an expansion chamber or aspiration box operating with a large cotton fan, all of which were integral parts of the purifier unit. The two collecting boxes for receiving the fractions were fitted with "breather" bags and the assembly as a whole functioned satisfactorily as a closed system.

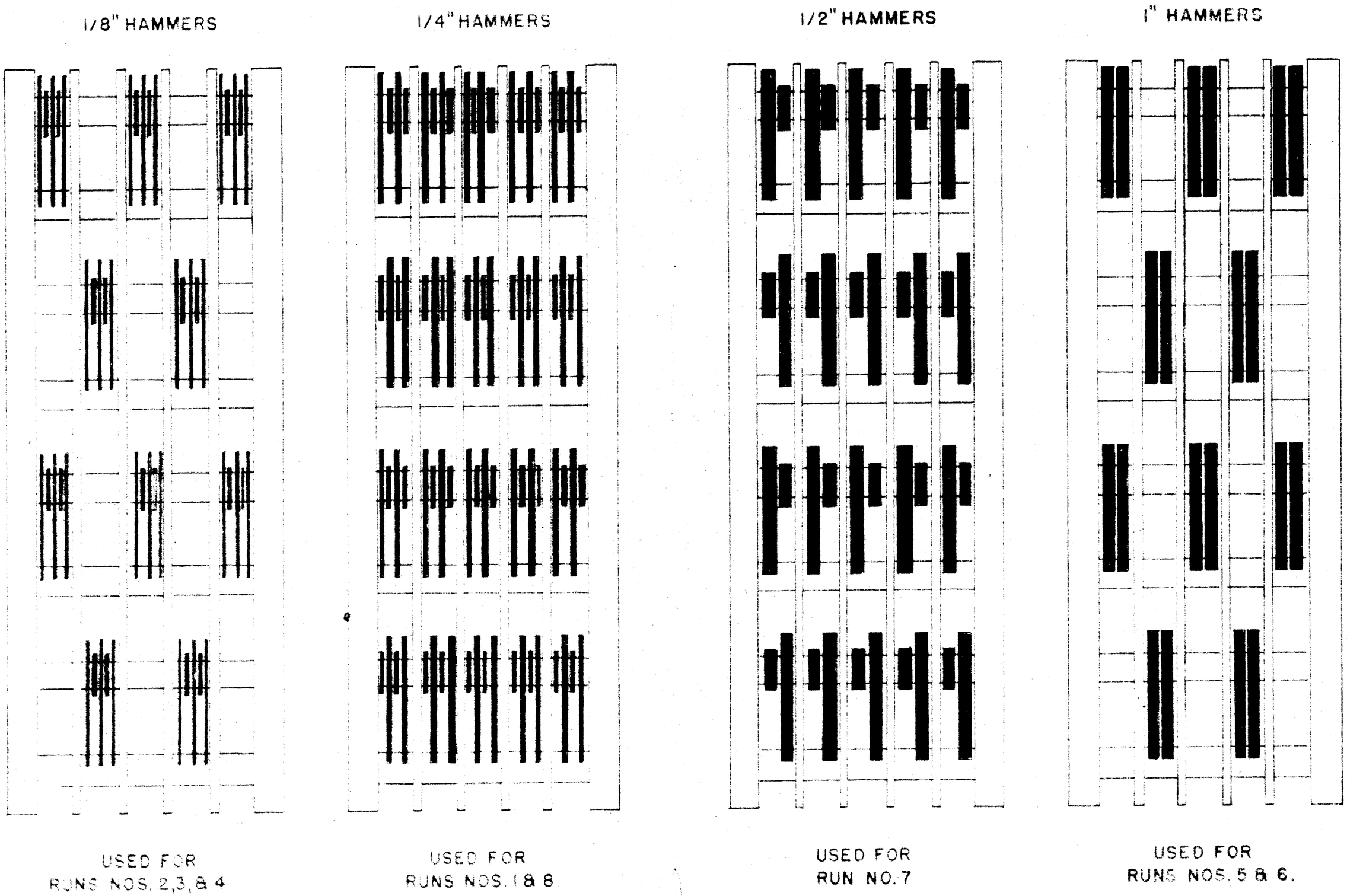
The top and middle trays were equipped with frames fitted with U. S. standard 30 mesh bronze screens 18" wide by 72" long. The bottom tray was blanked off with sheet metal and served merely as a conveyor to carry the "through" material to the discharge funnel. In order to obtain a constant feed rate, an automatic ratchet type screw feeder was installed. For delivering material to both screens simultaneously, a two-way distributor chute equipped with an adjustable slide gate was mounted just beneath the feeder outlet. For obtaining equal loading of each screen, the slide gate was adjusted to allow approximately 25% more material to the upper screen since the lower screen had the task of handling both the material fed to it and that passing through the upper screen. The material passing through and that rejected by the screens dropped into separate funnels and thence to respective collecting boxes below.

It was found necessary to load the screens rather heavily not for increasing the rate of throughput, but in order to obtain effective concentration of the fraction rich in rubber, and experimental runs were made over a wide range of feed rates to determine the optimum rate and corresponding feeder setting which gave the highest percentage of crude rubber in the enriched fraction, commensurate with a not too excessive loss of rejected product. It will be noted in the following table that run No. 4, with feeder setting of 15 and speed transmission control at 4.00, produced the fraction of highest (optimum) crude rubber content, and the curves shown in Figure 2 indicate clearly the optimum feed rate (550 pounds per hour) at which the rubber concentration approached and passed a maximum point under the operating conditions maintained.


VII FIG. 2
① PERCENTAGE OF TOTAL RUBBER RETAINED IN ENRICHED GOLDENROD FRACTIONS. O LEFT HAND SCALE.
② PERCENTAGE RUBBER CONTAINED IN ENRICHED GOLDENROD FRACTIONS. △ RIGHT HAND SCALE.
PERCENTAGE TOTAL RUBBER RETAINED.
PERCENTAGE RUBBER CONTAINED.
FEED RATE LBS./HR.
80
60
40
20
0
3.0
2.5
2.0
50
100
200
300
400
500
600
700
800
1
2

VII FIG. 1

HAMMER ARRANGEMENTS FOR GOLDENROD EXPERIMENTS.



Run No.	Speed Reducr. Setting	Conveyor Control Setting	Feed Rate Lbs./Hour	Enrchd. Fraction (throughs) #/Hr.	Enrchd. Fraction (throughs) %	Rejected Fraction, incl. losses %	Crude Rubber Content % Orig. Mtrl.	Crude Rubber Content % Enrchd Mtrl.	Crude Rubber Content % Rejected Mtrl.
1	3.16	15	149	83	56.0	44.0	1.89	2.51	1.29
2	3.50	15	304	158	52.0	48.0	1.82	2.43	1.12
3	3.75	15	402	192	48.1	51.9	1.73	2.61	1.19
4	4.00	15	546	226	41.5	58.5	1.95	2.97	1.19
5	4.50	15	790	232	26.9	73.1	2.31	2.85	1.76

Accordingly, these optimum settings were used in concentrating about 64,000 pounds of goldenrod material for pilot plant extraction.

The following table gives a break down and analysis of total ground material processed through the 30 mesh screens.

	Weight #	% of Total Weight	Crude Rubber Content Percent	Crude Rubber Content Wt. #	% of Tot. Cr. Rubber Content
Original material	172,926	100.0	1.95	1422	-
Material enriched (throughs)	30,743	42.1	2.97	912	64.5
Material rejected (overs)	42,183	57.9	1.19	502	35.5

Purification and concentration of the leaf fraction apparently increased the crude rubber content from 1.95% contained in the original mixture, to 2.97% in the enriched fraction, equivalent to an enrichment of approximately 52.3%. Of the total 72,926 pounds of goldenrod stock processed, 30,743 pounds of enriched material were produced, representing 42.1% of the total weight, and containing 64.5% of the rubber contained in the original raw material.

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Agricultural Research Administration

Bureau of Agricultural and Industrial Chemistry

EXTRACTION, CHARACTERIZATION, AND UTILIZATION OF GOLDENROD RUBBER

PART 2
SECTIONS VIII THROUGH XVII

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EXTRACTION, CHARACTERIZATION, AND UTILIZATION OF GOLDENROD RUBBER

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VIII EXPERIMENTS ON CHEMICAL TREATMENTS IN CONJUNCTION WITH EXTRACTION OR MECHANICAL SEPARATION

Water Digestion of Goldenrod Leaves Prior to Extraction. A series of experiments were conducted on digesting goldenrod leaves with water alone at atmospheric pressure prior to the usual acetone and benzol extractions. The purpose of these experiments was to determine the effect on the yield and quality of the rubber obtained from digested material as compared to that produced by the two-solvent laboratory and pilot plant control extractions on the same variety of leaves. In addition experiments were carried out to explore the possibility of making a direct benzol extraction on both the unground and ground digested material without prior acetone extraction to remove the resinous impurities. Leaves ground to pass through a 30 mesh screen and boiled from two to four hours in water, filtered, washed, and dried, lose up to 40 percent by weight of the water soluble constituents. It was found to be necessary to extract with acetone after drying in order to remove water insoluble non-rubber material, but the amount of this was reduced appreciably to approximately two-thirds of that obtained by acetone extraction without prior digestion, and the acetone extraction can be shortened. Benzol extraction yields of 8 percent were obtained, which was more than 20 percent greater than the 6 percent yield from acetone-benzol extraction of the controls as shown in Table I.

In two laboratory experiments, 124 and 125, the leaves were boiled for 2 hours in water, filtered, washed, and dried. Dried leaves ground to pass through a 30 mesh screen were used in experiment 124, while unground dried leaves were used for experiment 125. After grinding the dried digested whole leaf material, benzol extraction was made directly for 24 hours in a soxhlet extractor without prior acetone extraction to remove resinous impurities.

Direct benzol extraction was also made for the same time on the dried material of experiment 124 ground to pass through a 30 mesh screen before water digestion. Acetone was used to precipitate the rubber from the benzol extract in each case, however, it was necessary to centrifuge the precipitates in order to agglomerate the rubber. Water digestion of whole leaf material gave a lower water soluble value than on ground leaves and also a lower rubber yield as shown in Table I. Furthermore, the vulcanizates gave lower tensile strength as shown in Table II.

The solution method of precompounding in pot stills was employed on the benzol extracts from the digested material and the controls. All chemicals were added in solution except 5.5 parts zinc oxide which was milled in after the precuring step. The rubber finally obtained in case of water digestion was found to be slow curing in culcanization, the highest tensile strength obtainable with the material available from these experiments was 1400 pounds per square inch after 60 minutes, compared to values up to 2000 pounds per square inch after 30 to 50 minutes curing for the control benzol extracts prepared by the usual acetone-benzol extraction procedure from the laboratory or pilot plant as reported in Table II.

Experiments 74 and 86 tabulated in Tables I and II correspond to

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VIII TABLE I, WATER DIGESTION AND CONTROLS

Exp. No.	Wt. of Charge lbs.	EXTRACTION: Extraction Time: Water Hours	Acetone Hours	Benzol Hours	Extracts: Water %	Acetone %	Benzol %	ANALYTICAL RESULTS: Acetone Precipitation: Rubber %	Soluble Resins %	Tit. Value
Laboratory 142	2.34	Control	24	24	—	15.6	6.4	---	---	4.45
Laboratory 139	2.20	2	24	24	36.5	10.66	7.72	---	---	4.40
Laboratory 159	2.20	4	24	24	40.7	10.7	7.92	---	---	4.80
Laboratory 124	2.20	2	—	24	40.2	---	13.71	6.20	7.51	4.45
Laboratory 125	1.41	2	—	24	31.9	---	10.72	4.40	6.32	4.42
Pilot Plant 74	77.8	Control	38	26	----	15.2	6.2	----	----	4.30
Pilot Plant 86	84.3	Control	35	26	----	16.4	7.06	----	----	4.30

VII TABLE II, WATER DIGESTION: COMPOUNDING, VULCANIZATION, AND TESTING

COMPOUNDING	FORMULA
Rubber	100.0 parts
Sulfur	3.5 parts
Thiotax	1.0 part
Flectol-H	1.0 part
Zinc stearate	5.5 parts
Zinc oxide	5.5 parts

VULCANIZATION AND TESTING DATA

Exp. No.	Vulc. Time Mins. at 260°F	Tensile strength p.s.i.	Ultimate Elong. %
Laboratory 142 (control)	50	1900	710
Laboratory 139	60	1400	800
	80	1305	750
Laboratory 159	60	1190	700
	70	1240	700
Laboratory 124	50	920	750
Laboratory 125	50	1060	725
Pilot Plant 74 (control)	30 (1)	2060	775
	50 (2)	1837	775
Pilot Plant 86 (control)	30	1950	750

(1) Straight benzene extract.
(2) Acetone precipitated rubber.

pilot plant runs 3 and 4 listed in the tabulation of the single cell pilot plant extractions (see Section II). Water digestion of leaves, followed by the acetone-benzol extractions, gives a higher rubber yield but lower tensile strength when compared to rubber obtained by the usual solvent extraction procedure.

In case of direct benzol extraction on the dried digested leaves it is apparently necessary to centrifuge the resin-rubber mixture after the addition of acetone to agglomerate the rubber or add a small amount of some coagulent, such as KSCN, to coagulate the rubber. The rubber obtained from the single solvent extraction procedure was observed to be slow curing in vulcanization, the highest tensile strength was 1060 pounds per square inch after 50 minutes curing as reported in Table II. Rubber obtained on this scale showed little promise of development to produce usable rubber from water digested goldenrod leaves.

Alkali and Acid Digestion of Tray Dried Leaves Prior to Extraction. Digesting of goldenrod leaves in an alkali medium followed by an acid medium was investigated as a means of improving the solvent extraction process: first, by reducing the bulk of the material thus increasing up to four fold the capacity of the extraction equipment, and second, by removing about two-thirds of the acetone soluble constituents thereby facilitating complete extraction of both resins and rubber from the concentrated residue. The bulk of the leaves was reduced and the rubber concentrated in the residue by digesting and removal of 75 percent of the non-rubber constituents present in the leaves according to the following procedure:

(1) Two hour digestion in 2% NaOH at 100°C. followed by three washes with boiling water.

(2) One-half hour digestion in 3% H_2SO_4 at 100°C. followed by three washes with boiling water.

(3) Residue air dried.

Washing procedure for the digested material from experiments 3, 6, 14, 17, and 23 was carried out on a vibrating screen while the remaining samples were washed on a stationary screen.

The air dried residues were extracted in laboratory Soxhlet extractors with acetone for 24 hours and then with benzol for 24 hours. Periodic weighing of the extracts showed that practically complete removal of resins and rubber was attained in four to six hours. The rubber (benzol extract) obtained from the concentrated residue which consisted of only 13.9 to 24.8 percent of the original weight of dry leaves showed a yield comparable to the control as calculated back to the original weight of the leaves, and four to six times as much when based on the digested weight. See Table III. The rubber yields for experiments 3, 6, 14, 17, and 23 were somewhat lower due to some material being washed through the vibrating screen during the washing process. In some cases the rubber recovery was higher than that obtained in the control. This is a desirat result which can be attributed to the breakdown of cell structure thus permitting better contact of benzol and rubber. The total acetone solubles

VII TABLE III, ALKALI AND ACID DIGESTION AND EXTRACTION

Exp. No.	CONTROLS Extract Acetone %	CONTROLS Extract Benzol %	Loss in Wt. by Digestion %	DIGESTED LEAVES Digested Basis Acetone %	DIGESTED LEAVES Digested Basis Benzol %	DIGESTED LEAVES Original Basis Acetone %	DIGESTED LEAVES Original Basis Benzol %
3	16.4	7.3	85.0	18.8	24.4	2.81	3.66
6	19.2	6.7	85.9	19.0	19.3	2.67	2.72
14*	9.9	2.7	82.0	13.2	5.9	2.38	1.06
12	16.1	7.0	78.7	17.7	24.9	3.92	5.53
17	15.4	7.0	86.1	20.0	23.3	2.80	3.20
20	17.3	6.4	79.5	24.4	25.5	5.00	5.20
23	15.0	7.9	84.2	21.9	20.9	3.50	3.30
26	17.2	7.0	75.2	20.1	30.5	5.10	7.50
29	16.8	7.9	76.1	22.6	32.6	5.40	7.80
32	15.7	7.3	75.6	21.6	31.7	5.10	7.75
35	20.9	7.8	78.9	22.1	29.3	4.60	6.20
38	15.9	7.4	78.8	23.0	35.8	4.90	7.50

* Local leaves harvested near laboratory used.

in the digested material were reduced to one-third or less as calculated on the original basis. It is believed that this decreased resin content aids in the decrease of time required for extraction and also aids in obtaining a more complete benzol extraction.

Vulcanizates of the dried rubber (benzol extracts) were prepared after milling in the required chemicals as listed in Table IV. All chemicals were added on the mill since the solution method of pre-compounding was not known at the time. Milling proved difficult due to the sticky nature of the unprecured rubber. In vulcanization the compounded stock was slow curing requiring 60 minutes to obtain satisfactory cures. For these early experiments, a laboratory made tensile tester was devised and used to obtain the tensile strengths of the prepared vulcanizates. The tensiles ranged from 800 to 1350 p.s.i. with the exception of experiments 3 and 20 which were extremely low as shown in Table IV.

Alkali and/or Acid Digestion of Leaves Followed by Either Ball Milling or Solvent Extraction. A series of experiments were carried out using alkalies and acids in various combinations in an attempt to make the rubber more easily separable from the resins and fibrous material. The various treatments are shown under "preliminary treatment" in Tables VI and VII. These tables show that an acid digestion causes about 50% reduction in weight and an alkali or alkali followed by an acid digestion causes a loss of about 75 percent in weight. Digestion of the leaves in boiling water as discussed above causes reduction in weight of 35 to 40 percent. (See Table V). This is significant when the output of any given extraction unit can be doubled or quadrupled by digesting the leaves before extraction.

The digestions were carried out using a ratio of 2/3 liters of 2 % NaOH or 3 % H_2SO_4 solution per 100 grams of leaves. After the digestion the liquid was drained or screened and the leaves were washed with three portions of water each equal to the original volume of acid or alkali used. Following digestion and washing of the leaves, the rubber was separated from the fiber and resin either by ball milling or solvent extraction. The analysis for resin and rubber is the percent acetone extract and percent benzol extract respectively on the original leaves. In figuring the percent extracted, the analytical data is assumed to be 100 percent.

Ball milling of digested leaves was conducted in ball mills of one quart to three gallons capacity with proportionate amounts of small pebbles. A ratio of 100 grams of original leaves, to 675 grams of half inch pebbles and 450 cc. of water was used. The ball milling time varied from 18 to 140 hours in order to effect a separation of the rubber from the fibrous material. (see Table VI). Samples 6 and 7 (Table VI) were dried and extracted with acetone before ball milling in order to eliminate the resin from the ball milled product. By digesting the leaves in 2 % NaOH at 100°C. for one hour, washing, and then digesting in 3 % H_2SO_4 at 100°C. for 1/2 hour, washing, and ball milling, it was found that the rubber could be separated within 18 to 24 hours as shown in Table VI, samples 5 and 7. In all cases the separated rubber appeared to contain large amounts of fiber and resin which is verified by the high percentage extraction and by an analytical separation which gave 36.2 percent benzol soluble (rubber).

VIII TABLE IV, ALKALI AND ACID DIGESTION-COMPOUNDING, VULCANIZATION, AND TESTING

COMPOUNDING	FORMULA
Rubber	100.0 parts
Agerite	1.0 part
Captax	1.0 part
Zinc oxide	6.0 parts
Stearic acid	5.0 parts
Sulfur	3.5 parts

TESTS ON VULCANIZATES*

Exp. No.	Tensile strength p.s.i.	Ultimate Elongation %
3	287	325
6	913	625
14	820	625
12	1175	700
17	947	575
20	379	350
23	858	575
26	1260	750
29	1050	625
32	1350	675
35	1270	800
38	1060	625

* All vulcanizations 60 mins. at 260°F.

VIII TABLE V.

Wt. of Untreated Leaves Gms.	TREATMENT	TREATED LEAVES		
		Weight Gms.	EXTRACT	
			Acetone %	Benzol %
100	Original (1/16")	100	17	7
100	Water Cooked	60	15	11
100	3 % H_2SO_4 Cooked	50	26	15
100	2 % NaOH Cooked	25	20	35.5
100	"2 %NaOH plus 3 % H_2SO_4 Cooked"	25	20	35.5

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VIII TABLE VI

Sample	Analysis Original Leaves: Resin % Acetone Extract	Rubber % Benzol Extract	PRELIMINARY TREATMENT: Alkali Digestion followed by 3 water washes	Acid Digestion followed by 3 water washes	Other	% Loss in Wt.	BALL MILL: Hours Time	% Yield	% Extracted (from % Rubber in original leaves)
1	18.15	2.95	(2nd) Part 1 1% NH_4OH 100°C 1/2 Hr.	(1st) Parts 1, 2 & 3 3% H_2SO_4 100°C 2 hrs.			40	1.0	33.9
					(2nd) part 2 air dried and ground to 40 mesh	50	140	0.0	0.0
			(2nd) Part 3 1% NH_4OH 24°C 1/2 Hr.				64	6.9	234.0
2	18.15	2.95	(1st) 2% NaOH 100°C 2hrs.	(2nd) 3% H_2SO_4 100°C 1/2 Hr.			66	7.6	258.0
3	18.15	2.95	(1st) 2% NaOH at 30# steam for 1 hr.	(2nd) 3% H_2SO_4 100°C 1/2 hr.			72	10.2	346.0
4	18.15	2.95	(1st) 2% NaOH 100°C 3 hrs.	(2nd) 3% H_2SO_4 100°C 1/2 hr.			88	4.9	166.0
5	21.3	4.91	(1st) 2% NaOH 100°C 1 hr.	(2nd) 3% H_2SO_4 100°C. 1/2 hr.			18 to 46	6.1 to 14.8	124.0 to 302.0
6	21.3	4.91		(1st) 3% H_2SO_4 100°C. 3 hrs.			48	5.2	104.0
7	21.3	4.91	(1st) 2% NaOH 100°C. 1 hr.	(2nd) 3% H_2SO_4 100°C. 3 hrs.			24	5.5	112.0

34.9 percent acetone soluble (resin) and 28.9 percent acetone and benzol insoluable (fiber). Vulcanizates prepared from these samples were hard and inelastic. Physical tests were not obtained due to lack of proper equipment.

For one experiment the progress of the ball mill extraction was followed by periodically withdrawing samples and observing them under the microscope. Due to the length of time required for ball milling operation and the poor quality of rubber obtained these experiments were discontinued.

Solvent extraction of chemically treated leaves was conducted after digesting with 2 % NaOH, 3 % H_2SO_4 or a combination of the base and acid with various conditions. The leaves were then dried and extracted with acetone and benzol, using 100 gram samples in a Soxhlet type extractor and extracting for 24 hours with each solvent.

The digestion caused weight losses varying from 50 % to 80 % resulting in greatly increased yields from a given size extractor. Tables VII and VIII show the preliminary treatment given the leaves, the percent loss in weight effected by the treatment, and the percent yield which is actually the grams extracted from 100 grams of treated leaves. In all cases the treatment facilitated the extraction of rubber. The yields obtained were higher than the untreated leaves as shown by analytical data in Tables VII and VIII. Microscopic examinations indicated more complete extraction on the treated than on the untreated leaves.

The rate of extraction of the treated leaves was also accelerated as discussed more fully in Section II on rate studies (See rates of extraction of treated goldenrod leaves and Section II Figs. 4, 5, 6, and 7).

The above work was done before solution compounding or tensile testing was available, therefore data on physical properties were not obtained on the few vulcanizates prepared. These experiments were discontinued because of prohibitive cost of chemicals for treatment, and the necessity of alkali and acid resistant equipment which would not be available under war conditions.

<u>Alkaline Ball Milling of Leaves.</u> Rubber was obtained from goldenrod material by ball-milling with dilute sodium hydroxide, followed by neutralization, additional ball-milling, and separation of the "wormed" rubber by screening. A description of two experiments follows:

Rubber was obtained from 800 g. goldenrod leaves by ball-milling with 8 kg. stones and 4 l. N/1 NaOH for 47 hours, neutralizing with H_2SO_4, and ball-milling for an additional 8 hours. The yield was 7.2 percent on leaves assaying 4.1 percent rubber. The product contained 30 percent acetone-extractable material and 65 percent benzol-extractable material (rubber). The yield of actual rubber was therefore 4.7 percent. Titration value by the Physical Chemistry Section was 4.40, indicating little oxidation. This rubber may be of interest because it has not been touched by organic solvents. The vulcanizate by the standard formula was poor; its tensile strength was 430 p.s.i. and elongation was 715 percent.

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Raw goldenrod, 600 grams, was milled for 4 1/2 hours, using 3 liters of I.O.N. NaOH and 12 kilos of stones. Neutralization by the addition of 250 ml. of 12 N H_2SO_4, followed. A small amount, 1 gm., of cetyl alcohol was added to keep foaming down. Then the liquor was subjected to 20 hours of neutral milling. The balling of the rubber, after this treatment, was very satisfactory.

Although a good yield of 73.8 g. was obtained, this rubber was of a very poor grade. The resin content was approximately 23 percent and fiber and other acetone and benzene insolubles amounted to about 31 percent. The rubber was purified by solution in Skellysolve B, centrifugation, saponification with aqueous sodium byhydroxideand washing with water. After this purification, the rubber contained 17 percent acetone soluble material and 81 percent benzene soluble material. A vulcanizate on the purified rubber by the standard formula had a tensile strength of 1420 p.s.i. and an elongation of 675 percent. Values with diphenyl guanidine were 1420 p.s.i. and 600 percent.

Conclusions of Experiments on Chemical Treatments in Conjunction with Extraction or Mechanical Separation.

1. Benzol extraction of water digested goldenrod leaves gave slightly higher yields of rubber than the untreated controls, however, the vulcanizates were slow in curing and the tensile strength values obtained were somewhat lower.

2. Alkali and acid digested leaves can be almost completely extracted in four to six hours. The benzol extract varied from 10.3 to 35.8 percent on the digested basis as compared to 2.95 to 7.9 percent for the controls and in most instances the total rubber yield on the original basis was as high or higher than the controls.

3. Digestion of goldenrod leaves has decreased the bulk of material to be extracted as follows:

Water digestion	35 to 40 percent
Acid digestion	50 percent
Alkali digestion	75 percent
Alkali and acid	75 to 85 percent

4. Rubber obtained by aqueous ball milling was contaminated with resins and fibrous material and the vulcanizates obtained from these samples were hard and inelastic.

5. Rubber produced by the alkaline ball milling procedure when purified by solution in Skellysolve B, centrifugation, saponification with aqueous sodium hydroxide, and washing with water, gave a vulcanizate of 1420 p.s.i. tensile strength and an elongation of 675 percent as compared to 430 p.s.i. and elongation of 715 percent for the unpurified sample.

VIII TABLE VII

Sample	Analysis of Original Leaves: Resin Acetone Extract	Analysis of Original Leaves: Rubber Benzol Extract	PRELIMINARY TREATMENT: Alkali Digestion followed by 3 water washes	PRELIMINARY TREATMENT: Acid Digestion followed by 3 water washes	PRELIMINARY TREATMENT: Other	% Loss in Weight
1	18.15	2.95	(1st) 2% NaOH 100°C 3 hrs.	(2nd) 3% H_2SO_4 100°C 1/2 hr.	Air dried and ground to 32 mesh	82.3
2	18.15	2.95	(1st) 2% NaOH 100°C 1 1/2 hrs.	(2nd) 3% H_2SO_4 100°C 1 1/2 hrs.	Oven dry at 60°C 6 hrs. Air dried 44 hrs.	74.0
3	21.3	4.91	(1st) 2% NaOH 100°C 3 hrs.		Dried at 60°C air dried 44 hours	73.2
4	21.3	4.91		(1st) 3% H_2SO_4 100°C 3 hrs.	Dried 3 hrs. at 85°C airdried 24 hr.	50.0
5	21.3	4.91	(1st) 2% NaOH 100°C 1 hr.	(2nd) 3% H_2SO_4 100°C 3 hrs.		77.4
6	21.3	4.91	(1st) 2% NaOH 100°C 3 hrs.	(2nd) 3% H_2SO_4 100°C 1 hr.	Unground	78.6
7	21.3	4.91	(1st) 2% NaOH 100°C 3 hrs	(2nd) 3% H_2SO_4 100°C 1 hr.	Unground	78.6
8	21.3	4.91		(1st) 3% H_2SO_4 100°C 3 hrs.		48
9	21.3	4.91		(1st) 3% H_2SO_4 100°C 3 hrs.		48
10	21.3	4.91		(1st) 3% H_2SO_4 100°C 3 hrs.		

VIII TABLE VIII

Sample	SOLVENT EXTRACTION				% Rubber Extracted	Remarks
	% Yield		% Yield Original Air Dry Basis			
	Acetone	Benzol	Acetone	Benzol		
1	11.6	16.94	1.87	2.98	100.8	Vulcanized to fairly good sample
2	31.7	12.61	8.25	3.27	110.8	No vulcanizate
3	19.3	28.4	5.2	7.58	153.5	No vulcanizate
4	33.3	14	16.7	6.25	127.0	No vulcanizate
5	28.6	24.7	6.45	5.58	113.5	No vulcanizate
6	14.6	33.8	3.14	7.25	148.0	Extracted with benzol and precipitated with acetone
7		53.8		11.6		Benzol extract only
8	32.7	12.8	17.1	6.7	136.5	Vulcanized to a soft strochy sheet (Large Extractor)
9	33.8	10.3	17.6	5.4	110.0	Small Extractor
10	Alcohol 36.2	12.7	Alcohol 18.9	6.6	134.5	

IX RETTING OF GOLDENROD

Microbial Disintegration Preliminary to Solvent Extraction.

Introduction. Investigations were conducted to determine the feasibility of utilizing microbial activity or "retting" for the purpose of obtaining goldenrod leaves in such a physical and chemical state as to facilitate the extraction of rubber. In the extraction process it appeared advantageous to reduce the bulk of the goldenrod to be extracted, to break down the cell structure so as to permit easier and more complete removal of resins and recovery of rubber, and to eliminate some of the extraneous substances present in the goldenrod. These requirements indicated that some form of controlled microbiological decomposition such as occurs in advanced stages of retting, which would wholly or partially solubilize or disperse sugars, pectins, proteins, hemi-celluloses, celluloses and other plant constituents without deteriorating the rubber, would be desirable.

Retting is the steeping of plant material and is usually divided into three distinct stages. The first stage may be considered as physical in which the material is submerged in water causing swelling, elimination of air, and solution of water soluble substances. The second stage consists of two steps: (1) the microorganisms act on the extracted solubles creating anaerobic conditions; (2) the anaerobic condition favors the biological breakdown of the non-solubilized plant constituents. In the third stage, the retted tissues are washed free of decomposed substances and dried.

The original investigations were made with goldenrod leaves on small laboratory scale. The results of these studies warranted larger laboratory experiments leading to development of this step on a pilot plant scale.

PRELIMINARY LABORATORY EXPERIMENTS

The first experiments were conducted on leaves in beakers to which solutions containing various salts were added in order to determine if the microorganisms indigenous on the leaves would serve as a natural inoculum. This was found to be unsatisfactory possibly due to the fact that only dry leaves were available. Since the desired flora was not present on the leaves, the possibility of obtaining an inoculum that would be readily available and easily handled was investigated. Retting of plant material is generally accomplished by submergence in stagnant waters, therefore local swamp waters were tried. Several experiments using swamp waters were conducted in jars, containing one-quarter pound of leaves. Some of the variations included temperature, aeration, the use of chopped and unchopped leaves as well as acid and alkali pre-cooked leaves. Swamp water was found unsuitable as an inoculum.

Digested sludge from a local sewage plant was then tried in combination with swamp water with the results summarized in Table I. Good digestion is obtained only if the acid liquor is drained after three days, otherwise the leaves will remain in a pickled condition. Better decomposition of leaves was also noted when the leaves were kept moist with inoculum. Additional

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experiments indicated that digested sludge could serve satisfactorily as a source of inoculum.

TABLE I

ACTION OF COMBINED SWAMP WATER AND DIGESTED SLUDGE UPON GOLDENROD LEAVES UNDER VARYING CONDITIONS AT 30°C. (ONE POUND LEAVES IN 10 GALLON CROCK.)

Treatment	Duration of Test (Days)	Lowest pH	Observations
Leaves submerged, no withdrawal of liquor, no aeration	7	4.4	High acidity produced tending to pickle the leaves. Leaves crisp and firm to touch.
Leaves submerged, solution aerated, liquor not changed	7	4.5	Leaves preserved. Retting prohibited due to high acidity.
Leaves submerged for three days without aeration. Liquor drawn off. Moist leaves mixed once a day for four days.	7	5.5	Leaves not pickled. Leaves in advanced state of decomposition.
Leaves submerged for three days with periodic aeration. Liquor removed. Moist leaves mixed once a day for four days.	7	5.4	Leaves in fair state of decomposition.
Leaves not submerged but moistened by sprinkling at daily intervals to maintain moist conditions. Leaves undisturbed.	7	5.6	Leaves in advanced state of decomposition.
Leaves not submerged but moistened by sprinkling at daily intervals to maintain moist conditions.	7	5.8	Leaves in advanced state of decomposition.

A series of experiments with digested sludge as the inoculum were conducted on green, undried goldenrod leaves. In order to obtain sufficient rubber for testing purposes, five pound batches of leaves were used. Pertinent data and details of the variables involved are given in Table II. Inoculum prepared by diluting one part of digested sludge to 20 parts water supplies a desirable population of microflora. Maximum acidity is reached in three days inhibiting further decomposition unless the acid liquor is withdrawn. The use of a nutrient with the inoculum is not essential. Daily sprinkling with the inoculum favored decomposition. Upon completion of each experiment the retted leaves were washed with tap water, dried at 60° C. and analyzed for bone dry weight, percent acetone solubles, percent benzol solubles and tensile strength of the rubber extracted (benzol solubles). The reduction in weight of the dry material varied from 27 to 43.7 percent.

IX TABLE II

RETTING OF FIVE POUND BATCHES OF GREEN LEAVES (3.175 LBS. BONE DRY WT.) USING DIGESTED SLUDGE AS THE INOCULUM AT 30° C.

Exp.	Treatment	Duration of Test (Days)	Lowest pH	Observations	Digested Leaf Bone Dry Wt. Lbs.	Loss in Wt. %
1	Leaves submerged in diluted sludge water three days, drained and then sprinkled daily with digested sludge water.	7	5.7	Active fermentation for first three days. Leaves progressively decomposed during aerobic sprinkling period. Leaves easily torn by handling.	2.31	27.0
2	Leaves submerged in diluted sludge water and left in this anaerobic state for three days. Water withdrawn and leaves sprinkled daily with sludge followed by water sprinkling.	8	5.5	Pronounced fermentation. Leaves sticky and in state of good decomposition.	1.79	43.6
3	Anaerobic three days. Water withdrawn. Leaves moistened with digested sludge and water. Thereafter leaves moistened by intermittent recirculation of same liquor.	11	5.2	Active fermentation for three days. Decomposition of leaves not severe. Some tendency of leaves to pickle.	2.13	32.7
4	Anaerobic three days. Aerobic stage maintained by sprinkling with digested sludge fortified with NH_4NO_4 (5 gms.), and KH_2PO_4 (5 gms. per l.)	11	5.9	Anaerobic fermentation active. Leaves in good state of decomposition.	1.78	43.7

(Table continued)

IX TABLE II-con't.

RETTING OF FIVE POUND BATCHES OF GREEN LEAVES (3.175 LBS. BONE DRY WT.) USING DIGESTED SLUDGE AS THE INOCULUM AT 30° C.

Exp.	Treatment	Duration of Test (Days)	Lowest pH	Observations	Digested Leaf Bone Dry Wt. Lbs.	Loss in Wt. %
5	Anaerobic three days. Liquor withdrawn. Aerobic stage sprinkled daily with sludge solution.	11	5.5	Anaerobic fermentation normal. Aerobic breakdown slow but leaves finally sticky and show decomposition.	2.2	30.7
6	Leaves not submerged (no anaerobic stage). Leaves maintained in moist condition by daily sprinkling with digested sludge inoculum.	11	5.6	Progressive digestion of leaves.	1.82	42.6

Data on laboratory extractions of the above retted material for rubber and resins and the corresponding vulcanizates are summarized in Table III. Acetone extracts (chiefly resins) varied from 11.8 to 17.0 percent as compared to approximately 16 percent for unretted goldenrod leaves. The yields of benzol extract (rubber) were normal for the first, third, and fourth experiments and above normal for the other three.

IX TABLE III

YIELDS AND TESTS OF EXTRACTIVES OF RETTED GOLDENROD LEAVES

	Extraction					Testing	
Exp.	30 mesh Leaves Anal. gms	Acetone Extract gms	Acetone Extract %	Benzol Extract gms	Benzol Extract %	TS psi.	Ult. Elong. %
1	871.0	121.8	16.3	45.5	6.07	1557	650
2	785.5	87.1	17.0	40.6	7.92	1337	600
3	929.8	132.2	16.6	46.0	5.80	1635	675
4	759.6	106.0	15.4	41.4	6.00	965	625
5	1028.1	106.4	11.8	74.2	8.2	987	617
6	824.2	70.0	12.5	50.8	6.9	860	662

The tensile strength of the compounded rubber from the benzol extracts averaged about 30 percent higher for the first three experiments than for the last three. Little difference was noted in the ultimate elongation.

An examination of the data presented in Tables II and III indicated that the best procedure for retting of goldenrod leaves is as follows: submerge leaves in dilute sludge inoculum for three days, drain spent liquor, moisten daily with dilute sludge inoculum followed by mixing, and ret for total of 7 to 11 days.

Large Scale Laboratory Experiments. The feasibility of retting goldenrod leaves as a possible adjunct in the extraction of rubber was indicated in the preliminary experiments. In order to determine if retting would proceed in a similar manner on a larger scale, experiments were conducted in wooden barrels on ten-pound batches of dried leaves. Leaves were submerged for three days, drained, left unsubmerged, and retted for a total of 7, 11, and 21 days. Another series of leaves were not submerged, but kept moist during the retting period. A second experiment was conducted to determine more accurately the number of days necessary for satisfactory retting. Further experiments were made varying the concentrations of the sludge inoculum. Additional experiments were conducted with the whole goldenrod plant cut into pieces averaging two inches in length.

Approximately 150 pounds of dried goldenrod leaves were thoroughly mixed and then divided into ten pound samples. A sample was put into each of six barrels, covered with water until the barrel was half full (about 20 gallons), and allowed to remain overnight. The following day three gallons of digested sludge was added to each barrel and mixed. For the aerobic

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digestion experiment the liquid of three barrels was drained after one-half hour contact with the leaves. Daily thereafter the leaves were wetted with four to five gallons of inoculum prepared by mixing one part sludge with five parts water. After one-half hour the excess liquor was drained. For the anaerobic-aerobic experiment the leaves were left submerged for three days before the initial draining. Thereafter, the treatment was the same as for the aerobic experiment. Duplicate runs were made in the same barrels.

At the end of 7, 11, and 21 days, the contents of one barrel of each of the aerobic and anaerobic-aerobic series were removed and washed. In order to rid the retted leaves of the sludge accumulated by repeated inoculations, washing of the leaves was necessary. After trying several methods of washing with screens of various meshes a combination of 16 and 120 mesh screens used simultaneously proved satisfactory. The leaves were washed until little or no color was observed in the wash water. The washed leaves were allowed to drain in a cloth bag and squeezed by hand to remove as much water as possible. The retted material was then dried in a forced draft oven at 140° F. for the first four hours and at 120° F. for the remainder of the drying period. Data pertaining to retting, extraction, and testing of rubber for the anaerobic-aerobic method of retting are summarized in Table IV and for the aerobic method in Table V.

It appears from these data that retting offers the following advantages: it reduces the bulk of the material handled, decreases the time required for both resin and rubber extraction, favors more complete extraction of rubber, and generally reduces the resin content of the rubber extract. The bulk of the material was reduced by 51.5 to 73 percent for the aerobic retting and 48.5 to 70.8 percent for the anaerobic-aerobic retting. These figures may be slightly higher than the actual reduction due to some leaves being lost during the washing process. Rubber yields (benzol extract) for the 7 and 11 day rets were higher for the ground retted material than for the control, although the unground retted leaves showed yields comparable to the ground control sample. The 21 day period of retting had an adverse effect on the rubber yield possibly due to the loss of leaf fragments during the washing of the extensively disintegrated leaves. Extraction efficiency on retted material was 95 to 100 percent of the available rubber based on the finely ground unretted leaf material which analyzed 5.46 percent rubber. The necessity of grinding retted leaves decreased with the increase in disintegration of leaves by retting as shown by the percent benzol extract. Retting decreased by more than one-half the amount of resins present in the leaves before benzol extraction, therefore making possible the almost complete removal of excess resins by acetone thus yielding a rubber of higher purity and quality. Microscopical examination of the extracted leaves indicated that in general long retting periods and grinding before extraction favor the more complete extraction of rubber. The tensile strength of the compounded rubber as shown in Tables IV and V was comparable to that obtained from the unretted control and superior with the addition of a booster accelerator such as DPG to the compounding formula. The reduction in bulk of 50 percent and the reduction in extraction time of 60 to 75 percent will greatly increase the capacity of an extraction plant.

IX TABLE IV

RETTING, EXTRACTION, AND TESTING DATA FROM ANAEROBIC-AEROBIC RETTED GOLDENROD LEAVES

(EXTRACTION PERIODS-24 HOURS)

Retting			Extraction				Analytical
Ret No.	Time of Retting Days	Reduction in wt. %	Ground & Unground	Extract Acetone %	Extract Benzol %	Rubber in Extracted Leaves Microscopic Tests	Resins in Rubber %
Control			Ground	14.5	3.2	Much	11.6
1	7	48.5	Ground	8.1	5.2	Considerable	6.96
			Unground	7.2	2.7	Considerable	21.4
1-A	7	50.0	Ground	7.4	4.0	Considerable	11.6
			Unground	6.4	3.1	Much	21.5
2	11	53.5	Ground	7.2	5.5	Much	8.25
			Unground	4.8	4.0	Little	14.6
2-A	11	51.0	Ground	7.8	4.3	Little	10.8
			Unground	7.0	3.3	Much	18.5
3	21	65.0	Ground	5.6	3.6	Little or none	8.75
			Unground	5.4	3.3	Much	10.6
3-A	21	70.8	Ground	5.1	3.0	Little	5.15
			Unground	5.1	2.6	Much	3.95

"A's" are duplicate runs.

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IX TABLE IV-con't.
VULCANIZATION AND TESTING

Ret No.	Physical Chemical: Titration Value	Physical Chemical: Viscosity	Vulc. No.	Vulcanization: Curing Time at 260° F. min.	Vulcanization: Tensile Strength psi.	Vulcanization: Ultimate Elong. %	Vulcanization: Tensile Strength DPG psi.
Control	4.40	0.704	286 232	60	1075	710	1370
1	4.75	0.655	295	30	1530	700	2105
	5.00	0.660	293	60	880	690	
1-A	5.10	0.660	339	45	1100	700	1450
	5.40	0.646	355	45	920	625	
2	5.00	0.660	309	60	1170	635	1710
	5.05	0.650	313	30	860	675	
2-A	5.20	0.658	346	45	870	575	1310
	5.20	0.650	354	60	920	650	
3	5.00	0.653	324	60	1070	650	
	5.20	0.660	325	45	1060	650	1390
3-A	5.20	0.695	361	45	1050	675	1630
	4.95	0.660	334	30	1050	700	1520

"A's" are duplicate runs.

IX TABLE V

RETTING, EXTRACTION, AND TESTING DATA FROM AEROBIC RETTED GOLDENROD LEAVES
(EXTRACTION PERIODS-24 HOURS)

Retting			Extraction				Analytical
Ret No.	Time of Retting Days	Reduction in wt. %	Ground & Unground	Extract Acetone %	Extract Benzol %	Rubber in Extracted Leaves Microscopic Tests	Resins in Rubber %
Control			Ground	14.5	3.2	Much	11.6
4	7	51.5	Ground	7.5	4.3	Little	6.8
			Unground	6.8	3.6	Much	16.5
4-A	7	59.5	Ground	6.9	4.7	Little	3.7
			Unground	6.6	4.6	Little	5.7
5	11	60.0	Ground	6.1	4.5	Considerable	6.6
			Unground	5.9	3.6	Little	8.6
5-A	11	52.6	Ground	8.0	5.3	Little or None	4.5
			Unground	7.5	4.6	Little	7.5
6	21	73.0	Ground	4.5	2.4	None	5.5
			Unground	4.5	2.4	Little or None	5.0
6-A	21	65.0	Ground	6.1	4.2	Little	4.6
			Unground	5.8	4.2	Little or None	6.9

"A's" are duplicate runs.

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IX TABLE V-con't.

VULCANIZATION AND TESTING

Ret No.	Physical Chemical: Titration Value	Viscosity	Vulc. No.	Vulcanization: Curing Time at 260° F. min.	Tensile Strength psi.	Ultimate Elong. %	Tensile Strength DPG psi.
Control	4.40	0.704	286 232	60	1075	710	1370
4	4.95	0.662	310	60	1025	610	1040
	5.25	0.648	294	45	1090	675	
4-A	5.10	0.657	360	45	1055	650	1630
	5.00	0.675	340	30	1360	700	1820
5	4.85	0.680	312	45	1330	650	
	5.05	0.657	318	45	1070	650	1400
5-A	4.75	0.668	314	30	1290	650	1585
	5.25	0.650	338	45	1210	625	1720
6	5.15	0.649	333	15	1150	650	1420
	5.10	0.648	326	30	940	700	
6-A	5.05	0.658	347	15	1060	700	1550
	5.25	0.673	345	60	1110	600	1480

"A's" are duplicate runs.

Extraction Rates of Retted Goldenrod Material. These rates were determined in the laboratory on 100 grams of material from each of the retting experiments by extracting first with acetone for 24 hours and then with benzol for 24 hours. During the extraction with each solvent, the extracts were weighed at the end of 1/2, 1, 4, 12, and 24 hours. The retted material investigated included that obtained from both aerobic and anaerobic-aerobic experiments retted for periods of 7, 11, and 21 days. Duplicates of all runs were made. Since no appreciable differences were noted in the extraction rates of the two types of retting, aerobic and anaerobic-aerobic, the results were averaged with the duplicates as tabulated in Table VI. The percent acetone extract versus time is shown graphically in Figure 1, and percent benzol extract versus time in Figure 2.

IX TABLE VI

RATE OF EXTRACTION STUDIES OF RETTED GOLDENROD MATERIAL

Results Calculated to Dry Weight of Original Leaves											
			Hours Extraction					Hours Extraction			
Days Retted	Type of Retting		1/2	1	4	12	24	1/2	1	4	12	24
			% Acetone Extract					% Benzol Extract				
7	A-A(1)	Ground	6.80	7.21	7.98	8.50	8.85	2.84	4.02	6.28	6.55	6.80
7	A-A	"	3.05	4.15	6.05	6.75	7.05	1.15	1.95	2.74	3.04	3.24
7	A(2)	"	3.84	5.18	6.68	6.96	7.08	1.17	3.00	4.37	4.65	4.70
7	A	"	4.56	6.50	7.18	7.47	7.67	2.66	4.07	4.75	5.10	5.29
		Average	4.56	5.76	6.97	7.42	7.66	1.95	3.26	4.54	4.81	5.01
7	A-A	Ungr'd	3.09	3.40	5.15	6.18		0.72	0.93	2.06	2.58	3.30
7	A-A	"	1.40	1.60	4.00	4.70	4.90	0.10	0.50	1.90	2.50	3.00
7	A	"	3.32	3.76	5.87	6.35	6.68	1.86	2.59	3.89	4.22	4.37
7	A	"	3.78	4.36	5.53	6.30	6.60	1.40	1.94	3.30	4.07	4.17
		Average	2.89	3.28	5.14	5.88	6.06	1.02	1.49	2.79	3.34	3.71
11	A-A	Ground	4.55	5.64	7.40	8.08	8.47	2.02	2.89	3.52	3.62	3.97
11	A-A	"	6.08	6.41	7.02	7.48	7.54	3.21	4.33	5.03	5.35	5.40
11	A	"	4.60	5.68	7.15	7.44	7.72	1.61	2.98	4.26	4.60	4.88
11	A	"	5.00	5.55	6.28	6.56	6.60	2.72	3.84	4.24	4.32	4.44
		Average	5.06	5.82	6.96	7.39	7.58	2.39	3.51	4.26	4.47	4.67
11	A-A	Ungr'd	3.04	3.72	5.98	6.95	7.15	0.88	0.98	2.06	2.74	3.24
11	A-A	"	2.70	3.44	4.94	6.42	6.70	1.12		2.32	3.54	4.00
11	A	"	3.31	4.45	5.78	6.35	6.82	1.14	1.89	2.84	3.69	4.07
11	A	"	3.04	4.08	5.35	5.76	6.00	1.36	1.84	2.80	3.12	3.30
		Average	3.02	3.92	5.51	6.37	6.67	1.12	1.57	2.50	3.27	3.63
21	A-A	Ground	3.26	4.02	4.60	4.72	4.96	0.85	2.04	2.92	3.06	3.10
21	A-A	"	4.06	4.20	5.52	5.38	5.43	0.81	1.65	2.45	2.48	2.56
21	A	"	3.43	4.72	5.50	5.56	5.78	0.88	2.45	2.98	3.04	3.12
21	A	"	2.30	2.89	4.03	4.18	4.37	1.00	1.67	2.22	2.24	2.40
		Average	3.26	3.94	4.86	4.96	5.14	0.88	1.95	2.64	2.70	2.79

(1) Anaerobic-Aerobic; (2) Aerobic

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IX TABLE VI-con't.

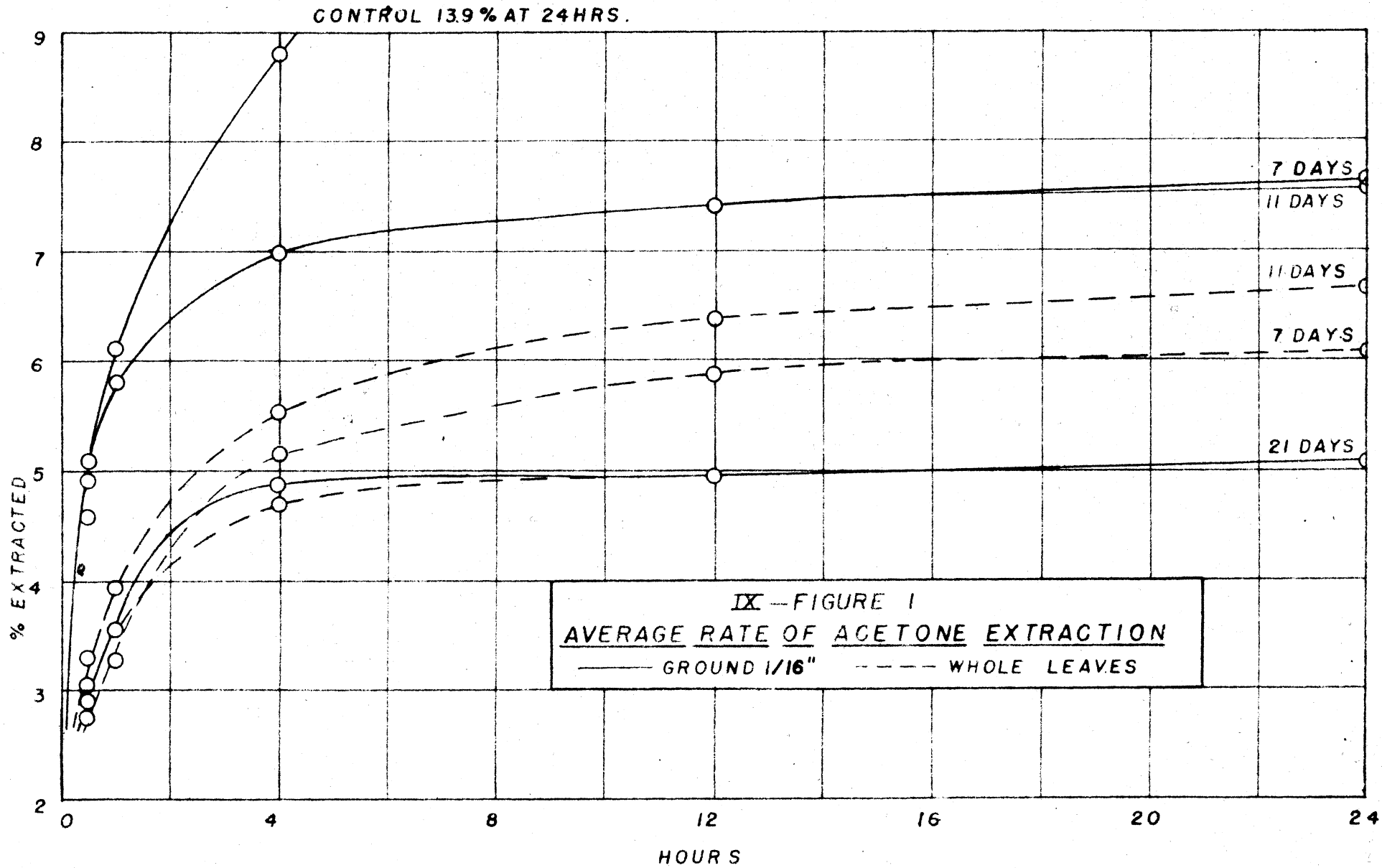
Results Calculated to Dry Weight of Original Leaves												
			Hours Extraction					Hours Extraction				
Days Retted	Type of Retting		1/2	1	4	12	24	1/2	1	4	12	24
			% Acetone Extract					% Benzol Extract				
21	A-A	Ungr'd	2.40	3.16	4.32	4.38	4.55	1.63	1.83	2.10	2.34	2.40
21	A-A	"	3.15	3.78	4.97	5.40	5.67	1.33	1.96	2.66	3.08	3.22
21	A	"	2.80	4.20	5.40	5.60	5.67	1.96		3.36	3.71	3.78
21	A	"	2.59	2.97	4.05	4.37	4.38	1.24	1.94	2.38	2.48	2.54
		Average	2.73	3.53	4.68	4.94	5.09	1.54	1.92	2.62	2.90	2.98
0	Control	Ground	4.9	6.1	8.8	11.6	13.9	2.1	2.2	3.3	4.3	5.2

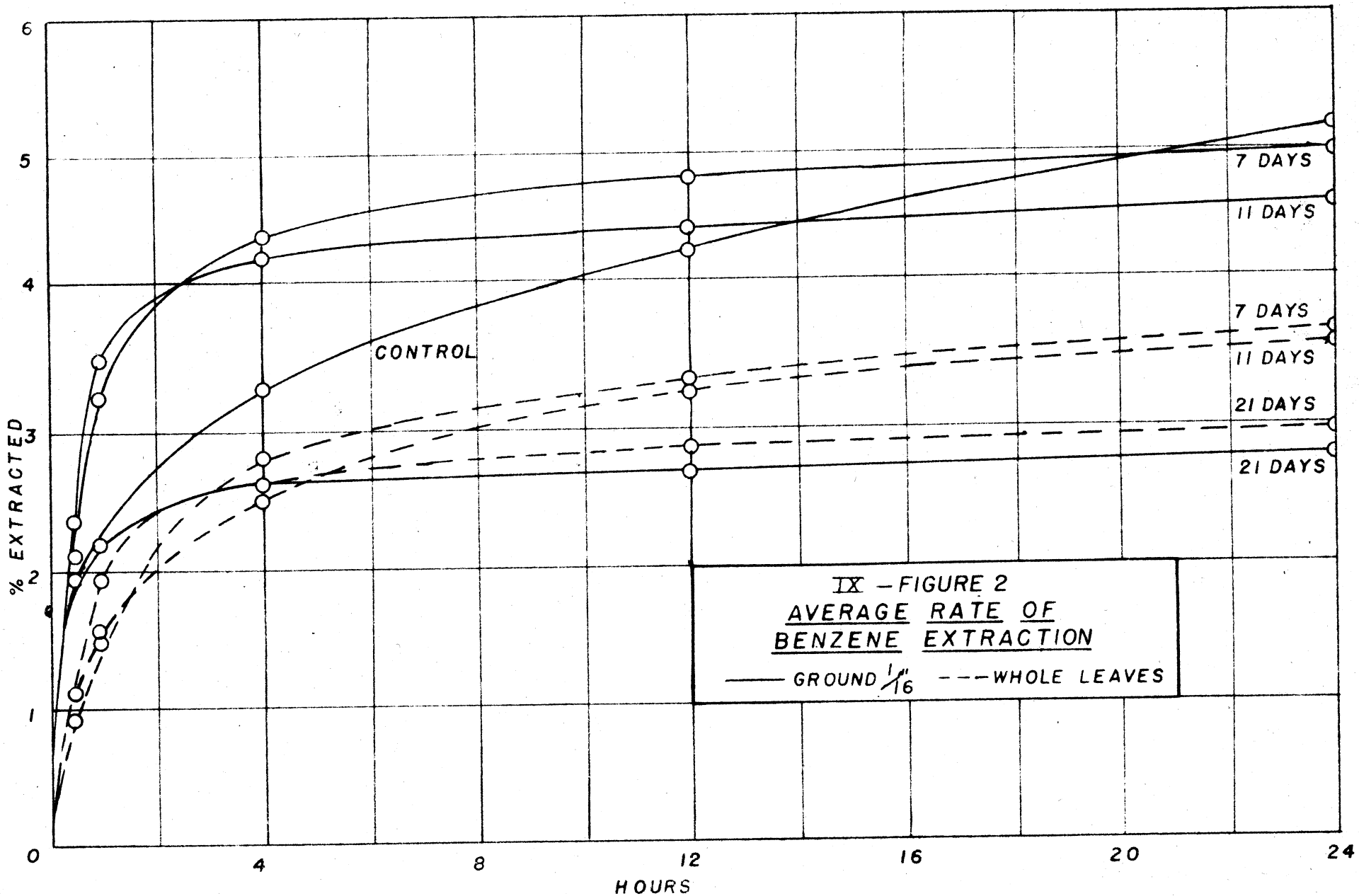
The original leaves contained 14 percent acetone soluble material, or "resins". The 7 and 11 days' retting both removed 50 percent of the acetone solubles and the 21 days' retting removed 65 percent. As shown in Figure 1, the rates of extraction of the remaining resins increased appreciably with the number of retting days; and all rets were extracted more readily than the ground control. For the 21 day ret, practically all of the acetone solubles were removed in four hours. Grinding of the retted leaves in a Wiley mill through a 1/6 inch screen aided the rate of extraction for the 7 and 11 days' ret but had a negligible effect on the 21 day ret.

The results of the benzol extraction rates showed trends similar to the acetone extraction. As shown in Figure 2, the extraction rates increased with increase in the retting period. In addition, all retted materials were extracted more readily than the unretted ground control sample. The ground leaves from the 7 and 11 days' retting experiments extracted more readily than the unground. Grinding appeared to have a negligible effect on the 21 day retting experiment. The bulk of the rubber from the 7 and 11 days' retted and ground material was extracted in four hours as compared to 16 hours required to obtain a similar amount of rubber from the unretted control.

Anaerobic-aerobic Retting. A study of the previous tables will show that for similar retting periods the anaerobic-aerobic retting yields about 20 percent more rubber than the aerobic, therefore the remaining retting experiments were limited to anaerobic-aerobic studies. Experiments were conducted using ten pounds of leaves in each of six barrels; two were retted for 11 days, two for 16 days, and two for 21 days. Previous retting experiments had shown that a retting period of 11 to 21 days was desirable.

The inoculum used for this series of experiments was the liquid prepared by diluting one part of digested sludge with 15 parts water. After mixing and settling of the heavy particles, four gallons of the supernatant liquid


CONTROL 13.9% AT 24 HRS.
9
8
7
6
5
4
3
2
% EXTRACTED
0
4
8
12
16
20
24
HOURS
7 DAYS
11 DAYS
11 DAYS
7 DAYS
21 DAYS
IX — FIGURE 1
AVERAGE RATE OF ACETONE EXTRACTION
GROUND 1/16"
WHOLE LEAVES


6
5
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3
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% EXTRACTED
4
8
12
16
20
24
HOURS
7 DAYS
11 DAYS
CONTROL
7 DAYS
11 DAYS
21 DAYS
21 DAYS
IX – FIGURE 2
AVERAGE RATE OF
BENZENE EXTRACTION
GROUND 1/16"
WHOLE LEAVES

was added to the leaves in each barrel. Sufficient water was then added to cover the leaves. A slatted cover with weights was put on top of the leaves to prevent flotation. At the end of the three day submergence (anaerobic) period, the spent liquor was drained. During the remaining retting period, the leaves were inoculated daily with two gallons of inoculum which remained in contact with the leaves for 15 minutes before draining.

During the three day anaerobic phase, the titratable acidity increased and the reaction varied from a value of pH 5.4 to 5.0. In the aerobic phase the titratable acidity decreased and the pH increased to a value of 6.0 at the end of the retting period. The temperature of the retting mass varied from 28° C. to 31° C.

At the termination of the retting period the material was washed <u>in situ</u> two or three times with measured volumes of water and the drainings were carefully collected. An aliquot of the wash waters was analyzed for total solids which in turn were submitted to an acetone and a benzol extraction. The loss of benzol extract (rubber) due to washing and draining of the retted leaves varied from 0.023 to 0.193 percent and may be considered as negligible. The washing and drying data are summarized in Table VII.

The leaves were dried in a forced draft oven for six hours at 140° F. and for 7 to 17 hours at 125° F. Due to the nature of the air-circulation and to the fact that the retted material was spread on paper placed on trays only surface drying was possible. Observations of the drying material also indicated that drying was retarded by lumping and retention of some solid sludge especially with material obtained from the 16 day and 21 day retting periods. The reduction in weight approximated 30 percent for the 11 day period, 36 percent for the 16 day, and 38 percent for the 21 day period.

Information concerning rubber evaluation of this series of retted goldenrod leaves is presented in Table VIII. The tensile strength of the rubber obtained from the retted leaves was slightly better in some cases than unretted control in spite of the fact that the resin content of the rubber was somewhat higher. Microscopical examinations showed that very little or no rubber was present in the extracted ground retted leaves and also in the 21 day unground retted material. The percent acetone extract was considerably less than in a control, showing that some resins were removed during retting.

<u>Effect of Inoculum Upon Retting.</u> A study was made using a diluted sludge, a concentrated sludge, and a clear culture in order to determine if the presence of sludge particles can be eliminated; and to determine at the same time if comparable reduction in weights can be obtained, with shorter drying periods of the retted material.

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IX TABLE VII

WASHING AND DRYING OF RETTED GOLDENROD LEAVES

(AIR DRY WEIGHT OF UNRETTED LEAF SAMPLE-10 LBS.)

Washing							Drying			
Time Retted Days	No. of Times Washed	Wash Water Gals.	Solids in Wash Water %	Acet. Extr. of Solids %	Benz. Extr. of Solids %	Based on Original Wt. of Leaves: Acetone Extract in Solids %	Based on Original Wt. of Leaves: Benzol Extract in Solids %	Time in Hours 140°F	Time in Hours 125°F	Air Dried Wt. Lbs	Reduc. in Wt. %
11	2	12	0.19	3.96	1.30	0.071	0.023	6	7	7.05	29.5
11	2	12	0.10	3.82	0.85	0.069	0.015	6	7	6.95	30.5
16	3	18	0.23	6.24	5.13	0.21	0.174	6	17	6.6	34.0
16	3	18	0.15	5.90	3.34	0.14	0.077	6	17	6.3	37.0
21	3	17	0.13	6.78	5.31	0.13	0.101	6.5	13	6.06	39.4
21	3	12	0.25	6.57	7.73	0.16	0.193	6.5	13	6.3	37.0

IX TABLE VIII

RETTING, EXTRACTION, AND TESTING DATA ON ANAEROBIC-AEROBIC RETTED GOLDENROD LEAVES
(EXTRACTION PERIODS-24 HOURS, RETTING PERIODS, 11, 16, 21 DAYS)

Retting			Extraction			Analytical	
Ret No.	Time of Retting Days	Reduction in wt. %	Ground & Unground	Extract Acetone %	Extract Benzol %	Rubber in Extracted Leaves Microscopical Tests %	Resins in Rubber %
Control	0		Ground	18.3	7.2	5-10	4.2
7	11	29.5	Ground	10.2	7.4	Trace	7.4
			Unground	8.4	5.6	5-10	9.4
7-A	11	30.5	Ground	8.4	8.6	None	14.6
			Unground	7.7	6.5	25-30	19.5
8	16	34.0	Ground	8.8	7.3	Less than 3	7.1
			Unground	8.7	7.5	Less than 3	5.5
8-A	16	37.0	Ground	8.1	7.9	0-5	12.6
			Unground	7.6	7.3	15-20	10.3
9	21	39.4	Ground	8.2	7.0	None	10.3
			Unground	9.7	7.3	None	5.3
9-A	21	37.0	Ground	8.4	7.9	None	13.4
			Unground	8.3	9.3	None	9.6

"A'S" are duplicate runs.

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IX TABLE VIII-con't.

VULCANIZATION AND TESTING

Ret No.	Physical Chemical: Titration Value	Viscosity	Vulcanization: Vulc. No.	Curing Time at 260° F. min.	Tensile Strength psi.	Ultimate Elong. %	Tensile Strength with DPG psi.
Control	4.95	0.690	376	45	970	650	1735
7	5.00	0.660	370	45	990	600	1645
	5.10	0.656	378	60	740	600	1155
7-A			373	30-45	690	650	1310
	4.80	0.657	371	30	550	700	1080
	5.35	0.663	396	45	665	700	975
8	5.15	0.644	377	15	770	650	1290
	5.00	0.656	372	30	1030	625	1675
8-A	5.05	0.662	392	45	830	625	1260
	5.05	0.653	379	60	565	550	1310
9	5.10	0.658	375	15	1160	600	1430
	4.93	0.660	374	10	1140	675	1420
9-A	5.25	0.660	390	30	610	600	850
	5.23	0.654	380	15	925	625	1240

Dilute sludge was prepared by adding one part of original digested sludge to 15 parts water. The concentrated inoculum had twice the amount of digested sludge. The culture inoculum was prepared as the dilute inoculum with the addition of two grams of peptone per gallon of solution. These were allowed to remain 24 hours before using. For the dilute inoculum only the supernatant liquid was used. The concentrated inoculum was thoroughly mixed before using. The culture inoculum was stirred only slightly before use so as to keep the lighter particles in suspension.

To each of three barrels were added six pounds of goldenrod leaves which were then retted by means of the three prepared inoculants. Two gallons of inoculum and approximately 20 gallons of water were added to the corresponding barrels. Retting was then conducted according to the anaerobic-aerobic procedure. After three days, the liquor was removed and thereafter, daily, two gallons of the required inoculum were added and drained after 15 minutes. Inoculum was prepared as required. At the end of the 11 day retting period, the retted leaves were washed, pressed, and dried. Washing and drying procedures were similar to the previous series of experiments. A pressing operation using a small hand press was included in order to facilitate drying by removing as much water as possible.

The ret conducted with the dilute inoculum using only the supernatant liquid washed easily and the wash water drained readily. Although the leaves did not appear to be completely decomposed, they showed the greatest reduction in weight (40 percent). The retted material using the cultured inoculum washed and drained slowly, and although the leaves appeared well decomposed they showed only a reduction of 29 percent due to adhering sludge particles. The leaves retted with the concentrated sludge inoculum contained sludge particles resulting in a non-decrease in weight although the leaves were well decomposed. Wash water drained very slowly. Data pertaining to drying and analyses of the wash water are given in Table IX. The rubber (benzol extract) lost in the water from the pressing operation was negligible. Although the drying time for all rets was six hours at 140°F. and six hours at 125°F, the rets using culture and concentrated inoculum required periodic shredding, while drying due to the lumping, which tended to keep the centers moist. Determinations made for pH and total acidity gave trends similar to those in previous experiments in which the acidity increased rapidly during the three day anaerobic submerged phase and decreased slowly during the aerobic phase approaching a value of pH 5.7.

Extraction and testing data of rubber obtained are summarized in Table X. The rubber recovered from leaves retted with dilute inoculum had a tensile strength comparable to the control. The culture inoculated, retted leaves gave similar results. The concentrated inoculum gave lower tensile strength. The yields from all the rets in general were as good or better than the unretted control. Of the three types of inocula, the dilute inoculum in which only the supernatant liquor was used gave the best results as measured by, (1) reduction in weight, (2) yield of rubber from ground material, (3) thorough extraction as shown by microscopical examination of extracted leaves, and (4) high tensile strength when an accelerator such as D.P.G. is used in the compounding formula.

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IX TABLE IX

WASHING AND DRYING OF RETTED GOLDENROD LEAVES USING THREE TYPES OF INCCULA ON SIX POUND SAMPLES FOR A RETTING PERIOD OF 11 DAYS.

Inoculum	Washing: No. of Washes	Washing: Wash Water Gals.	Washing: Solids in Wash Water %	Washing: Acet. Extr. of Solids %	Washing: Benz. Extr. of Solids %	Based on Original Wt. of Leaves: Acetone Extract in Solids %	Based on Original Wt. of Leaves: Benzol Extract in Solids %	Drying: Time in Hours 140°F	Drying: Time in Hours 125°F	Drying: Dried Wt. Lbs.	Drying: Reduc. in Wt. %
Culture	2	6	0.16	4.54		0.036		6	6	4.25	*29.0
Concentrated	2	7	0.19	4.05		0.050		6	6	6.1	* 0
Dilute	2	10	0.11	3.82		0.034		6	6	3.6	40.0
Liquid Pressed Out with Hand Press:											
Culture		2	0.35	5.19	3.17	0.031	0.019				
Concentrated		2	0.55	4.06	1.32	0.037	0.012				
Dilute		2	0.24	6.71		0.027					

* Low Reduction in Wt. Due to Sludge Retained by Leaves.

IX TABLE X

THE EFFECT OF INOCULA UPON RETTING OF GOLDENROD LEAVES.
(ACETONE AND BENZOL EXTRACTION PERIODS-24 HOURS EACH)

Inoculum	Retting: Time of Retting Days	Retting: Reduction in wt. %	Extraction: Ground & Unground	Extraction: Extract Acetone %	Extraction: Extract Benzol %	Analytical: Rubber in Extracted Leaves Microscopical Test %	Analytical: Resins in Rubber %
Control	0	29.0	Ground	18.3	7.2	5 to 10	4.2
Culture	11	29.0	Ground	9.6	6.2	Less than	5.2
			Unground	9.3	8.3	None	7.9
Concentrated	11	0	Ground	10.2	3.96	15 to 20	12.6
			Unground	10.2	7.75	5 to 10	9.0
Dilute	11	40.0	Ground	9.0	7.4	None	6.1
			Unground	8.7	7.5	0 to 5	7.9

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IX TABLE X-con't.

VULCANIZATION AND TESTING

Inoculum	Phisical Chemical: Titration Value	Viscosity	Vulc. No.	Vulcanization: Curing Time at 260° F. min.	Tensile Strength psi.	Ultimate Elong. %	Tensile Strength with DPG psi.
Control	4.95	0.690	376	45	970	650	1735
Culture	5.05	0.649	409	30	1000	625	1460
	5.15	0.661	394	30	755	650	1620
Concentrated	5.18	0.648	410	15	705	625	965
	5.38	0.682	408	60	595	500	975
Dilute	4.68	0.667	393	45	880	700	1710
	5.00	0.676	395	30	920	700	1300

Additional Experiments. Temperature changes due to bacterial action during the anaerobic-aerobic retting process were determined on 37 pounds of dried leaves packed in a wooden barrel. A thermometer was placed in a pipe containing glycerine. The pipe was inserted into the center of the retting leaves and temperatures were recorded daily. Over a period of 14 days the temperature increased from 28°to 31°C. in accordance with room temperature.

Effect of retting the whole plant was observed upon fresh goldenrod plants gathered locally. The plants were chopped into pieces approximately two inches in length, and 20 pound samples were weighed into each of three barrels. Anaerobic-aerobic retting procedure was followed using dilute, concentrated and cultured inocula for a retting period of 16 days. Before using the inocula, the coarse particles were removed by means of cheesecloth. The leaves were well retted by all three inoculants. The bark separated from the woody portion and was in a fair state of decomposition. The stems remained practically intact except for the smaller ones which showed some indication of being retted. Reduction in weight was 30.9 percent for the concentrated inoculum, 40.6 percent for the dilute inoculum and 46.6 percent for the culture inoculum. Evaluation of rubber was omitted since earlier tests had shown very low rubber content present in this wild type of goldenrod.

Conclusions based on Laboratory Experiments. (1) A simple retting method has been developed as an aid in the extraction of rubber from goldenrod.

(2) Retting reduced the bulk of the material to be handled in the extractors by at least 40 percent.

(3) Resin and rubber extraction periods were considerably shortened, requiring one-third to one-fourth of the time necessary for unretted leaves as shown by extraction rates.

(4) Microscopical examinations show that rubber was more completely extracted from ground retted material than from ground unretted leaves.

(5) The yields and quality of the rubber obtained by retting was comparable, and in some cases, better than that obtained from the unretted control.

(6) Rubber losses due to washing of retted material were negligible.

(7) An anaerobic-aerobic retting procedure was used at 30°C. consisting of three days submergence in dilute sludge inoculum followed by a four to thirteen day period in which the leaves were not submerged but moistened daily with fresh inoculum.

(8) Easily obtainable digested sludge, diluted with 15 parts water proved to be a satisfactory source of inoculum with or without the addition of peptone.

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RETTING INVESTIGATIONS CONDUCTED ON PILOT PLANT SCALE AT WAYNESBORO, GEORGIA

Retting of goldenrod on a large scale was conducted at Waynesboro, Georgia, between September 23, 1943, and December 9, 1943. In general, the conditions of retting were based on the laboratory experiments completed at the Southern Regional Research Laboratory on the 1942 crop of hand-stripped leaves. A discussion of these large scale retting experiments, the processes involved in the preparation of the retted material for extraction and analysis, and testing data are presented. Briefly, the chronological treatment of the goldenrod at Waynesboro was as follows: (1) harvesting and preparation of the goldenrod for retting, (2) retting under various conditions, (3) washing, (4) pressing, (5) shredding, (6) drying, and (7) shipping.

Harvesting and Preparation for Retting. The goldenrod used for these experiments was selection 3-S-79 from various fields. The crop was harvested with either a corn binder or a rice binder and loaded onto trucks equipped with canvas covers to protect the goldenrod from sunlight which was believed to be detrimental to the quality of the rubber in the leaves. Hand picking of foreign plant material from the goldenrod for Ret Nos. 1 and 3 was necessary due to the presence of excess weeds and grasses. Listed in Table XI are the fields and the condition of the goldenrod as received from these fields.

TABLE XI
INFORMATION ON GOLDENROD, SELECTION 3-S-79, USED IN LARGE SCALE RETTING TRIALS

Ret No.	Field	Condition of Goldenrod	Binder Used for Harvesting	Preparation of Retting Material	Ratio Percent Leaf	Ratio Percent Stems	Green Wt. Lbs. Charged
1	Bates Red Bay	Weedy	Corn	Machine cut (Papec Cutter)	(a) 37.5	62.5	5002
2	Manley	Good	Rice	Small Leaf Stripper	(a) 92.7	7.3	1206
3	F. M. Cates	Grassy	Rice	Small and Large Leaf Stripper	31.0	(b) 69.0	2078
4	F. M. Skinner	Good	Rice	Machine-Cut Air-Separated	21.7	(b) 78.3	2033
5	Mrs. F. Cates	Good	Rice	Machine-Cut Air-Separated	21.7	(b) 78.3	2105

(a) Includes leaf plus bloom.
(b) Includes stems plus bloom.

Attempts made at the drying plant to obtain satisfactory leaf material for retting were not wholly successful. This necessitated modifications in the experiments as originally planned. Instead of pure leaf material it was necessary to use machine-cut (Papec cutter) whole plants for the first retting experiment, machine stripped material with only partial removement of stems for Rets Nos. 2 and 3, and machine-cut whole plants from which some of the heavier pieces of stems had been removed by a machine air separator for Rets Nos. 4 and 5.

Composition of Plant Material. A number of general harvest samples of machine air-separated material was carefully separated by hand and showed the following proportions: 20 percent leaf, 30 percent stems, and 50 percent bloom (Mr. P. C. Wakeley). The fourth and fifth retting experiments consisting of machine air-separated material had a leaf content comparable to that of the general harvest, 21.7 percent (Table XI). On the other hand, the goldenrod used in Ret No. 3 was passed through "leaf" strippers and therefore the material obtained had a higher percentage of leaf than the material in the last two retting experiments. The second experiment, also using machine stripped material, showed a much higher leaf content which in this case may be attributed to immature green blooms included with the leaves.

Description of Retting Tanks. Four cypress tanks, each with a capacity of 600 gallons and each of which could hold approximately 1200 pounds of plant material were used for retting. Two similar tanks were set aside for preparing the inoculum. The four retting tanks were equipped with removable false bottoms four inches from the true bottom. These false bottoms had 3/8" holes 1-1/2" apart. During the course of experimentation it was found necessary to fasten the false bottoms in order to aid in the prevention of the whole retting mass from floating during the first three days or anaerobic phase. The two make-up tanks used for preparing the sludge were equipped with swing suction pipes so that clear supernatant inoculum could be withdrawn. A centrifugal pump located between the two tanks was connected with a system of pipes and valves making it possible to use the pump for a three fold purpose: (1) to pump the inoculum from either of the makeup tanks to each of the retting tanks; (2) to circulate the inoculum during the preparation procedure; and (3) to pump sludge from a tank truck outside to the make-up tanks.

Inoculum. Digested sludge for preparing the inoculum was easily obtainable from the sewage plant at Camp Gordon located near Augusta, Georgia. The digested sludge was transported in a tank truck and was pumped into the make-up tanks by means of a flexible hose connected to the centrifugal pump. A total of 2,772 gallons of sludge was consumed in preparing the inoculum required for the 10,319 pounds of green goldenrod material retted in the first four experiments.

The inoculum was prepared by diluting 50 gallons of sludge to 550 gallons (ratio 1:10), and then adding a nutrient consisting of about one ounce of Bacto-peptone and one quart of corn steep liquor. Although the tap water used for dilution had an average pH of 9.3, the inoculum averaged pH 6.5.

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After circulating the mixture for ten minutes and settling overnight, the supernatant liquid was used for inoculating the goldenrod material. About 175 gallons of the clear liquor (inoculant) was added to 1000 pounds of goldenrod material. This is a relatively high concentration of plant material to liquid inoculum.

Conditions of Retting. The anaerobic-aerobic procedure was followed for four of the five experiments. In general, the plant material was covered with inoculum (150-200 gallons) and after three days the spent liquor was drained. This was followed by periodic inoculation with 150 to 200 gallons of inoculum so as to completely cover the leaves, and then, after a two to three hour soaking period, the excess liquor was drained. Mixing of the retting mass during the daily inoculations was found necessary in order to aid removal of excess acidity which would cause pickling and therefore prevent decomposition. The procedure was modified for Ret No. 4 in that the material was inoculated every second day rather than daily.

Ret No. 5 was entirely different insofar as an inoculum prepared with chicken manure was used and, in place of daily inoculations, the plant material was kept completely submerged throughout the retting period. The spent liquor was drained and new inoculant added only at the end of the third and tenth day of ret. The inoculum was prepared by adding one bushel of chicken manure, one ounce of peptone, and one quart of corn steep liquor to 600 gallons of water. After circulating and settling, the supernatant liquid was used as the inoculant. In this case the excess acidity formed in the retting mass was neutralized by the addition of one-half pound of bicarbonate of soda whenever necessary during aeration.

Data pertinent to the conditions of retting are given in Table XII. Temperature of the retting mass taken at a depth of ten inches varied from an average of 25° C. for Ret No. 1 to an average of 12° C. for Ret No. 5. Although higher temperatures were desirable, no control was possible due to the lack of heating facilities in the building. It was found that the retting mass would heat to some extent if inoculated every second day rather than daily. This procedure was used for Ret No. 4 in order to attempt to maintain a higher temperature. Also, to aid in obtaining a higher temperature at the start of each ret, the goldenrod material was moistened with inoculum on the first day and remained in that condition overnight to promote heating. Typical heat distribution in the goldenrod material due to self heating was as follows: two inches below the surface, 34° C.; six inches below the surface, 47° C.; 16 inches below, 44° C.; and 24 inches below, 24° C. Upon the addition of inoculum the temperatures became more uniform throughout the retting mass and averaged as shown in Table XII.

The lowest pH of the drain liquor varied from 4.40 to 4.50 for the five rets. These low values were attained at the end of the anaerobic phase (first three days of ret). The pH then increased gradually until at the end of the retting periods when the highest values were reached, the pH varying from 5.50 to 5.91.

IX TABLE XII

CONDITIONS OF LARGE SCALE RETTING OF GOLDENROD

Ret No.	No. of Days Retted	Retting Procedure	Type of Culture	Frequency of Aerobic Inoculation	Aerated	Temperature of Retting °C			pH of Liquor	
						Low	Average		Low	High
1	22	Anaerobic-Aerobic	Digested Sludge	Daily	No	21	25		4.42	5.50
2	20	Anaerobic-Aerobic	Digested Sludge	Daily	No	19.5	23		4.40	5.30
3	18	Anaerobic-Aerobic	Digested Sludge	Daily	Yes	16	19		4.55	5.91
4	20	Anaerobic-Aerobic	Digested Sludge	Every Second Day	Yes	15	17		4.21	5.68
5	21	Anaerobic[b] (Submerged)	Chicken Manure	(a)	Yes	10.5	12		4.51	5.71

(a) Inoculum changed at end of third and tenth day of ret.
(b) Excess acid neutralized with bicarbonate of soda.

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Aeration of the retting mass was found beneficial in obtaining a more homogeneous retting mixture. In retting large batches there is a tendency for the top portion to ret more readily than the bottom portion which could not be easily mixed. The difference was noticeable in that the leaves at the top were more "tender" than those at the bottom. Also, the material at the bottom of the tank was of a deep green color instead of the brown retting color and had a pickle odor for a longer period of time (as previously stated, pickling prevents decomposition). This difficulty was partially overcome for Rets Nos. 3, 4, and 5 by aerating - a process which was also believed helpful to microbial action during the aerobic phase. Aeration was accomplished by attaching a 1/2 inch pipe, 6 feet long to an air hose of a DeVilbiss air compressor. One end of the pipe was pointed and had four 3/16 inch holes, two inches from the point. The air going through the retting mass was controlled by a valve located at the end of the pipe connected to the air hose. In order to aerate, the pointed end was pushed through various sections of the retting mass and each time the air was allowed to bubble through for several minutes.

Washing the Retted Material. Upon completion of the retting periods of 18 to 22 days for the five retting experiments, the retted mass was washed two to four times with tap water (pH 9.3). In general, the procedure for washing was to cover the material with water and drain. Subsequent washes consisted of thoroughly mixing the retted mass while adding and draining the water. The pH of the wash liquor drained tended to approach neutrality with increase in number of washings. As shown in Table XIII, the pH averaged 5.58 for the first washes and 6.18 for the last washes.

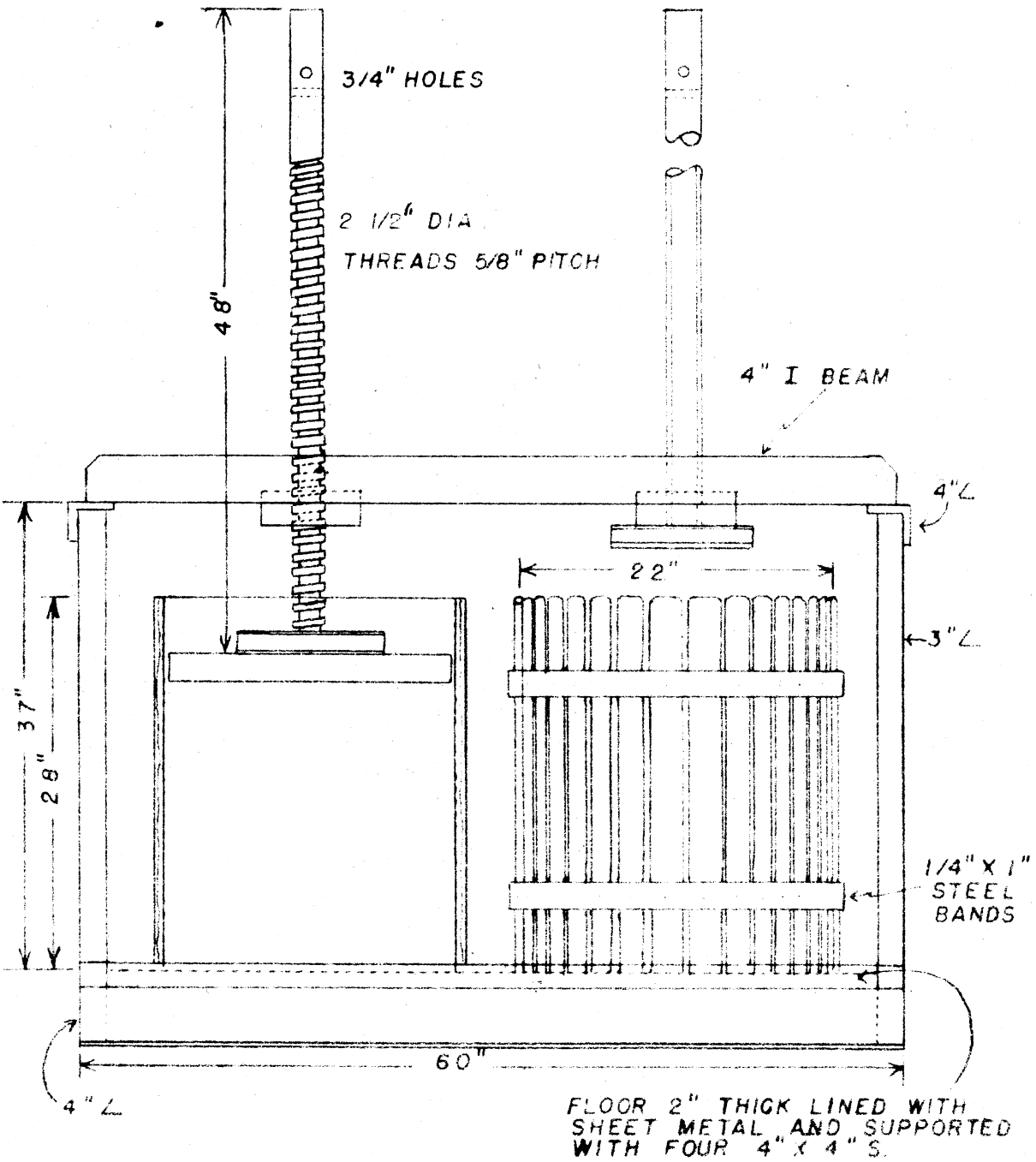
Pressing. After draining two to three hours, the excess water in the washed retted material was removed with a two-drum hand press shown in Figure 3. The number of times each drum was filled for each ret, the moisture content after pressing, and the man hours required for the pressing operation are tabulated in Table XIII. Each press drum full consisted of filling the drum, pressing to approximately one-half the volume, and then refilling before the final pressing. Pressing was not necessary for Ret No. 1 since it had dried sufficiently on the floor before the press was made available.

Shredding. In order to obtain a more uniform and a shorter drying period for the retted material, it was found necessary to break up the numerous lumps of various sizes contained in the pressed retted material. The lumps cake over during the drying process, leaving the center moist thus requiring a longer drying time in order to obtain a uniformly dried material.

The difficulty was eliminated for Ret Nos. 3, 4, and 5 by putting the pressed material through a shredder. The shredder consisted of a wooden roll five inches in diameter and 43 inches long, the surface of which was equipped with iron fingers 1/2 inch long, 1/8 inch in diameter, and spaced 1-1/2 inches apart. The roll, located at the bottom of a hopper 12 inches deep, revolved at a speed of 690 r.p.m. against a movable board which in this case was adjusted to 1/8 inch from the protruding fingers of the roll. The shredder is a simple but very effective apparatus for disintegrating the pressed retted material and accounted for the 50 percent decrease in drying time as well as for the uniformly dried material.

IX- FIGURE 3

FRONT VIEW OF PRESS USED FOR PRESSING RETTED LEAVES



IX TABLE XIII

WASHING, PRESSING, AND DRYING OF RETTED MATERIAL

DRYING TEMPERATURE-160-165°F

Ret No.	Washing: pH of Wash Liquor: 1st Wash	Washing: pH of Wash Liquor: Last Wash	Pressing: No. of Drums Full	Pressing: Time Man-Hours	Pressing: Moisture after Pressing %	Shredding: Time Man-Hours	Drying: Time in Hrs.	Drying: No. of Trays	Drying: No. of Dollies
1	5.34	6.17					6	151	17
2	5.44	6.08	5	10	71.5		5	45	5
3	5.96	6.22	12	20	70.9	3	4-5	99	11
4	5.88	6.26	12	18	71.5	3	3-5	117	13
5	5.31	6.18	12	18	72.0	3	3-4	99	11

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Drying. The shredded retted material was loaded into boxes and transported to the dry kiln building to be dried in a large tray drier having a capacity of ninety 4' x 5' trays, the bottoms of which were 1/4 inch mesh wire screens. The trays were constructed so that a tier of nine trays with baffles in between each tray could be stacked on dollies which were moved along a track into the drier kiln. The kiln compartment was insulated with rock wool and designed so that air, heated by means of steam coils, could be circulated in either of two directions. The baffles between the trays provided a means of directing the air through the drying material rather than over the surface. The circulating air was passed down through the top of the drying material for one-half of the drying period and up through the bottom for the other half.

Drying data for the five experiments are given in Table XIII. The drying temperature was maintained at 160-165° F., and the drying time varied from three to six hours. Rets No. 1 and 2, which were not shredded after pressing, dried in six and five hours respectively. Drying was not uniform since many caked-over lumps were damp in the centers. Rets No. 3, 4, and 5, for which the shredder was made available to break up the lumps, were examined at the end of three hours drying time. They were found to be thoroughly dry except for spots in the center of some trays where the screen sagged and touched the baffles below, thus preventing air from passing through; therefore making it necessary to increase the drying time. However, it may be stated that pressed and shredded retted goldenrod can be dried in three hours at 160-165° F., by passing the circulating air through the material.

Results. The reduction in weights for the five retting experiments each involving 1200 to 5000 pounds of green goldenrod is tabulated in Table XIV. The decrease varied from 21.0 to 41.6 percent on a bone dry basis as compared to an average decrease of 50 percent for the ten-pound leaf samples retted in the laboratory for a similar period of time. This difference may be attributed to the fact that the material retted at Waynesboro contained a large proportion of bloom and stems as shown in the data presented in Table XI. This was the best "leaf" material available with the equipment on hand. Because of the excess bloom and stems present in the material used for these large scale retting experiments, they are not comparable to the laboratory experiments in which 100 percent leaves were used. Stems and bloom do not ret as readily as the leaves. In addition, the temperature of the retting material averaged 12° to 26° C., as compared to 28 to 31° C., for the laboratory rets, and indications are that low temperatures have an adverse effect on the action of the microorganisms involved. From the time of the first retting experiment in September through the fifth experiment in December, the temperature decreased and the amount of bloom on the plant increased. In spite of these difficulties marked reduction in weights were obtainable.

The leafy portion of the material retted in the large scale retting experiments for 18 to 22 days appeared to be similar to leaves retted 11 to 14 days at the laboratory.

IX TABLE XIV
REDUCTION IN WEIGHT

Ret No.	Charged to Tanks: Green Wt. Lbs.	Mois-ture %	Bone Dry Weight Lbs.	After Retting and Drying: Kiln Dry Weight Lbs.	Mois-ture %	Bone Dry Weight Lbs.	Reduction in Wt. Bone Dry Basis %
1	5002	55.0	2251.0	1566	8.0	1441	36.9
2	1206	63.4	441.4	280	8.0	258	41.6
3	2078	56.4	906.0	693	8.0	638	29.6
4	2033	55.5	904.7	755	5.7	712	21.3
5	2105	56.8	909.4	768	6.6	717	21.0

Shipping. The dried retted material was shipped in bales, boxes, or burlap sheets to the Southern Regional Research Laboratory for extraction of rubber and for evaluation of the rubber obtained.

EXTRACTION OF RETTED GOLDENROD AND EVALUATION OF RUBBER

The treatment of the retted goldenrod material received from Waynesboro, Georgia, was as follows: Prior to extracting, the material was put through a three way separation process in order to obtain an enriched leaf portion. This leaf portion was ground and then the resins and rubber extracted with acetone and benzol, respectively. The benzol extract (rubber) was precipitated with acetone to reduce the resins in the rubber and then precured, compounded, vulcanized, and tested.

Obtaining an Enriched Leaf Fraction. In order to facilitate separation, the lumps present in the retted material were disintegrated by passing the retted material through a hammer mill containing one inch hammers and no screen. This was especially necessary for Rets. Nos. 1 and 2 which were very lumpy due to the fact that the material was not shredded before drying. In the separation procedure the thin long stems and grass were then removed by sifting through a three mesh screen. The material for Rets Nos. 1, 4, and 5 passing through this coarse screen was subjected to a three way separation in a "cyclone" separator which consisted of a wooden box containing inclined compartments for separation of leaf and stem fraction, an air fan, and a cyclone in which the bloom was collected. This three way separation procedure was omitted for Rets Nos. 2 and 3 since the material had not been ensilage cut and therefore did not contain numerous short stems. Tabulated in Table XV are the results of the separation. Weight of the stem fraction includes that obtained by sifting and by air separation when the two processes were used. Ret No. 1 contained the greatest portion of stems as would be expected since retting included the whole plant. The proportion of stems and bloom increased progressively with the remaining four experiments and the increase was probably due to the date of harvesting the goldenrod.

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IX TABLE XV
SEPARATION OF RETTED GOLDENROD

Ret No.	Fraction: Leaves Lbs.	Stems Lbs.	Bloom Lbs.	Total Lbs.
1	635.0	946.0	6	1587
2	253.5	21.5	Negligible	275
3	537.0	115.0	Negligible	652
4	463.0	243.5	40	746.5
5	400.0	306.0	43	749

IX TABLE XVI

Ret No.	Analysis of Separated Material: Benzol Extract: Leaf Fraction *%	Leaf Fraction *Lbs.	Stem Fraction %	Stem Fraction Lbs.	Bloom Fraction %	Bloom Fraction Lbs.	Total Lbs.	Unretted Control: Available Rubber: Original Material Bone Dry Wgt. Lbs.	Benzol Extract *%	Benzol Extract *Lbs.	Rubber Unrecovered %
1	4.12	26.1	0.91	8.6	1.87	0.1	34.8	2251	1.37	30.9	15.5
2	5.86	14.8	0.52	0.1	-	-	14.9	441.4	3.23	14.3	0
3	4.28	23.1	0.52	0.6	-	-	23.7	906.0	2.88	26.1	11.5
4	4.07	18.9	0.91	2.2	1.87	0.8	21.9	904.7	2.27	20.5	7.7
5	3.79	15.2	0.91	2.8	1.87	0.8	18.8	909.4	1.65	15.0	0

*Resin free rubber.

A summary of the benzol extracts (rubber) obtained from each of the three fractions, and that potentially available as calculated from control samples are tabulated in Table XVI. Calculations of benzol extract of the control samples and leaf fraction are based on resin-free rubber. As noted in these two columns, the bulk of the rubber was recovered in spite of the fact that some bloom and a large portion of the stems containing some leaf material were discarded.

Grinding. The leaf fraction of the separated material as listed in Table XV was ground in a Jeffrey hammer mill using one inch hammers and 1/16 inch screen. It was estimated that about 85 percent of the ground material would pass a 40 mesh screen. All control samples were ground in a Ball and Jewell mill using a 1/32 inch screen. Preliminary grinding using a 1/8 or 1/16 inch screen was required for all controls except Ret No. 2 due to the presence of some stems which caused difficulty in grinding with the 1/32 inch screen in the mill.

Extraction of Retted Goldenrod. The ground retted goldenrod from the five retting experiments was extracted in the pilot plant system in order to obtain sufficient rubber and extraction data for evaluating the retting procedure. Ample ground material was obtained from the various rets to make the following extractions:

Ret No.	Cell Extractions Made	Average Wt. of Charge Per Extractor
1	10	63.5 lbs.
2	4	61.5
3	8	67.0
4	7	65.0
5	6	66.0
		64.6 lbs. average

The above figures show that the maximum average charge of ground retted material for each extractor was 64.6 pounds. Seventy-five pounds of ground and screened goldenrod material from the general harvest was the maximum which could be charged to an extractor. These results indicated that the average density of the retted material was 86.2 percent of the ground and screened goldenrod material from the general harvest.

Since the extraction system was in continuous operation during the extraction of the retted material, several extractions remained under solvent overnight. However, this period was not considered as part of the extraction time for either the acetone or benzol extraction. All extractors for each ret were given six hours of continuous extraction with acetone. The benzol extraction time was varied in that each extractor of Rets Nos. 1, 2, and 4 was extracted continuously for 12 hours, whereas for Rets Nos. 3 and 5, the total time of continuous benzol extraction was nine hours. Two extractors were in the acetone cycle and three in the benzol cycle. The temperature of acetone extraction was maintained at 140° F., and of benzol at 170° to 175°F.

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Acetone flow through the retted material in the extractors at a rate of 100 gallons per hour was maintained for Rets 1 and 2. The rate was reduced to 75 gallons per hour for Rets 3, 4, and 5 due to the development of pressures up to 50 pounds per square inch with flow rates above 75 gallons per hour as compared to a normal value of 15 to 20 pounds per square inch and 20 to 25 pounds per square inch for 75 gallons per hour. Excessive pressure on the system tended to cause solvent leakages at the gaskets in the extraction battery. It is believed that the higher pressures for Rets 3, 4, and 5 may have been caused by formation of an impervious film on the filters in the extractors by the bloom present in the retted material. For the benzol extraction, the rate of flow of benzol through the retted material was maintained at 40 to 45 gallons per hour. The pressure did not deviate from the normal value of 15 to 20 pounds per square inch.

The results indicate that a 12 hour benzol extraction at the rate of 40 to 50 gallons per hour maintained at a temperature of 170°to 175° F., is sufficient for completely extracting the rubber from ground retted goldenrod material. However, a nine hour extraction time is not adequate as shown by the "efficiency of extraction" in Table XVII for Rets Nos.3 and 5. The resin content in the crude rubber varied from 4.9 to 10.4 percent which is 1/4 to 1/2 that present in the crude rubber of the general harvest goldenrod. This indicated that a six hour acetone extraction time is sufficient for resin removal.

Extraction data for the ret control samples are tabulated in Table XVIII. Resin content of the benzol extracts obtained from the five retting control samples ranged from 5.9 to 48.0 percent. The high resin content and the titration value of ret controls 3, 4, and 5 indicated a rubber of poor quality. Therefore, the extraction of these control samples was repeated and the benzol extracts were acetone precipitated prior to evaluation. Significant comparisons cannot be made between the controls and the pilot plant extracted material due to the presence of excess resins in the control and to the fact that a large portion of stems and some bloom were removed from the retted material prior to extraction.

Purification by the acetone precipitation procedure consisted of adding the benzol extract to three volumes of acetone in order to precipitate the rubber and remove most of the acetone soluble resins. The resin content of the rubber from the pilot plant extracted retted goldenrod was reduced from an average of 8.0 to 1.7 percent. For the control samples the resin content was decreased from an average of 15.2 to 6.6 percent as shown in Table XIX.

IX TABLE XVII

SUMMARY OF PILOT PLANT EXTRACTION OF RETTED GOLDENROD

	Ret No. 1			Ret No. 2			Ret No. 3			Ret No. 4			Ret No. 5		
		Analytical			Analytical			Analytical			Analytical			Analytical	
	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*
Total lbs. material extracted	635			246			537			455			396		
Percent moisture in material	5.43	5.43	9.40	4.32	4.32	9.18	5.62	5.62	9.25	5.32	5.32	2.83	2.43	2.43	2.71
Total lbs. material extracted M.F.B.	600			236			506			430			386		
Lbs. of resins extracted	73.8			425			101.5			67.5			51.0		
Percent resins - as is basis	11.6	10.35	.90	17.3	17.9	4.12	18.9	15.2	1.25	14.8	12.40	1.23	12.9	12.75	1.44
Percent resins - M.F.B.	12.3	11.0	1.00	18.0	18.7	4.54	20.1	15.8	1.37	15.7	13.10	1.27	13.2	13.05	1.48
BENZOL EXTRACT															
Volume-gallons	18.0			8.12			13.45			10.2			7.42		
Total solids gms/cc	17.5			17.3			20.3			22.05			23.2		

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IX TABLE XVII-con't.

SUMMARY OF PILOT PLANT EXTRACTION OF RETTED GOLDENROD

	Ret No. 1			Ret No. 2			Ret No. 3			Ret No. 4			Ret No. 5		
		Analytical			Analytical			Analytical			Analytical			Analytical	
	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*	P. P. Ext.*	Raw Material	Residue P.P. Ext.*
Lbs. of Crude Rubber	26.23			11.72			22.8			18.8			14.35		
Percent resins	7.5			8.1			4.9			10.4			9.1		
Lbs. of resin-free rubber	24.3			10.77			21.7			16.83			13.01		
Percent resin-free rubber-as is basis	3.83	3.90	.52	4.38	5.60	.73	4.04	4.04	.67	3.71	3.85	.67	3.29	3.70	.62
Percent resin-free rubber-M.F.B.	4.05	4.12	.57	4.57	5.86	.81	4.28	4.28	.74	3.92	4.07	.68	3.37	3.79	.64
Efficiency of Extraction	98.2			78.4			100.0			96.5			89.0		

*P. P. Ext. = Pilot Plant Extraction

IX TABLE XVIII
RETTING CONTROL SAMPLES

Ret Control No.	Laboratory Extractions: Acetone Extract: Resin %	Acetone Extract: Resins Avg. %	Benzol Extracts: Crude Rubber %	Benzol Extracts: Crude Rubber Avg. %	Benzol Extracts: Rubber Resin-free %	Benzol Extracts: Resin %	Benzol Extracts: Resin after Acet. Ppt. %	Benzol Extract: Transmission Value	Benzol Extract: Viscosity	Analytical Results: Raw Material: Moisture %	Raw Material: Rubber Resin-free Avg. %	Residue after Extraction: Acetone Extract %	Residue after Extraction: Benzol Extract %
1	5.7 6.1	5.90	1.47 1.87	1.67	1.41	15.3		4.75	0.664	4.42	1.37	2.00 2.01	0.18 0.21
2	14.25 13.86	14.06	3.54 3.30	3.42	3.21	5.9		4.75	0.679	6.97	3.23	4.07 3.23	0.29 0.50
3	14.63 15.81	15.22	3.36 2.96	3.16	2.82	10.7		4.90	0.668	7.35	2.88	2.86 2.44	0.63 0.72
4	9.30 9.06	9.18	3.57 3.84	3.74	1.96	47.7		5.05	0.658	6.36	2.27	3.82 2.85	0.70 0.70
5	8.44 9.49	8.97	2.93 3.49	3.21	1.67	48.0		4.90	0.659	6.56	1.65	4.55 4.06	0.39 0.42
3	16.11 16.50 15.23	15.95		3.36	2.78	17.3	8.0			7.35	2.88		
4	11.28 11.02 10.25	10.85		2.67	2.12	20.6	7.9			6.36	2.27		
5	10.89 11.92	11.41		2.21	1.87	16.7	4.0			6.56	1.65		

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IX TABLE XIX

PERCENT RESIN CONTENT OF RUBBER IN BENZOL EXTRACTS

Ret No.	Retted Material: Before Precipitation	Retted Material: After Precipitation	Control: Before Precipitation	Control: After Precipitation
1	7.5	1.8	15.3	
2	8.1	1.6	5.9	
3	4.9	1.1	17.3	8.0
4	10.4	2.0	20.6	7.9
5	9.1	2.0	16.7	4.0
Avg.	8.0	1.7	15.2	6.6

The lower resin content of the rubber from the retted material as compared to that of the control can be attributed to two factors; first, retting decreases the resins in the goldenrod material, and second, a large proportion of stems and some bloom both of which contain resins and non-rubber benzol extracts were separated from the retted material before extraction.

Compounding, Vulcanization, and Testing. The rubber from the ret control samples extracted in large Soxhlets was pot cured and compounded according to the standard laboratory procedure. At the time that this work was conducted, the standard compounding formula was based on a crude rubber basis. Since then, formulas have been recorded on a resin-free basis, therefore, the formulas for the control samples were calculated and recorded on a resin-free basis. Due to the high resin content in the rubber obtained, milling was very unsatisfactory for control samples from experiments 3, 4, and 5 as shown in Table XX. The vulcanizates obtained were also poor in the same experiments. In order to obtain satisfactory rubber evaluation, it was necessary to repeat the extraction, vulcanization and testing for control samples 3, 4, and 5, the benzol extracts of which were acetone precipitated so as to reduce the resin content. Also recorded in Table XX are the compounding formulas, vulcanization, and testing data. The tensile strength showed an improvement with the three acetone precipitated control samples, but, in general, all were low and only four cures attained the tensile strength of 1000 p.s.i. Tread stocks were not prepared due to the inadequacy of control samples.

The rubber obtained from the pilot plant extracted retted goldenrod material and purified by the acetone precipitation method was evaluated by using the standard laboratory compounding formula and vulcanization procedure. The purified rubber was redissolved in benzol and 650 gram amounts from each of the five retting experiments were precompounded by the solution method. The chemicals, added to the benzol rubber solution and those added on the mill, are recorded in Table XXI. Benzol removal and precure were conducted in a Loomis jacketed mixer of 1/4 gallon capacity. Milling was very satisfactory with rubber from all five ret experiments; however, with the exception of the tread stock from Ret No. 3, both the gum and tread stocks handled and sheeted better on cold rolls. A complete series of gum and tread stock vulcanizates were made and the vulcanization and testing data recorded in Table XXI.

IX TABLE XX

RET CONTROLS-VULCANIZATION AND TESTING DATA COMPOUNDING FORMULA-RESIN FREE BASIS

		Ret Control No. 1	Ret Control No. 2	Ret Control No. 3	Ret Control No. 4	Ret Control No. 5	Ret Control No. 3 Repeat	Ret Control No. 4 Repeat	Ret Control No. 5 Repeat
Rubber-crude incl. resins	gms	26.7	42.7	38.8	44.6	36.1	56.115	47.50	23.38
Resins in crude rubber	%	15.3	5.9	10.7	47.7	48.0	8.0	7.9	4.0
Rubber-resin free	gms	22.6	40.2	34.6	23.3	18.8	51.63	43.75	22.44
Rubber-resin free	parts	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Resins-incl. with rubber	"	18.1	6.3	12.0	91.3	92.2	8.70	8.58	4.17
Sulfur	"	4.13	3.72	3.92	6.70	6.72	1.90	1.90	1.82
Thiotax	"	1.18	1.06	1.12	1.91	1.92	.54	.54	.52
Zinc Stearate	"	6.50	5.84	6.17	10.53	10.56	5.98	5.97	5.73
Flectol-H	"	1.18	1.06	1.12	1.91	1.92	1.09	1.09	1.04
Added on Mill									
Thiotax	parts						.54	.54	.52
Sulfur	"						1.90	1.90	1.82
Zinc Oxide	"	6.50	5.84	6.17	10.53	10.56	5.98	5.97	5.73
D.P.G.	"	.59	.53	.56				.54	

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IX TABLE XX-con't.

RET CONTROLS-VULCANIZATION AND TESTING DATA

	Cures Minutes at 260° F	Modulus at 300%	Modulus at 500%	Max. T. S. psi.	Ult. Elong. %	Remarks
Ret Control No. 1	10	235	550	860	600	Quite dry in milling but satisfactory
	20	235	705	1020	575	
	40	315	745	860	550	
	60	315	705	940	550	
Ret Control No. 2	20	130	330	770	675	Good milling - somewhat spongy
	40	210	400	920	650	
	60	210	400	830	600	
Ret Control No. 3	20	65	235	435	600	
	40	65	260	330	550	
	60	135	330	400	525	
Ret Control No. 4	40			< 45	100	Milled like clay - doughy - no tack -
	50			< 35	100	high resins
Ret Control No. 5	40			< 30	100	No tack, doughy - high resins -
	50			< 35	200	vulcanizates leathery
Ret Control No. 3 Repeat	20		138	138	500	Soft - vulcanizate contained bubbles
	40	105	370	1000	650	
Ret Control No. 4 Repeat	10	90		120	400	Milled well, sheeted, but vulcanizates
	20	140	455	915	675	were poor
	40	210	560	700	525	
Ret Control No. 5 Repeat	20	105	275	690	675	Very sticky, gummy - difficult to get
	40	205	555	1000	650	off rolls
0.5 Part D.P.G. Added						
Ret Control No. 1	10	200	640	960	600	
	20	235	705	1020	550	
Ret Control No. 2	15	130	380	960	650	
	30	160	400	670	575	
	45	185	490	800	550	
Ret Control No. 3	20	60	175	260	525	
	40	145	400	400	500	
Ret Control No. 4 Repeat	10	135	400	400	500	
	20	205	620	620	500	
	40	215		430	425	

All cures were made at 260° F., with the curing time ranging from 10 to 40 minutes. The tensile strength, elongation, and modulus of the tread stocks compare favorably with similarly compounded and vulcanized rubber from the general harvest goldenrod. Although the gum tensile strengths are somewhat lower than that of the general harvest rubber, they are much higher than the laboratory pot cured controls. Appreciable differences in tensile tests among the five retting experiments are negligible with the possible exception of the gum stock from Ret No. 2 which was lower than the other four rets.

SUMMARY

1. An anaerobic-aerobic retting procedure utilizing diluted sludge as inoculum has been developed as an aid in the recovery of rubber from goldenrod. Aeration and mixing of the retting mass proved helpful to the process.

2. Retting reduces the dry weight of the goldenrod leaves by at least 40 percent in laboratory experiments, and 21 to 36 percent on large scale experiments consisting of 1200 to 5000 pound mixtures of leaves, stems and bloom. The resin content of the leaves is reduced approximately 50 percent.

3. Pressing and shredding of retted material decreases by one-half the time required for drying.

4. The rates of extractions for resins and rubber by acetone and benzol show that retted goldenrod material can be extracted in 1/4 to 1/3 the time required for unretted goldenrod.

5. Rubber extraction of retted material is more thorough than extraction of unretted goldenrod as indicated by microscopic and analytical examination.

6. The quality of rubber obtained from retted material is superior to that obtained from unretted control samples of goldenrod.

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IX TABLE XXI
VULCANIZATION AND TESTING DATA OF RUBBER FROM RETTED GOLDENROD MATERIAL

Compounding Formula

Chemicals Added in Solution	Parts	Chemicals Added on Mill	Parts
Rubber, resin free	100.00	Sulfur	2.90
Sulfur	0.60	Thiotax	0.25
Thiotax	0.75	D.P.G.	0.50
Zinc Stearate	5.50	Zinc Oxide	5.50
D.P.G.	0.30	Carbon (for tread stock)	50.00

Physical Testing of Rubber

Sample	Cures Minutes at 260°F	Modulus at 300%	Modulus at 500%	Max. T. S. p.s.i.	Ult. Elong. %
Ret 1	10	205	745	1630	600
	20	275	1380	2140	575
	40	295	1440	1570	525
Ret 2	10	220	890	1080	525
	20	330		555	375
	40	330		490	350
Ret 3	10	240	725	930	525
	20	270	1355	1695	550
	40	300	1200	1200	500
Ret 4	10	100	500	1165	600
	20	205	1255	1630	550
	40	265	1335	1335	500
Ret 5	10	200	575	1490	625
	20	345	1380	1380	500
	40	310		620	425
Tread Stock 50 Parts Statex					
Ret 1	10	1000	2070	2540	575
	20	1440	2455	2455	500
	40	1700		2230	375
Ret 2	10	920	2040	2625	600
	20	1480		2805	475
	40	1770		2295	350
Ret 3	10	880	2000	2440	600
	20	1400	2600	2600	500
	40	1705		2390	400
Ret 4	10	865	2070	2630	625
	20	1445	2590	2590	500
	40	1710		2255	375
Ret 5	10	1000	2130	2600	600
	20	1445	2620	2620	500
	40	1695		2540	425

X ENSILAGE OF GOLDENROD

The purpose of this work was to study the ensiling of green goldenrod as a ready, practical means of storing and preserving this crop in the absence of air and light for a considerable period after harvesting and to determine whether the ensilage process has any degrading effect on the quantity and the quality of the rubber obtainable.

Preliminary ensilage studies were made in the laboratory before large scale field experiments were undertaken. A detailed account of this preliminary work is given in the first part of this Section, and the remainder of the Section deals with the large scale experimental runs and includes storage, rubber extraction, and testing data obtained.

PRELIMINARY LABORATORY EXPERIMENTS. No fresh goldenrod material was available for these experiments at this time and dried material was used instead. Two 1-kg. batches of air-dried whole goldenrod leaves, identified as GRG-75 or AG-629, were wetted with sufficient water to approximate a moisture content of 62 percent. The assay on the air-dried goldenrod used in this experiment follows:

% Moisture	% Acetone Extract		% Benzene Extract	
	As rec'd	M.F.B.	As rec'd	M.F.B.
9.45	15.4	17.0	5.4	6.0

The wetted batches were bottled and sealed, with only a tube outlet which was kept under water. The ensiling proceeded, in complete darkness, for a period of thirty-four days. The ensiled material was then air-dried in a circulating-air room, by spreading in a thin layer over a large surface. The pH of the material, taken prior to air-drying, was found to be 5.3 in run A and 5.1 in run B. Some of the drying data follows:

Run	Wt. of wet leaves (g)	Wt. of wet ensilage (g)	Air-dry matter (g) Orig. g'rod.	Air-dry matter (g) Ensilage	Moisture-free matter Orig. g'rod.	Moisture-free matter Ensilage	% Loss in dry-weight
A	2420	2354	1000	901	906	824	9.01
B	2420	2363	1000	902	906	828	8.50

Ensilage "A" was extracted without grinding. Ensilage "B" was extracted after grinding through a Wiley mill using a 1/16" screen. The extraction procedure consisted of 24 hours of acetone extraction to remove "resins." The residue was then nearly freed from acetone and then extracted for 24 hours with benzene to obtain "rubber." The conventional analytical procedure was also run on small (5 gram) finely ground portions of the ensilages to determine what the ultimate values would be. The

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results follow:

	ACETONE EXTRACT				BENZENE EXTRACT			
	"Analytical"		"Large Scale"*		"Analytical"		"Large Scale"	
	As rec'd	M.F.B.	As rec'd	M.F.B.	As rec'd	M.F.B.	As rec'd	M.F.B.
RUN								
A Whole	15.6	17.2	17.9	19.5	4.4	4.8	3.1	3.3
B Ground	15.1	16.4	16.5	17.9	4.5	4.9	4.8	5.2

(*) These four values are all probably higher than the true values. Especially in case "A", it is believed that the solvent was incompletely removed. The "resin" contents and yields from runs A and B were as follows:

Rubber from Run:	% Acetone Extract ("Resin")	% Yield (as resin-free rubber) As rec'd	M.F.B.
A	16.5	2.5	2.8
B	13.5	4.1	4.5

It will be noted that extraction of the ground ensilage not only gave more rubber but also a better rubber than extraction of the whole ensilage. Assuming the "analytical" figures to represent "resin-free" rubber, and using the "resin-free" yield values, extraction efficiencies of 58 percent for run A and 92 percent for run B were obtained. The high efficiency of the extraction on ground material indicates that ensilage has definitely increased the "availability" of the rubber present. This is further indicated by the efficiency obtained on the unground material.

When vulcanizates of these rubbers were made, it appeared that the more impure rubber gave the better tensile with D.P.G. However, by the standard formula, they both gave better tensiles than the best yet obtained on unensiled GRG-75. It must be noted that all the tensile strengths shown below are probably not the best obtainable, due to inadequacy of the amounts of rubber available in every case. Tensile strengths were as follows:

Vulcanization Method	Rubber from raw goldenrod	Rubber from whole ensilage	Rubber from ground ensilage
Standard	1000	1240	1350
With D.P.G.	No run	1860	1685

In order to more nearly complete the study of the effect of ensiling, analytical determinations of total nitrogen, non-protein nitrogen, and total sugars were run on the unensiled and ensiled materials. These values expressed as grams per kg. of the original goldenrod material are given below:

Summary of Analytical Results on Ensilage Experiment

	Before Ensilage	After Ensilage Run A (Whole)	Run B (ground)
Dry Matter	906	824	828
Total Nitrogen	22.6	21.1	22.0
Non-protein Nitrogen	5.1	7.6	7.3
Total Sugars (as invert)	51.5	13.7	12.7
Rubber content (by analytical method)	54.0	39.5	40.6
Resin-free Rubber (large scale extr.)	29.2*	23.1	37.3

(*) This figure calculated from a rubber yield of 3.3% (resin content of rubber = 11.6%)

CONCLUSIONS:

1. The grinding properties of the ensiled material were very superior to those of the raw goldenrod, with a marked increase in grinding speed being most notable. Even very fine grinding was accomplished with practically no gumming.

2. The analytical figures indicate that the rubber content was apparently reduced during ensilage. However, in spite of this drop in rubber content, the "availability" is increased. This is well illustrated by the fact that the net quantity of rubber obtained from one kilogram of goldenrod is greater after ensilage than before, when extraction is conducted on material ground in the same way.

3. It is shown that the total sugars content was greatly reduced due to ensilage.

4. The total amount of nitrogen remained unchanged but an increase in non-protein nitrogen was evident in the ensiled material.

LARGE SCALE EXPERIMENTS

Two large lots of goldenrod material of selection 3S79, 1943 crop, were ensiled at Waynesboro, Ga., in semi-farm-size concrete silos and six barrel size lots were prepared after encouraging results obtained in preliminary silage experiments conducted in the laboratory had indicated no apparent weight loss or reduction of quality of the rubber present due to this storage process. The ensilage was stored under optimum moisture conditions, until fermentation was substantially complete, after which the material was dried, fractionated in some cases, and then ground and extracted for evaluating the rubber quality as compared to that contained in control or check samples of the same material which had been dried at 145° F. without ensiling.

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Fifty-gallon steel drums with air-tight removable steel lids were used as storage silos for the small batches. The raw material used for filling the drums was freshly harvested whole goldenrod plant including stems, leaves, and blooms. This was chopped up in a Papec cutter in lengths not exceeding 3/4 in. and immediately packed as tightly as possible in the drums and held down with a number of slatted wooden cross pieces so arranged as to provide free unrestricted exit of the gases produced during the fermentation, and thus eliminate any possibility of bulging of the drums. A vent hole with threaded connection was then fitted into the center of the lid for connecting a glass or rubber tube to a small water trap or seal for excluding oxygen and also for observation of the rate of evolution of the gases, mainly carbon dioxide, from the fermenting material. Fermentation was considered practically complete after a period of 60-70 days, with the moisture content previously adjusted to 60-65%, whereupon the drum vent hole was sealed and the barrel made ready for shipment to the Southern Regional Laboratory for drying, separating, extracting, testing, etc.

Drums 1 and 2 were ensiled on Aug. 11, 1943, with whole goldenrod plant material which was Papec cut into 1 in. pieces. This material was not separated to remove stems and contained very little if any bloom. After fermentation was reasonably complete, the sealed drums were shipped to the Southern Regional Laboratory for drying and extracting in the laboratory and pilot plant. Similarly, drums 3 and 4 (combined) and also drums 4 and 5 (combined) were ensiled on October 22, 1943. Drums 3 and 4 were filled with whole green plant material harvested while the crop was at bloom stage and contained a considerable portion of stems and bloom. Drums 5 and 6 were ensiled on the same day with the same crop material as drums 3 and 4. Drums 5 and 6 were marked "separated" to indicate that the green contents had been air-separated prior to filling, for removal of a portion of the stems and bloom and other non-leaf material. The four drum silos were sealed without further treatment following the necessary silage period and shipped to New Orleans for drying and laboratory extraction for evaluation of the rubber.

After successful extraction of high quality rubber in the pilot plant from drum silages 1 and 2, two large scale storage runs were begun at Waynesboro. On November 27, two concrete silos measuring 5' diameter by 8' high were filled using selection 3S79 harvested from early planted well-developed stands. The raw stock at the mature stage contained a high percentage of stems and bloom and some of the bloom was chopped off before feeding through the Papec cutter set at 1 in. cut. It was necessary to add approximately 50 gallons of water to the contents of each silo in order to boost the moisture content up to 60%. The water was sprinkled continuously through a perforated can onto the stream delivered into the silos from the cutter. A fairly representative running sample of about 75# of the contents of each tank was collected by taking equal random "grab" samples at regular intervals during the loading. The total charge (including the water) filled into each silo was 3143# for No. 1, and 3366# for No. 2. The silos were then satisfactorily sealed using a properly formed earthen seal and this protected with a suitable weatherproof roof covering. The control samples were dried "as is" and shipped to New Orleans. Both of the silos

were unloaded after ensiling approximately 72 days and the contents dried at 165° F. in the large kiln drier at Waynesboro. Further details of the handling of the dried ensilage is given later in this text.

The sealed drums of ensilage goldenrod were opened promptly upon receipt at the Southern Regional Laboratory and were inspected carefully. In general, the material at the very top (approximately 6 in.) of each drum was very moldy and that at the bottom and along the sides was rather black and these portions were discarded before drying, but the remaining bulk of the ensilage was of a brownish yellow color. The material from each drum was dried separately (see table below) in a tray type drier at a temperature of 143-145° F.

Drum No.	Material Before Drying Net Wt. #	Material After Drying Net Wt. #	Loss in Weight %	Drying Time (hours)	Drying Temp. °F
1	146.5	52.0	64.4	10	143
2	136.5	54.0	60.4	15.5	143
3	202.5	82.5	59.3	24	145
4	212.5	85.5	59.9	24	145
5	201.0	76.5	61.8	23	145
6	185.5	70.0	62.3	26	145

The dried ensilage material from drums 1 and 2 was combined and ground "as is" for laboratory analysis and testing and for pilot plant extraction. The dried material from drums 3 and 4 was combined and was then processed through an aspiration-box type air-separator equipped with a cyclone for fractionating or removing as much as possible of the stems, and bloom and other non-leaf material. A fairly good separation of the leaves, stems and bloom was obtained by repassing the leafy portion successively for obtaining a concentrated leaf fraction which was finally ground for extraction later on. The identical procedure was carried out for the dried ensilage from drums 5 and 6. The following table shows a breakdown of the separation effected in both cases.

Before Separation		After Separation		
Drum No.	Dried Material	Bloom #	Stems #	Leaf (impure) #
1 & 2	Was not separated	-	-	-
3 & 4	119.5	17.5	28.5	73.5
5 & 6	153.0	12.0	74.0	65.5

It was originally planned that control samples would be taken of each drum for the purpose of evaluating the rubber quality before and after the ensilage process but none were received at the Southern Regional Laboratory.

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The ensilaged material from both of the large silos 1 and 2 was dried separately at Waynesboro in the kiln drier at 165° F. and then was separated with air-flotation equipment to scalp off a portion of the coarse stem material and some of the light chaff and bloom. It was finally baled and shipped to New Orleans, where it was subjected to further air-separation. The baled dry material from the two silos was combined and 1414# were concentrated down to 1014# of a fairly concentrated leaf material fraction by removing 336# of stems and approximately 60# of bloom, etc. Successive fractionation of the material in this way resulted in a considerable weight reduction and consequently an increased rubber content for final extraction in the two-solvent pilot plant extraction system. A 40# control sample, representative of each silo, was dried at Waynesboro after loading of the silos and was sent to the New Orleans laboratory for determining the possible rubber degradation during storage.

The dried ensilage material from the various drum and concrete silos was ground as follows:

Drums 1 & 2. Ground once through a Jeffrey hammermill with 1" hammers and a 1/32 in. screen.

Drums 3, 4, 5, & 6. Ground once through a Ball and Jewell mill with 1/8 in. screen and the first grind repassed through a 1/32 in. screen.

Drum Silo Controls. None received.

Concrete Silos 1 & 2. Ground once through Jeffrey hammermill using 1 in. hammers and 1/16 in. screen.

Concrete Silos 1 & 2, Controls. Ground once through a Ball and Jewell mill with 1/8 in. screen and first grind repassed through a 1/32 in. screen.

Pilot plant extractions were not made on all of the ensilage silos and controls as was originally contemplated but significant data obtained on a substantial bulk of this material indicated that goldenrod rubber quality was apparently not noticeably affected by ensiling. Separate pilot plant extractions and tests were made on drum silos 1 and 2 and on concrete silos 1 and 2 (Tables V and VI). Laboratory extractions were run on all of the drum silos (Tables I and II) and on the control samples for large silos 1 and 2, but none were available for the drum silos runs. Test data including laboratory extractions, vulcanization tests, etc., for large silo controls 1 and 2 are shown in separate tables (III and IV) as the results are considered valueless for two reasons, namely: first, it was necessary to concentrate the original material twice for the pilot plant extraction, and, second, because potcures made on the benzol extracts of goldenrod whole plant material containing a high percentage of stems and blooms are known to be of little significance due to the high proportion of non-rubber constituents in the benzol extract which cannot be separated from the rubber.

Fairly exhaustive laboratory extraction of the dried ground ensilage from drum silos 1 and 2 gave benzol extracts high in resin content and rubber of

high titration and low viscosity values. The crude rubber, unpurified by acetone precipitation, (Tables I and II), produced gumstock vulcanizates of only fair to poor tensile strengths even with the added accelerator booster, DPG. Past laboratory results have shown consistently that this is characteristic of whole plant material low in leaf or rubber content and containing a large percentage of stems and bloom. It is apparent that exhaustive benzol extractions made on this composition material, as is done in the laboratory, gives extracts which, even after acetone precipitation, do not resemble normal goldenrod rubber and probably contain a large amount of non-rubber constituents. On the other hand, benzol extracts obtained from pilot plant extractions made on identical material gave high tensile strength on Loomis vulcanizates and, even on potcure vulcanizates without D.P.G., because of the less exhaustive extraction given in the pilot plant as compared to the laboratory. Pilot plant extraction on drums 1 and 2 is a case in point (see Tables V and VI). The dried, ground ensilage from drums 3 and 4, which had been air-separated to remove considerable amount of the stems and bloom thereby increasing the rubber content, gave laboratory benzol extracts having considerably less resin content, and after acetone precipitation potcures were prepared which, although milling extremely sticky, gave vulcanizates of good tensile strengths with and without accelerator booster. However, the titration and viscosity values were "off", indicating again the presence of non-rubber constituents in the benzol extract. The dried, ground ensilage from drums 5 and 6, which had also been concentrated by air-separation to a fairly high rubber content, also gave laboratory benzol extracts of low resin content, and after acetone precipitation the vulcanizates were only fair. Titration and viscosity values were also "off". No positive significance need be given to this inconsistency which could be accounted for by many factors, such as non-representativeness of sample, contamination of end benzol extract with non-rubber impurities, etc.

Gumstocks of high tensile strength were prepared from the benzol extract obtained in the pilot plant extraction of drum silos 1 and 2 (Tables V and VI). The original material was very low in rubber content and although the crude rubber contained 8.8% resins and was not acetone precipitated, the vulcanizates showed high tensil values both with and without D.P.G. No Statex tests were made in this case.

Approximately 1.1# of crude rubber was obtained for these tests from 83# of the ground dried ensilage extracted in a single cell for 12 hours with acetone at 140° F., at an average solvent pumping rate of 100 gallons per hour, followed by a 12 hour extraction with benzol at 170° F., and an average solvent rate of 60 gallons per hour.

Rubber stock of very high quality, and in amounts large enough for precuring on the large Loomis machine, was produced in the pilot plant (see Tables V and VI) from goldenrod ensilage made in concrete silos 1 and 2. Both gum and carbon stocks of high tensile strengths (2535 p.s.i.) were obtained with stock precured on both the small (1#) and the large (20#) Loomis runs. The crude rubber content of this material, which had been thoroughly air-separated, was 4.41% and the benzol extract obtained from processing 975# of the raw

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material contained 11.5% resins and produced high tensile vulcanizates after acetone precipitation. However, before precuring, the benzol solution of this crude rubber was allowed to stand for some time and considerable of the non-rubber impurities settled out and were drained off at this stage. The large silo material was processed in the 8-cell pilot plant extraction battery using the two-solvent continuous system of extraction. Thirteen cell charges were made and the cycle adjusted for extracting the material for 6 hours with 92% acetone followed by 9 hours of extraction with 95% benzene. Processing of this ensilage was not exactly continuous as the plant was operated only 15 consecutive hours daily. Acetone at 140° F. was pumped through 2 extractors in series at a rate of 100 gallons per hour, while the benzene was put through at approximately 45 gallons per hour with three extractors connected in series.

Summary and Conclusions. (1) Laboratory investigations on goldenrod selection 3S79 before and after ensilage show no apparent change in the quantity of rubber obtainable by acetone-benzene extraction or of the quality of the rubber for producing gum and tread stocks.

(2) Gum and tread stocks of comparatively high tensile strength values were obtained from rubber extracted from a 975# lot of goldenrod ensiled in the two 5' diameter by 8' high concrete silos. Gumstock of high tensile strength was also prepared from an 83# batch of the goldenrod stored in drum silos 1 and 2. The control samples for affording an ideal basis for comparison of the rubber quality before and after the ensilage process were inadequate and meaningless in the case of the large silos, and were not available in the case of the drum storages. This, however, is really unimportant in the light of the high test values obtained and considering the large weight of material processed in this work. Appropriate size control samples for correct evaluation should be large enough, not only for obtaining close representation of the original material but for pilot plant processing to produce sufficient rubber for precuring with the small Loomis machine and for producing treadstock. This is especially true with material harvested during the bloom stage.

(3) Substantial evidence is presented in this report to indicate that ensiling is a highly recommended means for promptly storing and preserving this crop for a considerable period until it can be dried for subsequent processing. Ensilage is a well-known agricultural practice for preserving green fodder for edible purposes, and applied to goldenrod for rubber production, it not only affords a means of storing in the almost complete absence of air and light which are very injurious to goldenrod rubber, but the normal acid fermentation apparently reduces the total dry weight by approximately 10% and renders the material in a form which can be dried more quickly and consequently more economically. In addition, the dried material can be air-separated with comparative ease, grinds and handles easier in size-reducing machinery, and also extracts considerably faster with the solvents.

X-TABLE I

GOLDENROD ENSILAGE - DRUMS 1 - 6, Incl.

	Laboratory Extraction								Analytical Results					
	Acetone Extract		Benzol Extract								Raw Material		Residue after Extraction	
Sample Drum No.	Resins %	Resins Avg. %	Crude Rubber %	Crude Rubber Avg. %	Rubber, resin-free %	Resin %	Resin % after Acet. prec.	Titr. Value	Visc.	Mois-ture %	Rubber, resin-free Avg. %	Acet. Extr. %	Benz. Extr. %
1	8.0	8.2	2.3	2.5	1.86	25.7		4.70	0.662	4.87	1.75	3.41	0.27
	8.4		2.6			25.7		4.70	0.662	4.87		1.81	0.16
2	8.1	8.3	1.9	2.1	1.50	28.6		4.60	0.666	5.18	1.52	1.46	0.29
	8.4		2.3			28.6		4.60	0.666	5.18		0.85	0.30
3 & 4	19.2	16.7	3.1	3.5	3.04	12.6		4.80	0.682	6.49	2.98	1.50	1.12
	15.8		4.0			12.6		4.80	0.682	6.49		3.91	0.75
	16.5		3.4			12.6		4.80	0.682	6.49		3.47	0.76
	15.4		3.5			12.6		4.80	0.682	6.49		4.44	0.71
3 & 4 rerun			3.3	3.3	2.93	11.6	8.1			6.49	2.98		
5 & 6	19.2	19.1	3.8	3.7	3.38	8.3		5.25	0.673	6.42	2.94	1.77	0.60
	18.7		3.6			8.3		5.25	0.673	6.42		2.86	0.67
	19.0		3.7			8.3		5.25	0.673	6.42		2.36	0.55
	19.4		3.5			8.3		5.25	0.673	6.42		2.04	0.62
5 & 6 rerun			3.2	3.2	2.87	9.0	3.8			6.42	2.94		

X-TABLE II
GOLDENROD ENSILAGE - DRUMS 1 - 6, Incl.

Compounding Formula, Calculated to Resin-free, Rubber Basis.						
Drum No.	1	2	3 & 4	3 & 4	5 & 6	5 & 6
Rubber, crude, incl. resins, gms.	34.9	28.8	53.4	48.8	60.6	45.3
Resins in crude rubber %	25.7	28.6	12.6	8.1	8.3	3.8
Total solids $\frac{gms}{cc}$				.074		.053
Rubber, resin free, gms.	25.9	20.6	46.7	44.8	55.6	43.6
Rubber, resin free, parts	100.00	100.00	100.00	100.00	100.00	100.00
Resins, incl. with rubber, parts	34.6	40.0	14.4	8.82	9.05	3.95
Sulfur "	4.72	4.89	4.00	1.91	3.81	1.82
Thiotax "	1.35	1.40	1.14	.54	1.09	.52
Zinc Stearate "	7.41	7.69	6.29	5.99	5.99	5.71
Flectol H "	1.35	1.40	1.14	1.09	1.09	1.04
Added on mill:						
Thiotax "				.54		.52
Sulfur "				1.91	Not Milled	1.82
Z. Oxide "	7.41	76.9	6.29	5.99		5.71
DPG "	.67	.70		.54		.52

X-TABLE II-con't.
GOLDENROD ENSILAGE - DRUMS 1 - 6, Incl.

Sample Drum No.	Vulcanization and Tests: Cures Minutes at 260°F	Modulus at 300% psi.	Modulus at 500% psi.	Max. TS psi.	Ult. Elong. %	Remarks
	Gumstock - Standard Formula					
1	10	310		845	475	Sample dry, waxy, and had little tack and later became sticky.
	20	425		925	450	
	30	490		905	450	
2	20			150	300	Sample extremely sticky and hard to handle. Given additional precure.
3 & 4 combined	5	265	715	715	500	Extremely dry and crumbly - too overcured for proper milling.
	10	290	1090	1090	500	
	15	295	1185	1185	500	
	30	375		755	400	
	45	310		310	300	
3 & 4 combined	10	100	405	1350	700	Acetone precipitated. Very sticky.
	20	175	630	1755	700	
	40	270		880	475	

X-TABLE II-con't.
GOLDENROD ENSILAGE - Drums 1 - 6, Incl.

Gumstock - 0.5 parts DPG added.						
Sample Drum No.	Cures Minutes at 260°F	Modulus at 300% psi.	Modulus at 500% psi.	Max. TS psi.	Ult. Elong. %	Remarks
1	10	345	885	885	500	
	20	470		1100	450	
2	10	450		450	300	Vulcanizates of inferior quality
3 & 4	10	150	610	815	525	
	20	345	1275	1725	600	
	40	400		635	350	
5 & 6	20	205		310	350	Very sticky - hard to get off rolls
	40	265	915	915	500	

X-TABLE III

GOLDENROD ENSILAGE CONTROLS - SILOS 1 & 2

	Laboratory Extraction							Analytical Results					
	Acetone Extract		Benzol Extract					Benzol Extract		Raw Material		Residue after Extraction	
Control Sample	Resins %	Resins Avg. %	Crude Rubber %	Crude Rubber Avg. %	Rubber, resin-free %	Resin %	Resin % after Acet. prec.	Titr. Value	Visc.	Moisture %	Rubber, resin-free Avg.%	Acet. Extr. %	Benz. Extr. %
	5.62		2.80					5.30	0.653			3.96	0.27
	7.49	6.78	1.61	2.26	1.43	36.9		5.30	0.653	6.24	1.34	1.14	0.32
	7.22		2.31					5.30	0.653			1.32	0.35
Silo #1 (Bag # 2789)	6.69		1.82					5.50	0.646				
	6.50	6.62	1.50	1.71	1.45	15.3	1.3	5.50	0.646	6.24	1.34		
	6.77		1.74					5.50	0.646				
	6.50		1.76					5.50	0.646				
Silo #2 (Bag # 2788)	6.56		1.74					5.15	0.655			1.26	0.30
	6.01	6.34	1.67	1.67	1.23	26.0		5.15	0.655	7.08	1.13	1.58	0.33
	6.46		1.61					5.15	0.655			0.91	0.33
	5.89		1.75					5.10	0.655				
	6.35	6.07	1.58	1.63	1.38	15.2	5.3	5.10	0.655	7.08	1.13		
	5.76		1.59					5.10	0.655				
	6.30		1.60					5.10	0.655				

X-TABLE IV
GOLDENROD ENSILAGE CONTROLS - SILOS 1 & 2

Compounding Formula, Calculated to Resin-free Rubber Basis	Silo # 1	Silo # 2
Rubber, crude, incl. resins, g.	36.3	21.4
Resins in crude rubber %	36.9	26.0
Rubber, resin-free, g.	22.9	15.8
Rubber, resin-free, parts	100.0	100.0
Resins, incl. with rubber, parts	58.5	35.2
Sulfur "	5.55	4.74
Thiotax "	1.59	1.35
Zinc Stearate "	8.72	7.45
Flectol H "	1.59	1.35
Added on mill		
Zinc Oxide "	8.72	7.45

X-TABLE IV-con't.
GOLDENROD ENSILAGE CONTROLS - SILOS 1 & 2

Vulcanization and Tests.						
Control Sample	Cure min. at 260°F	Modulus at 300%	Modulus at 500%	Max. TS psi.	Ult. Elong. %	Remarks
Silo #1	40	270		350	400	Milled fairly well; did not stick; sheeted
	50	305		305	300	
Silo #2	15	155	350	350	500	Sticky, wouldn't sheet, yet produced better vulcanizate than Silo No. 1
	30	165	530	610	525	
	45	240	560	600	550	
	60	265	535	665	550	

X-TABLE V
GOLDENROD-ENSILAGE
PILOT PLANT EXTRACTIONS

	Pilot Plant Processing Results		Analytical Results			
			Raw Material		Residue after Pilot-Plant Extraction	
	Drums 1 & 2	Silos 1 & 2	Drums 1 & 2	Silos 1 & 2	Drums 1 & 2	Silos 1 & 2
Material Processed:						
Weight, lbs.	83	975				
Weight, lbs., MFB	78.8	900				
Moisture, %	5.03	7.82	5.03	7.82		
Acetone Extract. (Resins):						
Weight, lbs.		148				
Weight, %		15.2	9.27	15.2		2.51
Weight, % MFB		16.5	9.78	16.5		2.92
Benzol Extract:						
Volume, gallons	4.55	24.0				
Concentration-Solids gms./cc	0.0307	20.0				
Wt. Crude Rubber, lbs.	1.14	40.0				
Resins, %	8.8	11.5				
Rubber, resin-free, lbs.	1.04	35.4				
Rubber, resin-free, %	1.25	3.64	1.55	4.41		1.01
Rubber, resin-free, % MFB	1.32	3.96	1.63	4.79		1.17
Effic. of Benzene Extraction, %	81.0	82.5				

$$\text{eff. } \% = \frac{\%\ \text{rubber, resin-free, pilot plant}}{\%\ \text{benzol extract, analytical}}$$

X-TABLE VI
GOLDENROD-ENSILAGE
PILOT PLANT EXTRACTIONS

Compounding Formula. Calculated to resin-free rubber basis	Drums 1 & 2 (potcure)	Concrete Silos 1 & 2 (Small Loomis)	Concrete Silos 1 & 2 (Large Loomis)
Added in solution for precure	37.2 gms.	2813(cc)	50,151 (cc)
Resins, %	8.8	2.5	4.1
Total Solids (gms/cc)		0.237	0.169
Rubber, resin free (g)	33.9	650	8,165
Material produced (g)		637	8,898
Rubber, resin free (parts)	100	100.00	100.00
Sulfur "	3.34	0.60	0.660
Thiotax "	1.10	0.75	0.825
Zinc Stearate "	6.04	5.50	5.500
DPG "		0.30	0.330
Flectol H "	1.10		
Material milled (g)		250	250
Added on mill: (parts)			
Sulfur "		2.90	2.840
Thiotax "		0.25	0.175
DPG "	0.55	0.50	.470
Zinc Oxide "	6.04	5.50	5.50
Am't. of gum stock used for tread (g)		200.00	200.00
Carbon (Statex) (g)		86.00	88.00

X-TABLE VI-con't.
GOLDENROD ENSILAGE-PILOT PLANT EXTRACTIONS

Sample	Cures Minutes at 260°F	Modulus psi. at 300%	500%	Max. Tens. Strength psi.	Ult. Elong. %	Remarks
			Vulcanization and Tests			
			Gumstock-with compounding formula above.			
Drums 1 & 2, potcure	5	220		870	475	Very dry and spongy in milling.
	10	150	905	1810	600	
	20	225	1060	1695	550	
	30	225	1135	1395	525	
Silos 1 & 2, (Small Loomis)	10	205	620	1585	650	Milled well; sheeted
	20	280	1090	1720	600	
	40	305	1320	1320	500	
Silos 1 & 2, (Large Loomis)	10	240	880	1560	575	Very dry at first; softened up to mill very well.
	20	335	1300	1300	500	
	40	360		1145	475	
			Gumstock-.5 part DPG added.			
Drums 1 & 2, potcure	5	250	1285	1715	550	Very dry and spongy in milling.
	10	225	1360	1960	550	
	20	300	1510	1810	525	
			Tread stock-50 parts Statex added.			
Silos 1 & 2 (Small Loomis)	10	855	1640	2095	525	Carbon milled well on cold rolls.
	20	1185	2235	2370	525	
	40	1425		2170	425	
Silos 1 & 2 (Large Loomis)	10	900	2035	2470	500	Material took carbon slowly.
	20	1400		2535	475	
	40	1665		2300	400	

XI-ANTIOXIDANT TREATMENT OF FRESHLY HARVESTED LEAVES

A field test was made at the suggestion of Dr. H. L. Trumbull of the B. F. Goodrich Company, to determine the possible effect of application of a rubber antioxidant in counteracting any possible deterioration of the rubber during harvest collection, drying, and grinding of the leaves. Leaves, hand stripped from goldenrod consisting of selection 3-S-79 and harvested from F. M. Skinner field and Mrs. F. Cates field No. 2, were used for this experiment. As soon as 40 pounds of leaves were made available they were spread on two 4' x 5' trays each containing 20 pounds of leaves. Using a hand spray gun, the leaves of one tray were sprayed with Stalite Antioxidant emulsion manufactured by the B. F. Goodrich Company. The other tray of leaves was used as an untreated control. One gallon of Stalite emulsion, diluted with an equal amount of water, was consumed in treating a total of 228 pounds of green leaves. The dilution was necessary in order to obtain sufficient "wetting" which was also aided by mixing the leaves while spraying.

The amount of leaves stripped by eight to sixteen laborers averaged 80 pounds per day or a total of 456 pounds for almost six days. Daily, 40 pounds of antioxidant treated leaves and 40 pounds of untreated control were dried with the general harvest in the kiln drier for two hours at 160-165°F. A total of 228 pounds of green leaves were treated and dried to 117.5 pounds, whereas an equal amount for the control netted 116 pounds of dry leaves.

The control leaf material and the leaves treated with an antioxidant were practically free of stems and bloom therefore further separation was considered unnecessary. Grinding was carried out on these two lots of material by using the Jeffrey hammer mill with 1/16" screen and 1" hammers at the Southern Regional Research Laboratory. Extractions of 1 kg. batches of the control sample and of the antioxidant treated leaves were completed by extracting for 32 hours with acetone to remove resins and followed for 32 hours with benzol to obtain the rubber. Resin content of the benzol extract from the antioxidant material is slightly higher than that secured for the control sample (see Table I). The standard recipe was used in pre-compounding the benzol extracts in glass still pots for vulcanization.

Enough ground material, 100 pounds of control sample and 93 pounds of the antioxidant treated leaves, was available from each lot for a single cell extraction. The benzol stills were thoroughly cleaned and rinsed out with benzol before extraction. Conditions for extractions, and results of extractions, together with analytical determinations are indicated in Table II. The benzol extracts were precipitated with acetone to remove excess resins in the rubber. Benzol was used to redissolve the rubber in each case before precompounding in the small Loomis mixer.

Vulcanization and Testing. The antioxidant treated material and its control were each handled in two different ways, i.e., by the laboratory extraction and pot precuring method, and by pilot plant extraction, deresinification by repricipitation, and small Loomis precure for the larger samples. Results are shown in Table III.

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Milling of the two rubber samples from laboratory extractions was quite difficult as they were both extremely sticky. The control would not sheet but wasmanageable enough to mill a portion with 0.5 part D.P.G. The treated material was much too sticky and gummy for proper milling to be achieved and no D.P.G. values were obtained. Under the circumstances it would not be fair to draw any conclusion on the tensile strength values given for these two samples.

The acetone precipitated rubber from the pilot plant extractions was precured in the small Loomis mixer and tread and gum stocks were made. Again the control sample milled much better than the antioxidant treated and was much less sticky. The tread vulcanizates on the treated rubber gave higher tensile strength values than the tread on the control; however, this is not true with the gum vulcanizates. Tensile strength values on the control gum stocks with D.P.G. by both methods check very well. The higher resin content of the laboratory extracted rubber is due to the fact that it was not acetone precipitated, which probably accounts in part for its stickiness.

Summary of Results. 1. The titration values and viscosities of the benzol extracts from laboratory extractions of the control and antioxidant leaf material are practically the same, which indicates that the antioxidant emulsion has little or no effect on the quality of the rubber from goldenrod leaf material.

2. Resin content in the benzol extracts from both the laboratory and pilot plant extractions is higher in the case of the antioxidant treated leaves.

3. The control samples of rubber milled very much better than the antioxidant treated samples. This is true with laboratory samples which were not acetone preciptated as well as with the pilot plant samples where the excess resins in the rubber were removed by acetone precipitation.

4. Acetone precipitation of the rubber to remove excess resins is necessary in order to obtain the maximum tensile strength values.

XI-TABLE I LABORATORY EXTRACTIONS

Sample	% Moisture as rec'd	% Resins acetone ext. M.F.B.	% Rubber Benzol ext. M.F.B.	% Resins in Benzol ext.	Tit. Value Benzol ext.	Viscosity Benzol ext.	% Rubber Resins free M.F.B.	% Rubber Analyt. M.F.B.
Anti-Oxidant Control Bags 1604-1607 incl.	6.72	18.05	7.11	10.4	4.50	0.676	6.37	6.03
Treated with Anti-Oxidant Bags 1600-1603 incl.	6.62	18.39	7.04	13.9	4.60	0.682	6.06	6.70

XI-TABLE II PILOT PLANT EXTRACTIONS

Sample	Lbs. extracted	Pilot Plant Acetone		Pilot Plant Benzol Extraction				Analytical Determination				Eff. of Ext.
		Lbs. extracted	%	Crude rubber lbs.	Resin-free lbs.	% Resins in extract	% rubber resin free-basis	Raw Material Acetone ext.	Raw Material Benzol ext.	Residue Acetone ext.	Residue Benzol ext.	
Control-Bags 1604-1607 incl.	100	16	16	5.4	4.55	15.8	4.55	18.4	6.03	3.67	2.84	75.5
Treated-Bags 1600-1603 incl.	93	18	19.4	5.0	4.42	11.5	4.75	20.5	6.70	1.65	2.72	71.0

XI-TABLE III
ANTIOXIDANT EXPERIMENT-VULCANIZATION AND TESTING

	Lab. extraction Antioxidant Control	Lab. extraction Antioxidant Treated	Pilot Plant extract Treated & Control Samples
Added in Solution for Precure:			
Rubber, resin free gms	46.0	43.7	650
Rubber, resin free, parts	100	100	100
Resins, incl. with rubber parts	11.6	16.2	1.6
Sulfur, parts	3.90	4.07	0.60
Thiotax, parts	1.12	1.16	0.75
Zinc Stearate, parts	6.13	6.39	5.50
Flectol H	1.12	1.16	----
D.P.G.	----	----	0.30
Added on Mill:			
Zinc oxide, parts	6.13	6.39	5.50
D.P.G.	.56	----	0.50
Sulfur, parts	----	----	2.90
Thiotax, parts	----	----	0.25
Carbon (for tread), part	----	----	50.0

Sample	Stock	Cure Minutes at 260°F	Modulus at 300%	Modulus at 500%	Max. T.S. p.s.i.	Ult. Elong. %
Antioxidant Control Laby. Extraction	Gum	15	70	170	270	650
	no	30	70	270	545	675
	D.P.G	45	70	210	555	700
		60	70	340	680*	700
	Gum	15	80	280	800	650
	D.P.G.	30	135	440	950*	625
		45	105	280	280	500
Antioxidant Treated Laby. Extraction	Gum	30	<30	<30	<30	500
	no	45	<35	70	145	575
	D.P.G.	60	<35	140	445*	700
		75	70	---	70	300
Antioxidant Control Pilot Plant		10	235	---	870*	475
	Gum	20	195	---	195	<300
		40	270	---	305	325
		10	1065	2135	2335*	550
	Tread	20	1740	----	2330	400
		40	1865	----	2170	350
Antioxidant Treated Pilot Plant		10	165	590	590*	500
	Gum	20	---	---	260	<300
		40	295	---	490	350
		10	915	2070	2645*	600
	Tread	20	1565	----	2600	425
		40	1840	----	2430	350

XII-METHODS OF PURIFICATION OF RUBBER

The rubber extracted from goldenrod by benzol, after preliminary acetone extraction of resins for a practical length of time, is contaminated by a varying percentage of acetone soluble material. If the acetone soluble "resins" exceed 5-6 percent in the crude rubber, vulcanization reactions are adversely affected and the vulcanizates have poor physical properties. The percent resin in the benzol extract will vary, depending on the type of material, temperature, and time of both the acetone and benzol extraction. With pure leaf material extracted 24-36 hours with warm acetone the resin content of the rubber can be held to the minimum required, but with raw material contaminated by stems and blooms, even after long acetone extraction the amount of resin may reach 20 percent.

In addition to the acetone soluble resins, the benzol extract contains a small amount of a waxy impurity (described in Section XVII) which is precipitated with the rubber, but settles slowly from a benzol solution of rubber on standing. By pouring the benzol solution into a fairly large excess of acetone, the rubber and wax are precipitated and the supernatant acetone-benzol solution containing the resins can be decanted. The rubber is then redissolved in benzol and the wax is allowed to settle to the bottom.

Rubber can be extracted by several solvents such as benzol, naphtha, and chloroform, and is not soluble in alcohol or acetone but the resin is soluble in all of these. With the rubber dissolved in any rubber solvent, either acetone or alcohol would be effective for rubber precipitation. It was decided to use acetone for the laboratory studies, since in the pilot plant, acetone was to be used to extract the resin and the presence of alcohol would further complicate the solvent recovery operations.

At first it was believed that the presence of alkali in the acetone aided in the precipitation. Later work proved that nearly quantitative separation could be achieved with only acetone and the presence of alkali was of no value in this operation. Adding the rubber solution to the acetone or acetone to the rubber solution was found to make no difference in the extent of precipitation. However if the solutions were warm some rubber remained in solution. When the rubber is first precipitated it will form a colloidal suspension that will not settle for separation unless centrifuged. The presence of a trace of either KSCN or NH_4SCN will prevent the formation of this suspension and the rubber will coagulate and settle rapidly so that the solution of resins can be decanted. The lowest concentration of KSCN that would effectively coagulate the rubber was 0.01 g. per liter of acetone. The salt must be dissolved before the precipitation, because its addition later will not coagulate already dispersed rubber. Stirring was found to hasten precipitation and aid in the coagulation of the rubber.

The acetone used usually contained about five percent benzol, as available from pilot plant recovery. To obtain the greatest amount of

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precipitate with the smallest quantity of acetone, a highly concentrated solution of rubber in benzol is necessary. Benzol will dissolve as much as 0.4 gram per cc. of rubber, but this concentration is difficult to obtain and handle due to high viscosity. The most practical concentration is about 0.16 gram per cc. as produced in the pilot plant. Small variations from this concentration had no effect on the extent of precipitation. Two parts of acetone to one part rubber solution will separate out 98 percent of the rubber containing about 5% resin. Higher ratios of acetone to benzol will result in the precipitated rubber having a lower resin content. Since some resin and acetone solution is occluded by the precipitate, a washing of the precipitate or reprecipitation with fresh acetone will also lower the resin content to as little as 0.3%.

Fractionation. The rubber is incompletely precipitated if the ratio of acetone to benzol is low or if the solutions are warm. A three to one ratio of acetone to benzol at 50°C. precipitated only 77.5 percent of the rubber present, therefore all precipitations were at room temperature.

Acetone containing a trace of KSCN at 25°C. was poured slowly into a benzol solution containing five grams of rubber per 100 cc. The quantity and quality of the rubber precipitated at various ratios of acetone to benzol were determined, as recorded in Table I, and plotted in Fig. 1.

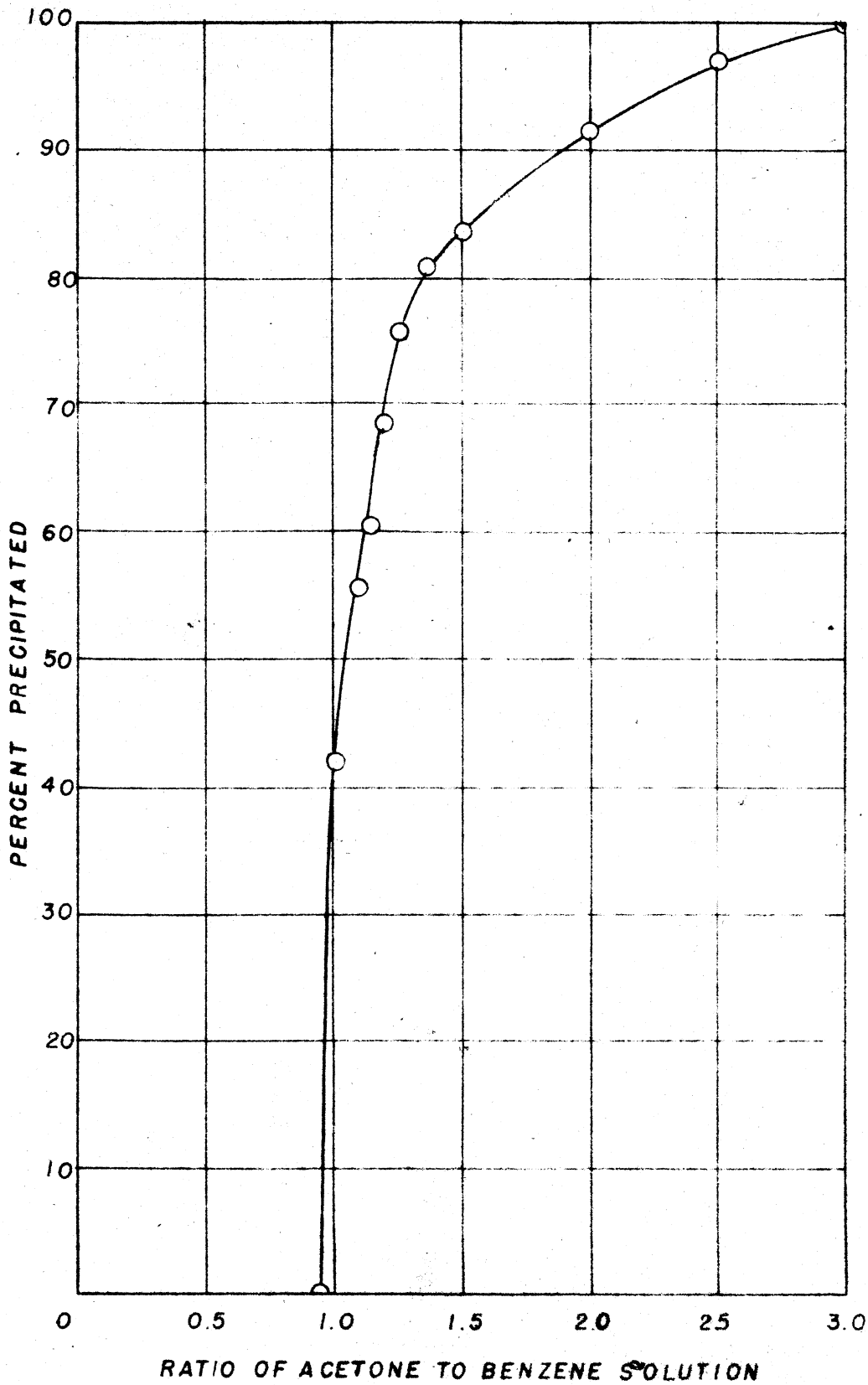
XII-TABLE I
PERCENT RUBBER PRECIPITATED BY DIFFERENT RATIOS OF ACETONE
BENZOL SOLUTION 5 G. RUBBER PER 100 CC.

RATIO ACETONE/RUBBER SOLUTION	% INCREMENT	TOTAL % PPT.
0.95	0.0	0.0
1.00	42.4	42.4
1.10	13.3	55.7
1.15	4.9	60.6
1.20	7.9	68.5
1.25	7.2	75.7
1.35	5.4	81.1
1.50	2.3	83.4
2.00	8.0	91.4
2.50	5.6	97.0
3.00	3.0	100.0

Apparently no rubber precipitated until the ratio of acetone to benzol was 0.95. The first rubber precipitated (42.5%) was in lumps and curds. On drying this material was not sticky and could be handled with ease. It had good tack but was slightly softer than smoked sheet. The subsequent fractions were unlike the first in that they were progressively more fluid at room temperature, and contained no lumps. They were very sticky, and on warming they were liquid. The first sample precipitated was redissolved and refractionated several times. Each time the first material to precipitate was less sticky and more closely resembled Hevea.

XII – FIGURE I

ACETONE PRECIPITATION OF RUBBER



The effect of fractionation of the rubber on the tensile strength is shown in Table II.

XII-TABLE II

	Sample	texture	% discarded	Resin %	Standard Formula Max. Strength	Standard Formula % Elongation	D.P.G. Formula Max. Strength	D.P.G. Formula % Elongation
A	Original extract	dark & sticky	0	4.3	1210	700	2160	650
B	Precipitated	light & sticky	5	1.4-2.2	1300	700	2170	525
C	fractionated	light & dry	60	0.3	2750	750	3720	650

Concentrated rubber solutions will precipitate on the addition of smaller quantities of acetone than will the more dilute solutions. The precipitation curve for a more concentrated solution would be of the same general shape as Fig. 1, except that it would be shifted to the left. The rubber in a sample of the pilot plant extract containing 13.8% total solids of which 5.8% was resins, was found to be 93 percent precipitated with an equal volume of acetone and completely with two volumes of acetone to one of the rubber solution. At this rubber solution concentration 0.65 volumes of acetone to one of rubber solution precipitated 75% of the available rubber. Several large scale precipitations were made at this ratio to obtain a better grade rubber in the pilot plant. This fractionated rubber vulcanized and tested better than the untreated extract, but a considerable loss of rubber was involved which the improvement in quality did not justify.

Special precipitation. Numerous special lots of crude rubber were precipitated in the laboratory so that test data and evaluations of quality would not be dependent upon the effect of resinous impurities in the sample. A three to one ratio of acetone to rubber solution was used in all cases so that little of the rubber would be lost. Data on the strengths of the rubber treated will be found in the Sections of this report to which the special samples pertain. The resin content of these samples was reduced to six percent or less.

RUBBER FROM GOLDENROD MATERIAL BY A SINGLE EXTRACTION FOLLOWED BY PURIFICATION

A benzol extraction of the leaves without preliminary acetone extraction yields a product containing about two thirds resin and one third rubber. This rubber was precipitated readily with acetone even in the presence of

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the large concentration of resins. Some tests were made by extracting the leaves with water followed by benzol or naphtha (Skellysolve B). The rubber was then separated by acetone precipitation. The water extracted some of the acetone soluble material and the rubber solutions in this case contained 45 percent rubber and 55 percent resin. It was nevertheless possible to obtain rubber of low resin content from these very impure extracts by acetone precipitation.

A simple and convenient laboratory method for obtaining rubber from goldenrod material consists of a single extraction with petroleum ether followed by precipitation of the rubber from the concentrated extract with acetone containing a little potassium thiocyanate to aid coagulation. This method eliminates the preliminary extraction with acetone and substitutes an inexpensive solvent for benzol. A modification of the process which improves the quality of the rubber is the saponification of the concentrated extract with alcoholic sodium or potassium hydroxide prior to precipitation of the rubber with acetone.

The green color of the rubber may be removed by bleaching with sulfur dioxide. Another modification of the method which adds to the yield by increasing extraction efficiently is to dry the goldenrod material completely and extract under anhydrous conditions.

EXPERIMENTAL

Extraction with Petroleum Ether Followed by Precipitation with Acetone. In a typical experiment, 800 g. of goldenrod leaves ground to 40 mesh were extracted in thimbles in four extra large Soxhlets with 3 l. Skellysolve B for 9½ hours. The extract was concentrated to about 500 ml. by distillation. One liter of 1 percent KSCN in acetone was added with rapid stirring, followed by 500 ml. of acetone. The coagulated rubber was separated after 2 hours by decantation, washed with two 200 ml. portions of acetone, dried in vacuo for 2½ hours at 65°C. yield 35.5 g. The rubber content of the starting material by analysis with the acetone-benzol method was 44 g. Carbon content of the product was 86.2 percent, hydrogen content 11.8. Theory for isoprene is: carbon 88.2, hydrogen 11.8. The product yielded an average quality vulcanizate of tensile strength 940 p.s.i. and elongation 500 percent.

In another experiment with 800 g. of the same lot of goldenrod leaves, Skellysolve B was used. In general the procedure was the same as just described, but the extract was concentrated to 400 ml., about 200 ml. of 1 percent KSCN in acetone added and the rubber precipitated with 500 ml. acetone. The rubber came down in about 5 minutes. It was separated by decantation and washed twice with 400 ml. portions of acetone.

The solvent was removed from the rubber in vacuo at 45°C. The product weighed 35.5 g. It yielded a vulcanizate by the standard formula which had a tensile strength of 1400 p.s.i. and an elongation of 815 percent.

Extraction with Petroleum Ether Followed by Saponification. Bleaching with Sulfur Dioxide. Since preliminary experiments had shown that the quality of the crude rubber was improved by saponification with alcoholic

potassium hydroxide, saponification of the concentrated extract prior to acetone precipitation was investigated. Sulfur dioxide bleaching was also tried, since this yielded a product resembling pale crepe in color. A control experiment in which the rubber was precipitated without chemical treatment was also made. In each experiment, 800 g. of the same goldenrod leaves were extracted for 14 hours with 2600 ml. Skellysolve B.

These leaves analyzed 7.7 percent rubber on the as received basis and 8.4 percent on the dry basis when finely-ground samples were analyzed by the acetone-benzol procedure.

Control Experiment. The Skellysolve B extract was concentrated to approximately 500 ml. The rubber was thrown down by addition of 250 ml. of 1 percent KSCN in acetone and 1500 ml. of acetone. The rubber was washed three times with acetone and freed from solvent by heating on the steam bath for about 15 minutes and then over-night at 65° in vacuo. It weighed 53.5 g. and had a "resin" content of 6.4 percent. The product thus accounted for 81 percent of the rubber in the original material. About 9 g. of rubber were left in the residual goldenrod material. The vulcanizate by the standard formula had a tensile strength of 1210 p.s.i. and an elongation of 750 percent. When diphenyl guanidine was used in the vulcanization the tensile strength was 2300 p.s.i. The vulcanizate was green.

Potassium hydroxide experiment: The Skellysolve B extract was concentrated to about 800 ml. and 200 ml. of alcoholic potassium hydroxide, 40 g. per liter, were added. The solution was refluxed for one hour on the steam bath and allowed to stand overnight. When examined, some solids were observed in suspension. The mixture was concentrated to 500 ml. and the rubber precipitated by the addition of 250 ml. of 1 percent KSCN in acetone and 1500 ml. of acetone. The rubber was washed by kneading three times with acetone, once with tap water and again with acetone. Solvents were removed by heating in vacuo at 84°C. for 4 hours and at 65° for 2 hours. The product weighed 50.0 g. It had a "resin" content of 4.2 percent. The vulcanizate was brown.

Tensile strength by the standard formula was 2325 p.s.i., elongation 725 percent.

Sulfur Dioxide Experiment. The first part of the procedure was the same as in the control experiment described above. The rubber after precipitation with acetone was dissolved in 500 ml. of benzol, 200 ml. of alcoholic potassium hydroxide added and the mixture refluxed for two hours on the steam bath. After standing overnight the alkaline-tested rubber mixture was heated on the steam bath, 6 g. calcium oxide added, and sulfur dioxide bubbled through for 2 hours. The mixture then stood in the dark for 2 days.

The rubber was thrown down by addition of 250 ml. of 1 percent KSCN in acetone and 1500 ml. of acetone. It was washed with acetone, taken up in 400 ml. of hot benzol and insoluble solids removed by centrifuging. After concentrating to 360 ml. the rubber was precipitated by the addition of

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200 ml. of 1 percent KSCN in acetone and 340 ml. of acetone. The rubber was washed with acetone and dried in vacuo at 85°C. for 16 hours. The product weighed 38.6 g. and contained 1 percent "resins". It resembled pale crepe in color, but was sticky. Previous small scale experiments had yielded less sticky products. It yielded a light brown vulcanizate with dark brown spots when vulcanized by the standard formula. Tensile strength was 1025 p.s.i. and elongation was 750 percent. It is likely that a simpler and less drastic procedure for bleaching with sulfur dioxide could be developed.

Saponification with sodium hydroxide or calcium hydroxide: In order to see if some other base could be used instead of potassium hydroxide, a series of experiments were made. About 7577 g. of goldenrod leaves containing 5.2% rubber were ground in the Wiley mill using a 1/32" screen. The material was extracted with Skelly B for 3 hours. The extract contained 685 g. of solids of which 365 g. were rubber. The concentrated extract was divided into 5 parts and treated as shown in the following:

Exp. No.	Treatment
1.	Refluxed 2 hours. 10 ml. 50% aqueous NaOH
2.	Refluxed 2 hours. 20 g. solid $Ca(OH)_2$
3.	No chemical treatment
4.	Refluxed 2 hours. 10 ml. 50% aqueous NaOH and then emulsified 200 ml. H_2O
5.	Refluxed 2-1/2 hours. 200 ml. alcohol + 7 g. NaOH

The above portions were then precipitated with acetone plus KSCN. In No. 5, it was necessary to wash the precipitate with water in order to remove soluble sodium compounds and allow the rubber to agglomerate. The yields and vulcanization results are given in the following:

Exp. No.	% Yield based on orig. G. R. Leaves		Tensile on vulc. crude	
	Crude rubber	"pure" rubber	Standard	D.P.G.
1.	5.6	3.0	1670*	2100*
2.	4.3	3.9	1560	2190
3.	3.9	3.7	1300	2240
4.	4.6	4.4	540	1110
5.	3.8	3.7	1980	2440

(*) The rubber from No. 1 had marked permanent set.

It will be noted that the best results were obtained with procedure No. 5 in which Skelly B extract was saponified with alcoholic NaOH, precipitated with acetone plus KSCN and the precipitate washed with water.

Procedure No. 5 was repeated on the same leaves ground on the Ball and Jewell mill with a 1/16" screen. The yield was 2.1 percent crude rubber or 1.9 percent resin free rubber. This low yield is in line with previous experience with coarsely ground goldenrod. The tensile was 1940 p.s.i. by the standard formula and 2110 with D.P.G. Incidentally, the residue from this last extraction was reground through a 1/32" screen, extracted, and

saponified in the same manner as the first extract. The product weighed 28.9 g., had a "resin" content of 3 percent, and yielded a vulcanizate by the standard formula that had a tensile strength of 2530 p.s.i. The tensile strength values from this series of experiments may be compared with a standard formula of 1000 p.s.i. from rubber obtained by the acetone-benzol method applied to the same vulcanizate goldenrod and with 1350 p.s.i. (standard) and 1860 p.s.i. (D.P.G.) obtained with rubber extracted by the acetone-benzol method from ensiled goldenrod from the same lot.

Extraction of Moisture-Free Goldenrod Material with Petroleum Ether. Since it was thought that the difficulty with which the last portions of rubber was extracted might be due to a film of moisture which protected the rubber from water immiscible solvents such as petroleum ether or benzol, extraction of moisture-free goldenrod leaf material was tried. The solvent used was Skellysolve B which had been distilled over calcium oxide. The goldenrod leaves had been ground through a Wiley mill using a 1/16" screen. Weighed samples were dried either 17 hours in vacuo at 75°C. or 5 hours in a forced draft oven at 105°C. One hour before the end of the drying period they were quickly introduced into paper thimbles, weighed to see that the loss of weight was that calculated from the analytical moisture figures, and replaced in the drying oven for an additional hour. Undried samples served as controls. The samples were extracted for three hours with Skellysolve B in Soxhlet extractors. The extractors used for the dried samples were provided with calcium chloride guard tubes. Care was taken that the rate of siphoning was the same in both the dried and undried sample. The solvent was removed from the extracts, the weight determined, and "resins" estimated by 6 hour acetone extraction of samples smeared on filter paper. The yield of "resin-free" rubber was calculated and in all cases found to be much higher in the dry extractions. This was particularly striking in the experiments with unground leaves.

The pertinent details of this series of experiments are summarized in Table III. It will be noted that the yield of "resin-free" rubber from the dry extractions was larger than expected from the amount of rubber estimated from the method of analysis then in use. This was especially true if the amounts of rubber found in the residues were taken into consideration. The method of analysis then in use was a 6 hour acetone extraction followed by a 6 hour benzol extraction applied to 5 g. samples. Steps were taken to improve this method by removing all moisture from the samples prior to the benzol extraction, by lengthening the extraction time and by regrinding the sample during the benzol extraction. This will be dealt with in another part of the report.

The quality of the rubber obtained by acetone - KSCN throw down from the last pair of extractions listed in Table A, was investigated. The results are as follows:

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Quality of Rubber by Moisture-Free Extraction

Method of extraction	Titr. value*	Viscosity* C.P. at 25°C.	Vulcanization by standard formula p.s.i.	Vulcanization by standard formula Elong. percent	Vulcanization with D.P.G. p.s.i.	Vulcanization with D.P.G. Elong. percent
Air-dried moisture 9.1 percent	4.45	0.677	1330	700	1885	635
Moisture-free	5.35	0.665	1050	710	1940	585

* By Physical Chemistry section.

Although there is some evidence that the rubber was affected slightly, it should be remembered that the drying conditions, 105° for 5 hours, were deliberately made rather severe. Since it will be shown that the favorable effect on extraction is due entirely to the removal of moisture, less severe drying conditions would be just as effective.

In order to determine whether the increased efficiency is due to heating, moisture-removal, or a combination of heating and moisture-removal, three methods of drying were employed:

(1) Moisture-removed at room temperature, over a desiccant, in vacuum; (2) low temperature heating in a vacuum oven; (3) high temperature heating in a forced draft oven. Further, in order to determine whether the drying treatment produced a permanent effect on the extractibility of rubber, some of the above treated samples were exposed and allowed to acquire the equilibrium moisture of the laboratory conditions.

The preliminary work had been conducted using Skellysolve B as a solvent. Therefore, one complete set as described above was extracted, in Smalley extractors protected with calcium chloride tubes. Anhydrous Skellysolve B was used as a solvent in this set. In another complete set, the samples were first extracted in customary fashion with acetone and then freed from acetone. They were then given the various drying procedures outlined above and finally extracted as above, but with anhydrous benzol as the solvent. Standard 5 g. analytical samples ground in a small Wiley mill using a 20 mesh screen were used. All extractions were for 6 hours.

The results given in Table IV show that the increased extraction efficiency when goldenrod material is dehydrated prior to extraction of rubber is due entirely to removal of moisture and not to any heating effect. One method of drying has no marked advantage provided rather complete dehydration is accomplished. The drying does not produce any permanent effect which remains after the samples are allowed to take up moisture from the air. To obtain increased extraction efficiency, the dried samples must not be allowed to regain any appreciable moisture after dehydration.

XII-TABLE III MOISTURE-FREE EXTRACTIONS OF GOLDENROD LEAVES

Lot number of Leaves	Rubber 1/ content Percent	Weight of material used Grams	Condition of material when extracted	Moisture content when extracted Percent	Wt. of crude P.E. extract Grams	"Resin" content of extract Percent	Yield of "resin-free" rubber Percent	Rubber found in residue Percent
AE 454	4.6 2/	180	ground	7.9	13.1	52	3.5	2.6 6/
				0.0 3/	21.0	37	7.1	1.6 6/
				7.9	13.9	51	3.8	1.8
				0.0 4/	20.3	41	6.7	1.2
AH 636	6.3 7/	80	unground	9.3	3.3	50	2.1	5.3
				0.0 4/	8.4	40	6.3	2.2
AH 878	7.6	1080	ground	9.1	59.4 5/	3.2	5.3	2.1
		760		0.0 4/	54.1 5/	1.3	7.0	1.3

1/ By 6 hr. acetone, 6 hr. benzol extraction.

2/ The rubber content found later on this sample by exhaustive extraction and regrinding of the residue averaged 7.2 percent. Incidentally, the rubber extracted from the reground analytical residues was 78 to 92 percent rubber by bromination.

3/ Dried in vacuo at 75°C. for 17 hours.

4/ Dried in forced draft oven at 105°C. for 5 hours.

5/ Rubber after acetone-KSCN throw down.

6/ By exhaustive extractions of the dried residues with dry benzol.

7/ 7.1 percent rubber was found later by the dry-regrind method.

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XII-TABLE IV EFFECT OF MOISTURE ON THE EXTRACTION OF GOLDENROD MATERIAL

Drying procedure	Treatment after drying and prior to extraction	Percent extracted: Skellysolve B extraction with no acetone extraction	Percent extracted: Benzol extraction of samples extracted with acetone prior to drying
Dried in vacuo at room temperature over sulfuric acid for 113 hours	Kept dry in vacuum desiccator over $CaCl_2$	12.4	6.0
	Allowed to stand in open for 2 days	10.3	4.6
Dried in vacuo at 55°C. for 18 hours	Kept dry in vacuum desiccator over $CaCl_2$	12.5	5.9
	Allowed to stand in open for 2 days	10.5	4.7
Dried at 105°C. in forced draft oven for 4 hours	Kept dry in vacuum desiccator over $CaCl_2$	12.4	5.5
	Allowed to stand in open for 2 days	10.4	4.5
Control, not dried		10.2	4.8

Rapid Method to Determine Total Solids and Rubber in Benzol Solution. In order to precompound the goldenrod rubber extracted in the pilot plant, it was necessary to determine by as rapid a method as possible the total solid content of the benzol extract and the percent of the solid that is rubber. This information was also required for carrying out the purification step of the process in the laboratory and pilot plant. The concentrated benzol extract (approximately 10%) was circulated one hour through the pump for uniform sampling. At the end of that time, while circulating, a 200 ml. sample was taken for the determinations after rinsing the sample line. The storage tank was then blocked off from the system. The two determinations are then made simultaneously.

Total Solids: Stir the sample well and measure out 10.0 ml. with a pipette or volumetric flask callibrated to contain. Rinse the container with benzol until all rubber is removed into a petri dish or cover. The benzol is evaporated over a steam bath in the hood and the sample is dried one hour at 90°C. and house vacuum. After cooling, the sample is weighed to 0.01 gram.

Percent Rubber: Stir the sample well and measure out 10.0 ml. with a pipette or volumetric flask calibrated to contain. This is added dropwise to at least 80 ml. and not more than 100 ml. of acetone containing 0.1% KSCN in a centrifuge tube. The pipette is rinsed with benzol until clean, using as small a quantity of benzol as possible. This is centrifuged five minutes at 2000 r.p.m. Decant the acetone layer and wash the rubber with acetone until it fails to color the acetone. The rubber is then quantitatively transferred to a weighed petri dish, using benzol to wash the centrifuge tube. Evaporate the benzol on a steam bath in a hood. Dry the sample at 90°C. with house vacuum for one hour. Cool the sample and weigh to 0.01 gram.

The accuracy of this method was ample as a control for pilot plant operation, and its rapidity (complete report within 2 hrs. after sampling) permitted a continual check on operating conditions. The method was exactly reproducible to the degree of accuracy indicated (±2%) which was sufficient for calculation of pilot plant compounding formulas.

Attempts to Purify and Process Goldenrod Rubber by Emulsification. At the time that this work was conducted it was urgently desired to reduce the stickiness property of the raw goldenrod rubber so that it could be readily handled. The formation of an artificial latex by emulsification and subsequent coagulation of the rubber with acids was considered. Studies were made using the following general procedure:

1. Benzol rubber solution and water solution of chemicals emulsified in blendor (high speed agitator type).

2. Mixture blended for 4 to 30 minutes.

3. Emulsion centrifuged to determine its stability.

(over)

4. Benzol distilled from emulsion under vacuum or at atmospheric pressure.

5. Rubber coagulated by addition of acid.

During the course of experimentation the effects of the following variables were studied; (1) type of emulsifying agents used, (2) order of addition of rubber solution, emulsifying agents, and other chemicals, (3) degree and time of blending or mixing, and (4) the acids and concentrations used for coagulation.

Either one or a combination of stearates and oleates of sodium, potassium, and ammonium served as the emulsifying agents which were prepared directly in the blender by addition of the oleic or stearic acid and one of the hydroxides. In several experiments, one or more of the following chemicals were added to the emulsion mixture; casein, zinc oxide, agerite, bentonite, and sulfur chloride, the last as a vulcanizing agent. Stirrers with speeds of 1500 and 5800 R.P.M. and blenders with a speed of 10,000 R.P.M. were used with mixing periods varying from 4 to 30 minutes. To coagulate the rubber from the emulsions, various concentrations of acetic, hydrochloric, and sulfuric acids were tried.

Several fairly stable emulsions were prepared from the above combinations; however, the rubber coagulated by the addition of acids was consistently sticky to some degree and unsuitable for handling. The best results were obtained with oleic acid and potassium hydroxide as the emulsifying agent, although it would have been preferred to use stearic acid because of its use as one of the compounding ingredients for final vulcanization. Dilute sulfuric acid gave the best results as a coagulating agent. From the standpoint of stability of emulsion, non-sticky properties and appearance of the rubber, a typical procedure and formula was as follows;

Ingredients added in the following order to a Waring blender rotating at 10,000 R.P.M.

(a) Benzol rubber solution - 40 cc. - concentration 0.125 g/cc.

(b) Oleic acid - 5.0% based on weight of rubber.

(c) Agerite - 0.1%.

(d) KOH - 50 cc. of 0.05 N. (added slowly).

(e) Water - 100 cc. added after five minutes of blending.

Blending was continued for a total of 15 minutes. The benzol was distilled under atmospheric pressure, with less difficulty due to foaming than was experienced in using vacuum. Rubber in the emulsion was coagulated with 1.8 cc. of dilute sulfuric acid (0.6 Normal), the rubber beginning to separate at pH 5.0. This product was sticky.

Three vulcanizates were made of rubber obtained by coagulating emulsions prepared with KOH and stearic acid, and using a 1500 R.P.M. stirrer and 50 grams of rubber in solution. The following tensile strengths were obtained;

Cure @ 260°F. Mins.	Tensile Strength p.s.i.	Ultimate Elongation %	Remarks
15	2295	600	No D.P.G.
10	3040	625	D.P.G. Added
30	2665	525	Tread Stock

The first two vulcanizates were prepared from a different batch than the last vulcanizate. The tensiles for the first two are higher than the average for untreated goldenrod rubber, whereas the tensile for the tread stock is comparable to that of untreated goldenrod rubber in similar stocks.

XIII PHYSICAL CHEMICAL INVESTIGATIONS

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XIII PHYSICAL CHEMICAL INVESTIGATIONS

A - EXTRACTION WITH SOLVENTS

Extraction of Rubber from Air-dried Goldenrod Leaves with Benzene Direct (omitting acetone extraction). The possibility of direct benzene extraction of dry goldenrod leaves, omitting acetone extraction, has been investigated. A report on a microscopic examination indicated that after five hours of hot extraction, almost all of the rubber had been extracted from whole leaves though a considerable amount of the resins still remained in the leaves.

Two methods of purifying the benzene extract were used. In the first, it was passed through a column of activated alumina. This left in the rubber a considerable percentage of a wax-like material which seemed to cause the vulcanizate to have almost no tensile strength. This step was therefore followed by acetone precipitation resulting in a product giving a fairly good vulcanizate. The second method used for purification of the benzene extract was acetone precipitation alone. This gave a a better vulcanizate. The detailed procedure of typical experiments will be given.

Method 1. 395 grams of ground air-dried goldenrod leaves were hot extracted for 24 hours by suspending in an extraction thimble directly above 1500 cc of boiling benzene containing antioxidants so that the reflux percolated through the sample. The extract, dark brownish green in color, contained 74 grams of total solids. It was passed through a column of activated alumina yielding a transparent orange yellow solution which was evaporated to dryness. A small portion of this product gave a vulcanizate of too low a tensile strength to measure. The main portion was therefore redissolved in benzene, precipitated with acetone, washed with water and dried.

The acetone-benzene mother liquor obtained on acetone precipitation was evaporated to dryness. The residue was taken up with ethyl alcohol and saponified with 5% KOH in ethyl alcohol. The greater part of the alcohol was distilled off. The residue taken up with water was extracted with several fresh solutions of diethyl ether. (1) The non-saponifiable fraction, 2.6 gm., orange in color, seemed to be crystallizable from acetone. (2). The saponifiable fraction was acidified in the HCl to precipitate the free acids. The solution was extracted with ether and the ether washed, dried, and evaporated to dryness. The residue, 1.16 gm., seemed to be crystalline in character.

Method 2. 370 grams were extracted for 6 hours over 3 liters of benzene as in method 1. The benzene extract was concentrated. The rubber was precipitated by acetone, washed and dried (46 grams). Its precipitation value was 4.30 cc and its resin content 19%.

The report on the vulcanizate was as follows:

Vulc. No.	Time of Cure	Tensile Strength	Ult. Elong.
	min.	p.s.i.	%
224C	30	1265	800
224A	45	1465	790
224B	60	1395	770

The following tabulation shows the rate of the benzene extraction of a 175 gram sample of ground dried goldenrod leaves when carried out by the same method as described above.

Total Hours	Total Grams Extracted	% Extracted
3	26.25	15.00
6	28.41	16.27
24	31.02	17.76

Rate of Extraction of Rubber by Different Solvents. The accompanying figure, XIII-A-1, shows the results obtained by hot extraction with benzene, toluene and xylene, starting with ground dried goldenrod leaves previously acetone-extracted in the pilot plant. 18-gram batches were hot-extracted by suspending each in an extraction thimble directly above the boiling solvent so that the reflux ran back through the sample. Fresh solvent was introduced at intervals and aliquots of the extracted solutions were evaporated to dryness in a nitrogen atmosphere to follow the rate of extraction. The residues after "exhaustive" extraction with benzene and toluene were further extracted with xylene as shown.

In the case of all three solvents, some 75% of the material extractable by the solvent in question was extracted within the first hour, about 85% within the first three hours. Apparently xylene is much more efficient than toluene or benzene. It extracts almost 15% more, i.e., 6.2% of total solids (rubber) instead of about 5.3% on the basis of the dried acetone-extracted leaves.

B - PURIFICATION

1. Adsorbents

The benzene extract of goldenrod rubber obtained in the pilot plant contained, in addition to the rubber, considerable amounts of "resins" including fats, waxes, pigments, traces of metals, etc. Preliminary results obtained with several activated adsorbents established the use of adsorbents as a possible method for the partial "purification" of these benzene extracts.

Experiments were carried out to establish the following:

(1) Evaluation of adsorbents in goldenrod rubber purification. This involved (a) estimations of the resin- and pigment-removing properties of the various adsorbents and (b) the effect of the adsorbent on the quality and yield of the rubber so obtained.

(2) The use of chromatographic technique (a) in the separation and analysis of pigments in the acetone extracts of goldenrod leaves and (b) in the removal of pigments from the pilot-plant benzene extracts of goldenrod rubber.

(3) The removal of metallic constituents (Cu, Mn and Fe) from benzene extracts of goldenrod leaves by adsorbents.

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(a) Removal of Resins.

Evaluation of Adsorbents. The following table summarizes the preliminary results of a systematic attempt to find the most suitable adsorbents for the separation of "resins" from benzene extracts of goldenrod leaves. Pilot plant benzene extract from goldenrod leaves was used for this set of experiments. It was first diluted from a concentration of 13.37 gm/100 ml. (16% by wt.), as received, to a concentration of 1.064 gm/100 ml. (approx. 1%).

One hundred ml. samples of this stock solution were added to 250 ml. centrifuge bottles containing 5.0 grams of the different adsorbents listed.

The silica gel was about 8 mesh to begin with. These granules were ground in a ball mill then screened to a 70-100 mesh size. The powdered material was then dried in an oven at 150° C. for 2 hours and allowed to cool to room temperature in a vacuum desiccator over P_2O_5.

The centrifuge bottles were shaken for 1/2 hr. in a Burrell shaker and allowed to stand over night to establish equilibrium. The bottles were centrifuged for 1/2 hour at about 1000 r.p.m. in an International centrifuge Size 1, Type SB. The supernatant materials were decanted into a funnel through folded filter paper. The filtrates were collected in a 100 ml. graduated cylinder and the volume and color noted. Ten ml. samples of the filtrates were taken for total solids estimations. The remainder of the filtrates were transferred to weighed flasks for evaporation and precipitation of the rubber. These solutions are called "Supernatant A".

By experimentation on the stock solution it was decided that the best coagulum could be obtained when the rubber was precipitated from a syrup with absolute ethyl alcohol. The "Supernatant A" solutions were evaporated to a syrup and the rubber precipitated with 100 ml. of absolute alcohol. The coagulum was allowed to stand at room temperature for 20 hours.

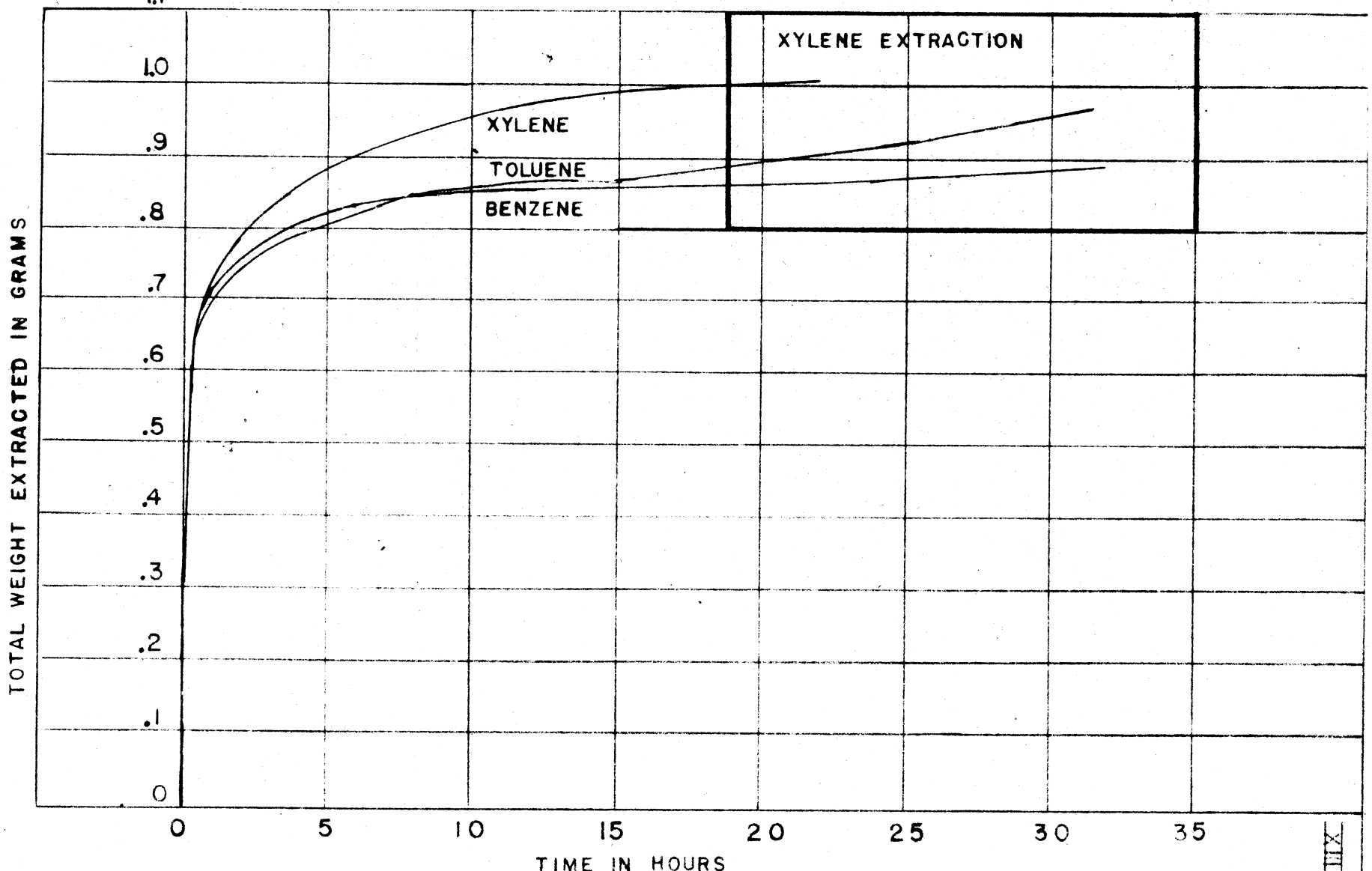
The supernatant liquor from the above precipitation was decanted into weighed evaporating dishes. The "rubber" was washed twice with small amounts of alcohol and acetone. The washings were added to the main supernatant and the combination evaporated to dryness under a stream of CO_2. This solution is called "Supernatant B".

The rubber precipitates were dried in an oven at 100° C. and placed in a desiccator, cooled to room temperature and weighed.

The data reported in the following table show (1) holdup by the various adsorbents, (2) the amount of rubber obtained using each adsorbent, (3) the amount of "resins" not adsorbed by the amount of adsorbent used, and (4) the efficiency of color adsorption by various adsorbents.

EXTRACTION OF GOLDENROD LEAVES

XIII A FIG. I



XIII A

TABLE I

EFFECTIVENESS OF ADSORBENTS IN OBTAINING RUBBER FROM BENZENE EXTRACTS OF GOLDENROD

Starting with 100 cc. of a benzene solution containing 1.064 gm. of pilot plant rubber.

Adsorbent	1 Holdup cc.	2 Rubber Obtained mg.	3 Resins not Adsorbed mg.	4 Color of Solution
None	6.5	881	15.4	Dark Green
"	7.0	876	17.4	"
Activated Charcoal Merck	28.0	557	6.0	--
	24.0	598	4.0	--
Wood Charcoal Merck	17.0	769	---*	--
	16.5	780	13.3	--
Animal Charcoal Sargent	12.0	792	8.9	Pale Yellow
	12.0	795	9.5	"
Black G-ELF Sargent	23.2	660	8.0	Water White
	23.2	661	9.5	"
Nuchar #2	28.0	600	7.4	--
	28.0	599	6.7	--
Al_2O_3 Merck	10.5	821	9.9	Pale Green
	11.4	810	10.2	"
Al_2O_3 Baker	10.2	810	11.2	Yellow Green
	10.2	810	13.0	"
MgO Baker's Heavy	14.0	753	15.2	Yellow
	13.0	745	12.2	"
MgO Baker's Light	39.2	506	6.6	Water White+
	40.0	507	6.0	"
Fuller's Earth Sargent	9.0	845	11.4	Green
	8.7	846	11.3	"
B.C. Clay	10.5	825	7.0	Pale Yellow
	11.0	811	7.0	"
Silica gel Sargent	12.5	740	3.9*	Green
	14.0*	749	5.0	"
Bentonite	11.2	814	5.8	Pale Green
	12.0	803	5.2	"

over

TABLE I-con't.

Adsorbent	1 Holdup cc.	2 Rubber Obtained mg.	3 Resins not Adsorbed mg.	4 Color of Solution
Nuchar	31.0	566	4.8	--
Eastman	32.5	530	6.0	--
Darco	25.2	478	25.0	--
Eastman	23.2	482	28.4	--
Norit	38.0	475	2.9	--
Eastman	19.0*	438	7.5	--

* Slight loss of sample

Four adsorbents were chosen from the original 17 as having properties that might be useful in goldenrod rubber processing. The adsorbents chosen were activated carbon - Merck, Al_2O_3 - Merck, Nuchar #2, and Black G-ELF - Sargent Company.

Each adsorbent was used to clean up approximately 100 grams of goldenrod rubber, Pilot Plant Run #3, by the slurry method. The samples of rubber obtained were submitted to Engineering and Development for evaporation and vulcanization using the solution method of compounding.

The results reported by the Engineering and Development Division are listed below:

(1) Using Nuchar #2

	Vulc. No.	Time of Cure	Tensile Str. p.s.i.	Elong. %
	210-A	60'	Very much undervulcanized	
	210-B	120'	465	700
	210-C	150'	270	600
	210-D	180'	570	725
	211-C	30'	Undervulcanized	
Acetone	211-A	60'	930	665
pptd.	211-B	90'	250	365

(2) Using Al_2O_3 - Merck Ignited

	Vulc. No.	Time of Cure	Tensile Str. p.s.i.	Elong. %	
	208-A	60'	690	850	Under
	208-B	80'	1385	750	vulc.
	208-C	100'	1125	675	
	208-D	120'	1235	665	
	209-A	60'	660	800	Under vulc.
Acetone pptd.	209-B	100'	1435	750	

(3) Using Activated Carbon - Merck

	Vulc. No.	Time of Cure	Tensile Str. p.s.i.	Elong. %
	180-B	80'	1120	800
	180-C	105'	1570	800
	180-D	120'	1270	775
	(188-A	80'	1660	850
Acetone	(188-B	100'	1800	800
pptd.	(188-C	120'	1830	725

(4) Using Black G-ELF - (Sargent)

	Vulc. No.	Time of Cure	Tensile Str. p.s.i.	Elong. %
	181-A	80'	1050	750
	181-B	60'	1110	750
	181-C	40'	1570	800
	181-D	35'	1330	800
	(189-A	40'	1920	775
Acetone	(189-B	30'	1880	850
pptd.	(189-C	50'	2115	775

It is evident from these values that the various adsorbents had different effects on goldenrod rubber. This might be caused by the removal of beneficial or of undesirable substances or by degradation of the rubber itself.

(b) Removal of Pigments.

Separation of Pigments from Acetone Extracts of Goldenrod Leaves. A pilot plant acetone extract was evaporated to dryness and the residue was extracted with petroleum ether. The petroleum ether extract was passed through an adsorption column of activated alumina and a chromatogram developed. The chromatogram exhibited evidence for the existence of 11 different pigments. The most prominent pigments were the chlorophylls and the carotenes. These zones were isolated from the chromatogram, the pigments were eluted and the eluates submitted to the Physics Section for spectroscopic study. They reported the definite identification of two of the pigments as chlorophyll and carotene.

Effect of Various Pretreatments of Goldenrod Leaves on the Chlorophyll. The chromatographic technique was employed in ascertaining the destructability of chlorophyll by various chemical reagents and treatments. Acetone extracts were made by the Engineering and Development Division of goldenrod leaves which had been predigested with 2% NaOH, 3% H_2SO_4, and with 2% NaOH followed by 3% H_2SO_4. They were evaporated to dryness and extracted with petroleum ether. The extracts were passed through adsorption columns of MgO and chromatograms were developed. Zones were eluted and submitted to the Physics Section for spectrographic analysis. Chlorophyll was found in the cases where the leaves had been digested (a) for 3 hours with 3% H_2SO_4, and (b) for 1 hour with 2% NaOH and 1/2 hour with 3% H_2SO_4. No chlorophyll was present in the case of 3 hour predigestion with 2% NaOH.

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Presence of Chlorophyll in Pilot Plant Goldenrod Rubber. A sample of pilot plant rubber was dissolved in benzene. The solution was passed through a column of activated alumina and a chromatogram was developed. The topmost zone was isolated and the pigment eluted from the adsorbent with acetone. The Physics Section reported that this solution gave a typical chlorophyll absorption spectrum curve.

Removal of Chlorophyll from Benzene Extracts of Goldenrod Rubber by Adsorbents. In the systematic study of the effectiveness of various adsorbents it was shown that all of the chlorophyll could be removed by the slurry method on benzene solutions by various activated carbons as well as MgO powder. Water white solutions were obtained showing that the carotene was also removed. These adsorbents are more effective on the weight for weight basis than aluminum oxide. The latter if used in large enough amounts will also remove all the chlorophyll completely but not the carotene from benzene solutions. For example, in the case of a solution obtained by benzene-direct extraction of dried goldenrod leaves a chlorophyll-free solution was obtained by passing the solution successively through four Al_2O_3 columns. The spectrogram of this solution was reported by the Physics Section to contain only carotene.

(c) Removal of Copper, Manganese, and Iron from Goldenrod Rubber.

During a visit to this Laboratory, Dr. J. McGavack emphasized the importance of keeping the Cu and Mn contents of rubber extremely low to avoid rapid aging and deterioration of the rubber. In this connection, he was given a number of small samples of goldenrod rubber for spectroscopic analysis in the U. S. Rubber Laboratory at Passaic, New Jersey. In his letter of October 30, 1942, he gave a report on these samples (see table II) and stated that there were indications that aluminum oxide treatment and benzene extraction, either when done direct or when done after base-acid hydrolysis, removes a large amount of Mn and Cu.

To test the validity of these indications it was decided to prepare a series of samples to be sent to Dr. McGavack for quantitative spectroscopic analysis. These were prepared in the following manner:

SAMPLE #1. A sample of the original goldenrod leaves (GRG-44) was used in the preparation of the following samples:

360 grams of these ground leaves were hot-extracted for 24 hours by suspending in an extraction thimble directly over 3000 cc. of boiling benzene so that the reflux percolated through the sample. The dark-brownish green extract containing 61.8 grams of total solids was divided into fractions as follows:

750 cc. of this benzene extract were evaporated to dryness resulting in 16 grams of residue (GRD-130) - SAMPLE #2.

750 cc. of the benzene extract were acetone-precipitated, washed and dried giving 6.3 grams of residue (GRJ-7) - SAMPLE #4.

The remaining 1500 cc. of the benzene extract were passed through two columns of activated alumina giving with the benzene washings 2450 cc. of a clear orange colored solution. This was divided into two equal parts; one-half was evaporated to dryness giving 6 grams of residue (GRD-131) - SAMPLE #3, and the other half was acetone-precipitated, washed and dried giving 4.5 grams of residue (GRJ-9) - SAMPLE #5.

Table III gives the results of the spectral analyses reported by Dr. McGavack.

Treatment with activated alumina apparently removes almost all of the Cu, Mn, and Fe. Acetone precipitation does not remove these metals. The increase in iron content of samples 4 and 5 over the corresponding samples 2 and 3 may be due to the presence of iron in the acetone used, which was discolored from the iron drum in which it was received.

TABLE II
SPECTROCHEMICAL ANALYSIS OF GOLDENROD SAMPLES
FURNISHED BY THE SOUTHERN REGIONAL LABORATORY
(Data furnished by U. S. Rubber Co.)

Treatment	G.L. Code	Parts per Million Cu	Mn	Fe
Oven-dried. 1942 (GRG-3)	624-6	4	60	80
Base-acid digest. of GRG-3 (GRD-62)	624-4	> 50	24	380
Acetone extract from (GRD-62)	624-1	> 50	9	< 10
Benzene extract from GRD-62	624-2	2	1	10
Residue after acetone-benzene extr. of GRD-62	624-3	> 50	23	3500
Benzene extr. of uncooked leaves purif. over Al_2O_3 and acetone pptd. (GRD-68A)	624-5	11	1	10

TABLE III
SPECTROCHEMICAL ANALYSIS OF GOLDENROD RUBBER SAMPLES
(Data furnished by U. S. Rubber Co.)

No.	Sample	Code	Parts per Million Cu	Mn	Fe
1.	Ground Leaves	GRG-44	15	94	480
2.	Benzene Extract of Leaves	GRD-130	3	10	5
3.	Benzene Extract of Leaves treated with Al_2O_3	GRD-131	0.2	0.3	1
4.	Rubber Ppt. from (2) by Acetone	GRJ-7	2	10	17
5.	Rubber Ppt. from (3) by Acetone	GRJ-9	1	0.5	17
6.	USF-rubber (control)	XR	1	0.5	11

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Summary of Experiments with Adsorbents. It has been shown that various activated adsorbents can be used to remove the greatest part of the "resins" from benzene solutions of goldenrod rubber. A systematic study has been made with a large number of adsorbents.

Goldenrod rubber obtained in the pilot plant contains chlorophyll and carotene. These can be removed completely from the benzene solution by adsorption on various activated carbons and by Magnesium oxide powder. These adsorbents are more effective weight for weight than activated alumina which fails to remove the carotenes completely.

The acetone extract of goldenrod leaves shows the presence of eleven or more pigments which could probably be isolated in a pure state chromatographically if the necessary expenditure of time were warranted. Chlorophyll and carotene have already been isolated and identified in this way as shown by spectrograms. Predigestion of goldenrod leaves for 3 hours with 2% NaOH destroys all of the chlorophyll as is indicated by the absence of chlorophyll in the subsequent acetone extract. Predigestion for 3 hours with 3% H_2SO_4 or for 1 hour with 2% NaOH followed by 1/2 hour with 3% H_2SO_4 does not destroy the chlorophyll.

In cooperation with the U. S. Rubber Company it has been shown that the benzene extract of goldenrod leaves contains appreciable quantities of Cu, Mn and Fe, and that these may be almost completely removed by adsorption on activated alumina but not by acetone precipitation.

C - PRECIPITATION VALUE (TITRATION VALUE) AND ITS SIGNIFICANCE IN CHARACTERIZATION AND EVALUATION OF RUBBER.

The solubility of a polymer depends upon the degree of polymerization; in general, it decreases with an increase in molecular weight. The direct determination of solubility for such substances is, however, usually very difficult and cumbersome as is pointed out in a recent article by Jirgensons (1).

When a non-solvent is added gradually to a dilute solution of a polymer with thorough mixing, a proportion of non-solvent to solvent is eventually reached in which the polymer is no longer completely soluble. At this point a turbidity appears due to incipient precipitation. Jirgensons (1) used this simplified method of titrating to the cloud-point in order to determine relative degrees of polymerization in each of a wide variety of substances, e.g., nitrocellulose, starch triacetates, polystyrene polymers.

In the case of rubber, Midgley (2) (3) distinguished between fractions of different molecular weight by means of their solubilities in mixed solvents

(1) Jirgensons, J., J. prakt. Chem., N. F. 161, 30 (1942).
(2) Midgley, T., Jr., Henne, A. L., and Renoll, M. W., J. Am. Chem. Soc. 53, 2733 (1931).
(3) Midgley, T., Jr., and Henne, A. L., J. Phys. Chem., 36, 2880 (1932).

and in this connection used the "standard precipitation point" as a characterizing property. This point was defined as the temperature at which a slowly cooled mixture of 0.85% of the rubber, 28.55% absolute alcohol and 70.60% benzene shows a sudden increase of turbidity. In the present investigation, a simple titration procedure similar to that of Jirgensons has been developed for distinguishing between various rubber samples. Various applications of the method have been made and information has been obtained as to its significance and limitations.

Experimental Methods

Titration. The procedure is as follows: One gram of the rubber sample is dissolved in 200 cc. of reagent grade benzene in a stoppered flask by allowing it to stand overnight or until solution is complete. To clarify the solution one gram of Merck's activated charcoal is added and the solution is slurried and allowed to settle at least 15 minutes. The slurry is then filtered through a filter paper on a Buchner funnel previously prepared by filtering a small benzene slurry of activated charcoal and filter cell and washing with benzene. The rubber solution is not added until the benzene comes through clear. No washing is necessary.

Total solids are determined on the clarified solutions by evaporating an aliquot in an impinging stream of nitrogen under a bell jar. The solution is then diluted with benzene to such a concentration that 100 cc. contains 0.175 gm. of total solids.

10 cc. of this solution is titrated in a 30 mm. test tube by adding absolute ethyl alcohol from a burette with agitation until the cloud-point is reached. The cloud-point is observed by looking through the solution at a black and white background illuminated by a fluorescent lamp and is easily discernible with a reproducibility of 0.05 cc. for values up to 5 or 6 cc. The temperature of the solution is now measured and the precipitation value is obtained by applying a slight correction, 0.05 cc. per 1° C., to the volume of alcohol required. The reproducibility decreases for larger volumes of alcohol; endpoints of more than about 25 cc. cannot be determined because of the high degree of dilution.

The preparation and storage of the rubber solutions should be carried out as far as possible in the absence of light, since exposure to light results in an increase in the precipitation value. The absolute alcohol should be protected from moisture.

The "precipitation value" (also called "titration value") is defined as the number of cc. of absolute alcohol necessary at 25° C. to produce a cloud-point in 10 cc. of a clarified benzene solution containing 0.0175 grams of sample.

Other methods of procedure were tried for making the solutions clear enough to be titrated. Aluminum oxide columns similar to chromatographic columns were employed and though effective, were too slow to be practicable. The precipitation value obtained seems to be independent of the method of

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clarification used; a sample of hevea smoked sheet gave the same value whether clarified by slurrying with activated carbon, by filtering through cotton, or by passing through a column of activated alumina.

The precipitation value is not very sensitive to errors in the rubber concentration. Solutions of hevea smoked sheet and goldenrod rubber of various concentrations were titrated; for hevea, it was difficult to obtain good cloud-points for concentrations above 0.3 grams per 100 cc. due to the tendency of the rubber to precipitate in the form of agglomerates. The results, shown graphically in XIII-C, figure 1, indicate that for hevea and goldenrod the same precipitation values would be obtained within the limit of error, 0.05 cc., for any concentration between 0.150 and 0.200 grams per 100 cc. of solution.

The effect of temperature on the precipitation values of hevea smoked sheet and goldenrod rubber was determined by performing the titration at various temperatures between 20° and 50° C. The data obtained, plotted in XIII-C, figure 2, can in each case be represented by a straight line within the limits of error through the range considered, each having a slope of about 0.05 cc. per ° C. Thus to correct precipitation values to 25° C., 0.05 cc. is subtracted for each degree above that temperature. This value has been assumed to be applicable to all types of rubber in the present investigation for temperature corrections of a few degrees.

Viscosity Measurements. Viscosities were measured by means of Ostwald viscosimeters as modified by Zeitfuchs (4), using the technique of Craxton (5).

They were determined at 25° C. in benzene solutions containing 0.175 gram per 100 cc. The same rubber solutions can be used for these determinations as are used for the precipitation value determinations if special precautions are taken to obtain the correct concentration. The viscosimeters were calibrated with benzene and checked against water. The results were calculated as absolute viscosities, η_a, in centipoises, at 25° C. The absolute viscosity of benzene at 25° was taken as 0.608 centipoise.

Throughout the following experiments precautions were taken against undue exposure to light.

Results and Discussion

Data for Various Samples of Rubber. Precipitation values and viscosities were determined for benzene extracts of goldenrod rubber obtained from the various pilot plant runs and also for specimens of different types of natural rubber. The results are tabulated in tables I and II, respectively.

(4) Zeitfuchs, E. H., Nat'l. Petroleum News, 31, 109 (1914); Proc. 9th Midyear Meeting Am. Petroleum Inst., Sec. III, Refining, 20, 104 (1939).
(5) Craxton, F. C., Ind. Eng. Chem., Anal. Ed., 14, 593 (1942).

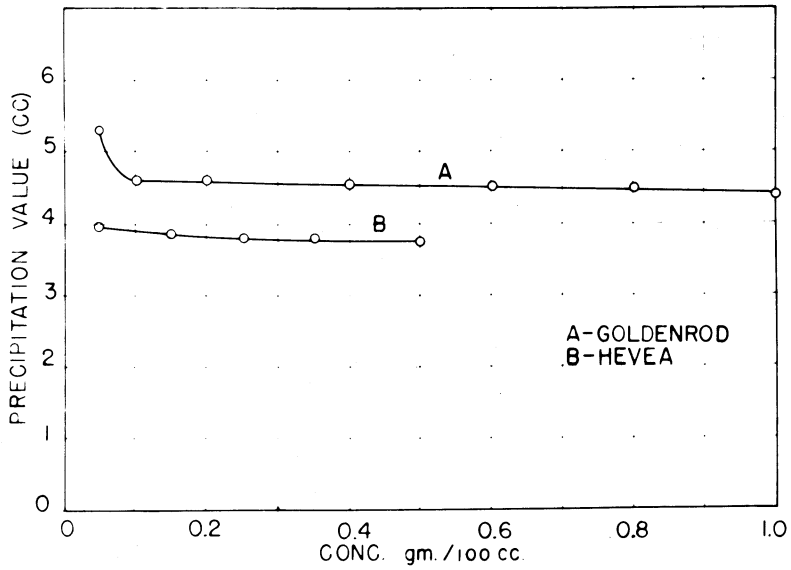

FIGURE 1. EFFECT OF CONCENTRATION ON THE PRECIPITATION VALUE

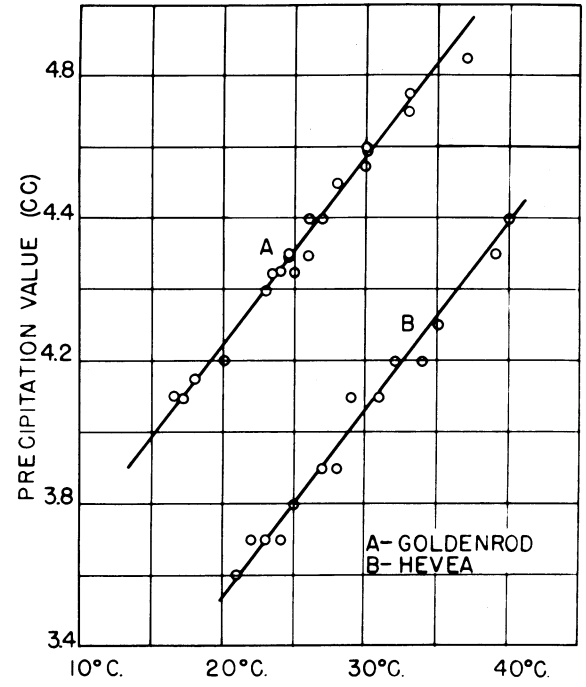

FIGURE 2. VARIATION OF PRECIPITATION VALUE WITH TEMPERATURE

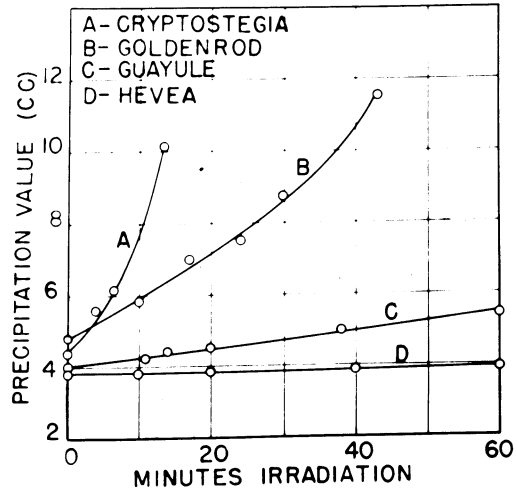

FIGURE 3.

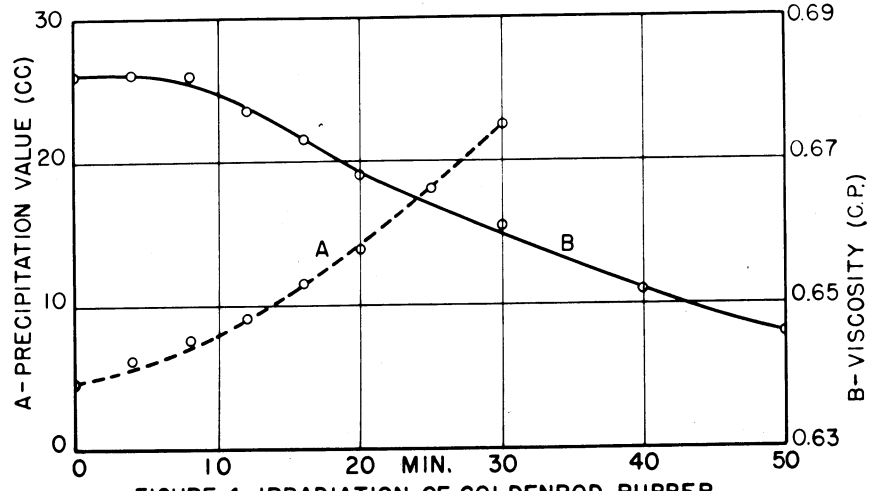

FIGURE 4. IRRADIATION OF GOLDENROD RUBBER.

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Leaving gutta percha out of consideration as an exception, the precipitation values varied from 3.80 cc. for hevea smoked sheet to 5.30 cc. for the poorest goldenrod rubber, Pilot Plant Run #2. In general the lower the precipitation value, the greater the viscosity of the rubber sample. No simple relationship exists, however, nor in view of other results reported below, would it be expected.

The average precipitation value and viscosity for the various pilot plant extractions of goldenrod rubber is 4.48 cc. and 0.681 centipoise, respectively. A poor grade of rubber gives a very high titration value and a low viscosity. Pilot Plant Run #2 gave the highest precipitation value, 5.30 cc., and a very low viscosity, 0.649 centipoise. This sample resulted from the extraction of "goldenrod leaves from dead and field-dried stems" and was very much degraded judging (1) from fractionation data given elsewhere in this report and (2) from the fact that the sample was extremely sticky and semi-liquid. On the other hand, Pilot Plant Run #17 (acetone precipitated) probably the best goldenrod rubber extract obtained, gave a precipitation value of 4.30 cc. and a viscosity of 0.728 centipoise. This sample was in a sense partially purified from degradation products since the acetone used in the preliminary extraction of the leaves contained some 20% of benzene and it has been shown that a mixture of acetone and benzene dissolves some of the lower molecular fractions of rubber. This sample of rubber was fairly hard and practically non-sticky. The relationship between the precipitation value and viscosity will be further discussed below in connection with additional data.

In the case of the goldenrod rubber samples, all those having precipitation values below 4.40 cc. had high viscosities, above 0.685 centipoise. For precipitation values above 4.80 cc. the viscosities were low, below 0.650 centipoise. There seems to be no definite relationship between precipitation value and viscosity, however, when the precipitation values lie between 4.40 and 4.80 cc., the corresponding viscosities vary inconsistently between 0.650 to 0.720 centipoise. These inconsistencies can be explained in the light of other experiments described below.

The values in table II can be considered characteristic only of the particular specimen tested and not necessarily of the variety of rubber since the samples were of unknown history. It is well known that rubber may undergo degradation on aging due, for example, to oxidation or light exposure. This is illustrated by the data given in table III for a sample of guayule rubber after various periods of time. The sample which was rather spongy in appearance was in the form of a large lump and was kept protected from light in a laboratory drawer. In ten months the precipitation value had risen from 3.90 to about 4.50 cc. and the viscosity had decreased from 0.98 to 0.73 centipoise. In the meanwhile the sample had become very sticky. This behavior is not, however, typical of all the guayule samples studied.

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TABLE I

PRECIPITATION VALUES AND ABSOLUTE VISCOSITIES OF PILOT PLANT GOLDENROD RUBBERS

Pilot Plant No. Run No.	Precipitation Value at 25° C.	η_a at 25° C. in benzene 0.175 gm. per 100 cc.
PP#	cc.	centipoises
2	5.30	0.649
3	----	-----
4	4.30	-----
5	4.30	-----
6	4.35	-----
7	4.25	-----
8	4.30	-----
9	4.30	0.689
10	4.25	0.692
11	4.40	0.698
12	4.50	0.697
13 (4 to 6 hrs.)	4.45	0.695
13 (7 to 24 hrs.)	4.55	0.655
14	4.35	0.692
15	4.75	0.662
15 (no Flectol H)	5.00	0.644
16	5.00	0.648
17 (1st 10 hrs.)	4.40	0.722
17 (2nd 10 hrs.)	4.65	0.677
17 (Acetone pptd.)	4.30	0.728
18	4.45	0.692
18 (Acetone pptd.)	4.35	0.693
19	4.35	0.698
20	4.60	0.663
21	4.45	0.665
22	4.60	0.652
23	4.55	0.680
24	4.55	0.663
25	4.50	0.680
26 (1st 12 hrs.)	4.45	0.703
26 (2nd 12 hrs.)	4.60	0.672
27 (1st 12 hrs.)	4.55	0.692
27 (2nd 12 hrs.)	4.55	0.666
28	4.80	0.670
29	4.45	0.683
30 (1st 12 hrs.)	4.35	0.716
30 (2nd 12 hrs.)	4.45	0.685
31	4.40	0.695
32	4.50	0.681
33	4.60	0.690
34	4.45	0.687
35	4.45	0.682
PP-a*	4.45	0.676
PP-e**	4.35	0.685
Average Value	4.48	0.681

* 1943 Crop, Sample 404-E-1

** 1943 Crop, Sample 408-E-79

TABLE II

PRECIPITATION VALUES AND ABSOLUTE VISCOSITIES OF VARIOUS NATURAL RUBBER SPECIMENS OF UNKNOWN HISTORY*

Sample	Precipitation Value at 25° C.	η_a at 25° C. in benzene 0.175 gm. per 100 cc.
	cc.	centipoises
Hevea (Purified crepe sheet)	3.90	2.4
Cryptostegia (smoked sheet)	3.95	1.9
Castilla (smoked sheet)	4.00	1.8
Hevea (smoked sheet)	3.80	1.8
Hevea (yellow crepe)	3.90	1.2
Kok-Saghyz	4.15	1.1
Guayule	3.90	0.98
Chilte (commercial)	4.05	0.98
Guayule (Mexican Resinous)	4.10	0.97
Guayule (Domestic Deresinated)	4.15	0.92
Guayule (Mexican Deresinated)	4.20	0.97
Guayule (Domestic Resinous)	4.20	0.85
Gutta Percha	3.65	0.73
Gutta Percha (aged sample)	4.15	0.66
Goldenrod (average)	4.48	0.68

* These values can be considered as characteristic only of the particular specimen and not necessarily of the variety of rubber.

TABLE III

EFFECT OF AGING OF SAMPLE OF GUAYULE (PC-437) ON PRECIPITATION VALUE AND VISCOSITY

Date	Precipitation Value	η_a at 25° C. in Benzene 0.175 gm. in 100 cc.
	cc.	centipoises
Jan. 16, 1943	3.90	0.98
Oct. 27, 1943	4.25	0.82
Nov. 18, 1943	4.50	0.75
Nov. 23, 1943	4.45	0.75
Jan. 12, 1944	----	0.73

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It has been found that in general, treatments such as mastication, heating and exposure to light, which are known to cause a decrease in the viscosity of rubber, cause an increase in the precipitation value.

Mastication. A sample of hevea smoked sheet was extensively masticated by a stepwise process in a mill by setting the rolls successively closer and closer together. Samples were taken off after treatment at each setting. The precipitation value changed progressively from the original value, 3.80 cc., as follows: 4.25, 4.60, 4.80, 4.85 cc. The viscosity of the final product was 0.68 centipoise as compared to 1.84 for the original unmasticated sample.

In another experiment the mastication was carried approximately to the extent usually attained for compounding. The viscosity had decreased from 1.84 to 0.73 centipoise and the precipitation value from 3.80 to 4.45 cc. This change in precipitation value corroborates the finding of Midgley, Henne and Renoll (6) that their "standard precipitation point" for a pale crepe rubber was reduced by milling.

Heat. The precipitation value of hevea smoked sheet was changed from 3.80 to 4.00 cc. by heating the solid for 6 hours at 120° C. in an air oven.

Irradiation. Exposure to light also is a cause of an increase in the precipitation value. XIII-C-e figure 3, gives a graphical representation of the results obtained in a preliminary experiment. The rubber samples were dissolved, clarified, and diluted to a concentration of 0.175 gm. per 100 cc. of benzene solution by the usual procedure. 10 cc. aliquots were then exposed in Pyrex test tubes at a distance of 12 cm. from a Mazda bulb, removed at the intervals indicated and titrated. As shown by the figure, the rate of degradation increased rapidly in the order hevea, guayule, goldenrod, cryptostegia. It was found that Agerite, Flectol H, and other antioxidants inhibited this reaction while the presence of chlorophyll and other activators enhanced the rate of the reaction. When a trace of chlorophyll was added to the original hevea solution, for example, a sixty minute exposure caused the precipitation value to change from 3.80 to 9.30 cc. instead of from 3.80 to 3.90 cc. This affords a possible explanation of the different rates of degradation of XIII-C,-e figure 3, since the rates increased in the same order as the depth of green color in the clarified solutions. The hevea solution was almost water-white and the cryptostegia, which was a benzene extract of the leaves, was quite green. It was observed that different goldenrod solutions give different rates according to the efficiency of the removal of the coloring matter.

The rate of change of the precipitation value during irradiation is greater at higher temperatures. Aliquot samples of a benzene solution of the goldenrod rubber, 0.175 gram per 100 cc. of solution, were placed in Pyrex

(6) Midgley, T. Jr., Henne, A., and Renoll, M. W., J. Am. Chem. Soc., 54, 3381 (1932).

test tubes 6 cm. from a Mazda lamp and irradiated for 1 hour. The original solution had a precipitation value of 4.40 cc. In the case of two sets of duplicates cooled by electric fan (temperature of the solution 31°C.) the precipitation values at 25° C. were 7.6 and 7.4 cc.; the corresponding values for two other sets of duplicates without fan cooling (55° C.) were 8.6 and 8.2 cc.

The following experiment was performed in the study of the relationship between the change in viscosity and precipitation value during irradiation. A large batch of a benzene solution of goldenrod rubber was clarified with activated carbon and diluted to a concentration of 0.175 gram per 100 cc. in the usual way. Twelve 50 cc. portions of this solution were measured into 125 cc. Pyrex Erlenmeyer flasks and placed in direct sunlight. As the irradiation progressed, they were removed one by one, placed in the dark, and their properties determined. The results are given in table IV and plotted in XIII-C,-o, figure 4.

TABLE IV.
EFFECT OF SUNLIGHT IRRADIATION ON PRECIPITATION VALUE AND VISCOSITY OF BENZENE SOLUTIONS OF GOLDENROD RUBBER

Exposure	Precipitation Value at 25°C.	Absolute Viscosity
Min.	cc.	centipoises
0	4.55	0.682
4	6.15	0.682
8	7.2	0.682
12	9.1	0.677
16	11.4	0.673
20	13.8	0.668
25	17.9	0.666
30	22	0.661
40	more than 25	0.652
50	more than 25	0.646

The precipitation value rose rapidly to more than 25 cc. so that it could not be followed after 30 minutes. In the meanwhile the viscosity had decreased from 0.682 to 0.661 in 30 minutes and was still falling after 60 minutes when it had reached 0.646 centipoise.

Investigation of Binary Mixtures of Rubber Samples. Benzene solutions of various kinds of rubber were prepared by clarifying with activated carbon and making up to a concentration of 0.175 gram per 100 cc. of solution in large batches. A considerable volume of some of these were then irradiated in sunlight to cause degradation as indicated by the decrease in viscosity and increase in precipitation value.

Pairs of these solutions were then mixed in varying proportions and the precipitation values and viscosities determined. For example, 1, 2, 3, etc. cc. of the first solution were pipetted into different test tubes and 9, 8,

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7, etc. cc. respectively, of the second solution were then pipetted in, so as to make the total volume 10 cc. in each case. The results are shown graphically in XIII-C,-o figures 5 to 9. XIII-C,-o Curve 10 is included here for consideration in connection with the discussion. This curve shows the precipitation values for mixtures of 0.175% solution of gutta percha with pure benzene instead of with another rubber solution of the same concentration. Thus, it is really a concentration curve of the type shown in XIII-C,-o figure 1.

In another experiment a clarified solution containing 0.175 gram of hevea per 100 cc. was exposed in a Pyrex flask to the light of a sunlamp and samples were removed after various periods. The precipitation value was determined for each sample and also for a mixture of 1 cc. of each sample with 9 cc. of the end product, which had a precipitation value of 10.50 cc. The results are given in table V.

TABLE V

IRRADIATION OF BENZENE SOLUTION OF HEVEA

Sample No.	Exposure Time	Precipitation Value	Precipitation Value of 1 - 9 mixture with Sample 6
	Hours	cc.	cc.
1	1	4.00	4.10
2	5	4.10	4.25
3	15	5.50	6.10
4	19	7.70	9.10
5	21	8.70	10.45
6	24	10.50	---

Significance of the Precipitation Value. XIII-C, curves 5 to 10 show quite clearly that while viscosity is roughly an additive property the precipitation value is not. The viscosity is known to be a function of the average molecular weight. From these curves the precipitation value seems to be a measure of the largest molecular weight present in the rubber in any appreciable amount and is more or less independent of the average molecular weight.

Consider the case of a 0.175% solution of hevea rubber irradiated so as to change its viscosity from 1.84 to 0.620 centipoise and its precipitation value from 4.05 to 14.0 cc. The addition of four volumes of the irradiated samples to one volume of the untreated sample lowers the viscosity of the latter by about 1.1 centipoise while the corresponding change in precipitation value is only 0.15 cc. XIII-C, (see figure 5). It is thus apparent that starting with these two hevea rubber solutions it would be possible to synthesize samples having a precipitation value of 4.10 ± 0.10 cc. and having any desired viscosity (average molecular weight) between 1.84 and 0.77 centipoise.

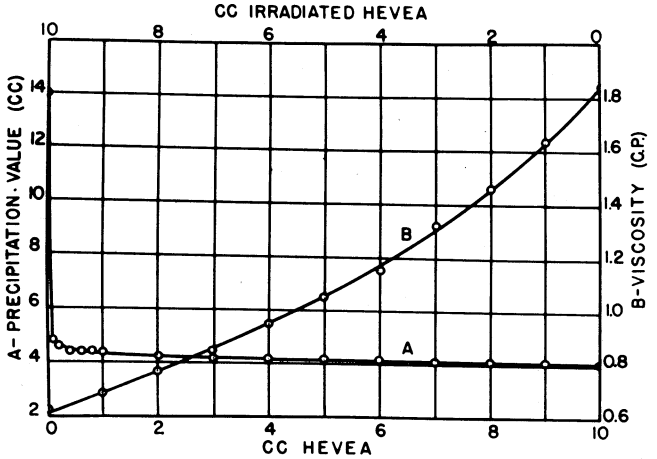

FIGURE 5.

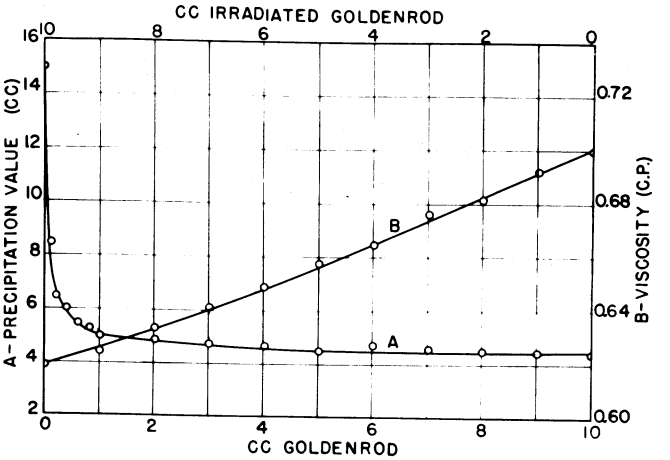

FIGURE 6

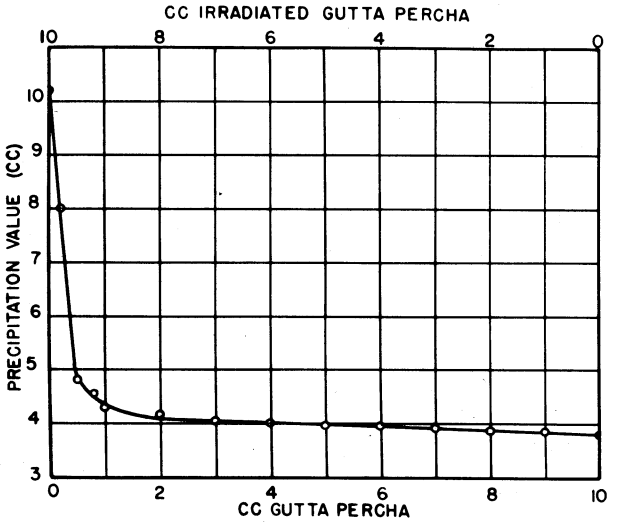

FIGURE 7.

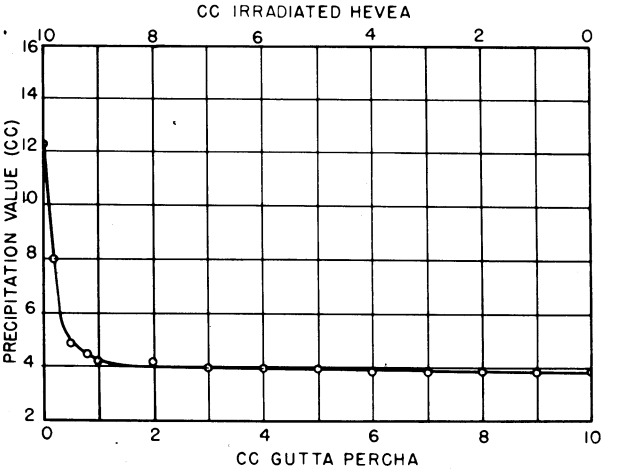

FIGURE 8.

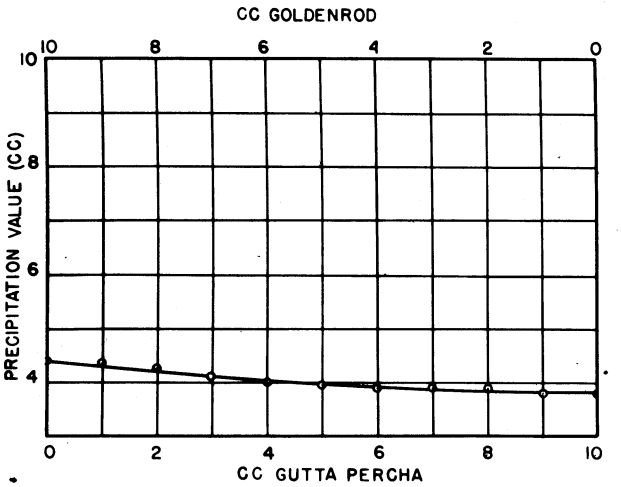

FIGURE 9.

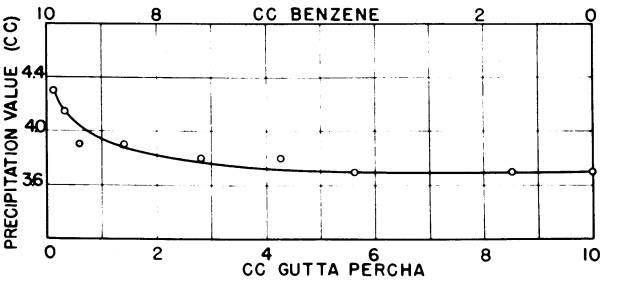

FIGURE 10

Samples with the same precipitation value may, in fact, differ markedly in their behavior depending on their history. This is illustrated by sample 3 in table V. A 1 to 9 mixture of this sample (precipitation value 5.50 cc.) and the end product (10.50 cc.) had a precipitation value of 6.10 cc. Consider, on the other hand, the mixture of hevea rubber having a precipitation value of 5.50 in XIII-C figure 5. From this curve, it is obvious that a mixture with nine volumes of a solution of precipitation value 10.50 cc. would have a precipitation value of about 10 cc.

This behavior also affords a possible basis for an explanation of the inconsistencies mentioned above in connection with table I. In the case of the various pilot plant goldenrod rubbers, when the precipitation values were between 4.40 and 4.80 cc., the corresponding viscosities varied inconsistently between 0.650 and 0.720 centipoise. This can now be accounted for by assuming slight differences in molecular-weight distribution in the pilot plant products.

Further, on the basis of this behavior, it might perhaps be anticipated that the relative changes of viscosity and precipitation value caused by irradiation would depend upon the thickness of the layers irradiated and thus upon the size and degree of natural or mechanical agitation of the sample being irradiated. Thus one might expect the precipitation value to increase more for a given fall in viscosity if a thin layer or a small batch is irradiated. In the case of a large batch, that part of the solution on the opposite side of the vessel from the light source may receive less intense irradiation and thus tend to lower greatly the precipitation value of the final mixed product, the viscosity of which may be very low. This would explain the differences in the relation of the precipitation value and viscosity of the goldenrod irradiation product obtained in XIII-C, figure 4 and those obtained for the large-batch irradiated solutions used to obtain the results of XIII-C, figure 6. In the former case a precipitation value of 25 cc. was reached when the viscosity had fallen to about 0.66 centipoise while in the latter, the precipitation value had risen to only 15.0 cc. though the viscosity had fallen to 0.62 centipoise.

The existence of inconsistency between the relative values of the viscosity and precipitation value for different rubber samples has a bearing on the application of the "standard precipitation point" of Midgley and co-workers. The underlying cause of the inconsistency is the fact that precipitation value is not very sensitive to changes in the concentration of the rubber solution used while the viscosity is. This is illustrated by a comparison of XIII-C figure 1 with figure 6, and figures 7, 8, and 9 with figure 10. The data of Midgley, Henne, and Renoll (2) seem to show that this holds also for the concentration used in the determination of the standard precipitation point. It therefore follows that neither the pecipitation value nor the "standard precipitation point" alone can be satisfactorily used to characterize a rubber. Both may prove of value, however, when considered in conjunction with the viscosity. For example, if two goldenrod samples gave the same viscosity, it could be concluded that the one with the lower precipitation value had an appreciable amount of a higher molecular weight fraction and

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that it must therefore have a larger portion of a lower molecular weight fraction as a counterbalance.

From the values for the precipitation valueand absolute viscosity for hevea smoked sheet, 3.80 cc. and 1.9 centipoise, respectively, and the corresponding average values for goldenrod rubber, 4.48 cc. and 0.68 centipoise, it is apparent that hevea has a much higher average molecular weight. Attention is called to the fact that this very high molecular weight is not necessary for the preparation of vulcanizates having good tensile strength and elongation; in fact, before compounding and vulcanizing, hevea is first broken down by mastication to a condition very close to that of goldenrod. This is shown by the precipitation value and viscosity of masticated hevea, 4.45 cc. and 0.73 centipoise. The corresponding values obtained for Pilot Plant Runs No. 17 and 30 are 4.40 cc. and 0.722 centipoise. Gum stock goldenrod rubber vulcanizates have been obtained in this laboratory which have tensile strengths of 2900 to 3600 lbs. per square inch and an ultimate elongation of 700-750%.

Summary. A simple titration method has been developed for determining the "precipitation value" of a sample of rubber. This constant is defined as the number of cc. of absolute alcohol necessary at 26° C. to produce a cloudpoint in 10 cc. of a clarified benzene solution containing 0.0175 gram of the sample. The precipitation value, which really depends on solubility, is shown to change relatively little over a considerable range of rubber concentrations. It increases progressively when the sample is degraded by treatments which decrease the viscosity, such as mastication, heating, and irradiation. It is shown that the precipitation value and viscosity of masticated hevea smoked sheet and of goldenrod rubber are about the same. Precipitation values and viscosities have been determined on goldenrod rubbers from various pilot plant runs, on a number of different kinds of natural rubber, and on various binary mixtures of these and other samples of rubber partially degraded by irradiation. It is concluded that, unlike viscosity, the precipitation value - and therefore the solubility - is not always a measure of the average molecular weight. It is, however, a function of the highest molecular weight fraction present in an appreciable amount. In conjunction with the viscosity value, it sometimes gives information about the relative molecular weight distribution in two samples.

D-FRACTIONATION AND ITS GRAPHICAL REPRESENTATION IN THE CHARACTERIZATION AND EVALUATION OF RUBBER

A systematic investigation was made of the fractionation of goldenrod and other rubber samples (1) to develop a suitable technique, (2) to determine the best method for the representation of the fractionation data obtained, (3) to ascertain the reproducibility and the significance of the results, and (4) to compare the molecular weight distribution of various goldenrod rubbers with each other and with rubbers from other natural sources.

Method of Obtaining and Analysing Data. a. Procedure. The method of fractionating used is essentially the precipitation method used by Dr. B. L. Johnson described in a letter from Dr. J. N. Street of the Firestone Rubber Company dated March 3, 1943. In brief, it involves the following steps. About 2.5 grams of the rubber sample is freed from resins by allowing it to stand in acetone for 18 to 24 hours in the dark after which the rubber is dried in vacuo. Two grams of this sample are weighed into a tall 400 cc. beaker with 2% of its weight of antioxidant (Flectol H) and dissolved in 200 cc. of benzene. (Toluene was used by Dr. Johnson). The solution is brought to 25° C. in a constant temperature bath and successive definite quantities of methyl alcohol are added to precipitate the rubber. After each addition, the temperature is raised until turbidity disappears and then the solution is allowed to stand in the 25°C. bath until a precipitate forms and settles. Each successive precipitate is separated by decantation, dried in a stream of nitrogen, weighed, and redissolved in benzene to make a 0.2 to 0.3% solution. The concentration of this solution is accurately determined and its relative viscosity is measured by means of a modified Ostwald viscosimeter. The intrinsic viscosity of the fraction, η_i is then calculated from the formula

$$\eta_i = \frac{2.303 \log \eta_r}{c} \quad \ldots\ldots$$

where η_r is the relative viscosity (with respect to pure benzene) and c is the concentration in grams per 100 cc. of solution. The higher the values of the intrinsic viscosity, the higher the average molecular weight of the sample. The successive volumes of methyl alcohol added to precipitate the various fractions depends on the type of rubber being fractionated. The whole procedure usually takes two or three days.

The whole procedure must be carried out as rapidly and with as little exposure to light and oxygen as possible so as to avoid degradation during the handling of the sample or of the separate fractions. The precipitates probably contain only traces of antioxidant so that they are very susceptible to light and oxygen. The intrinsic viscosity is very susceptible to concentration error and therefore the total solids of the solutions involved must be determined with suitable accuracy.

b. Typical Data. The results given in table I for a sample of goldenrod rubber from Pilot Plant Run #17 (1st ten hours) are typical of the data obtained by the technique employed.

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TABLE I

FRACTIONATION DATA FOR GOLDENROD RUBBER FROM PILOT PLANT 17 (1st ten hours).

Methanol cc.	Fraction No.	Ppted. %	Ppted. Cumulative %	η_a	η_r	Conc. g/100 cc	η_i	η_i x fract. ppted.
53	1	14.25	14.25	1.145	1.883	0.251	2.522	35.93
57	2	17.98	32.23	0.865	1.422	0.330	1.068	19.20
62	3	21.10	53.33	0.808	1.329	0.410	0.694	14.64
70	4	15.24	68.57	0.698	1.149	0.277	0.500	7.62
90	5	14.60	83.17	0.674	1.108	0.272	0.379	5.52
135	6	5.40	88.57	0.646	1.063	0.188	0.325	1.76
185	7	6.99	95.56	0.642	1.056	0.198	0.274	1.92
	Residue	4.18	99.74				Total	86.6
	Antioxidant added		2.00					
	Accounted for		97.74					

100 (η_i of original sample) = 87.2

c. Choice of Method of Graphic l Representation. As shown below, it has been found that these data can best be represented in the form of a histogram. The intrinsic viscosity of each successive fraction precipitated is plotted as ordinate against the cumulative percentages precipitated as abscissa. The histogram corresponding to table I is shown in figure 3.

d. Intrinsic Viscosity an Additive Property. It is already known that for rubber polymers the intrinsic viscosity of a mixture is the weighted average of the intrinsic viscosities of the constituents. This principle was used, for example, by Flory [J. Am. Chem. Soc., 65, 372 (1943)] in his work on polyisobutenes to show that there had been no degradation during fractionation. That this method of calculation of intrinsic viscosities for mixtures is valid in the case of goldenrod rubber was roughly confirmed by measurements of binary mixtures of two fractions obtained from a fractionation. The results obtained are given in table II.

TABLE II

INTRINSIC VISCOSITY OF MIXTURES

Fraction. I	Fract. II	Intrinsic Viscosity		Δ
		Observed	Calculated	
%	%			
0	100	.944	.944	0.0
20	80	.763	.803	-0.04
40	60	.656	.663	-0.007
60	40	.544	.522	+0.022
80	20	.441	.382	+0.059
100	0	.241	.241	0.0

e. Area of Histogram, a Measure of Experimental Error and Reproducibility. Since the intrinsic viscosity is an additive property, the area under the histogram should be independent of the size and number of the individual fractions. This is, $\Sigma\eta_i$ (% ppted.), the sum of the values in the last column of table I, should be equal to 100 times the intrinsic viscosity of the original sample. In the case of the fractionation data of table I, these two values are in excellent agreement. Differences in these two values can be taken as a measure of the experimental error. Differences between the histogram areas of duplicate samples indicate the reproducibility of the fractionation data.

Results. a. General. Experimental results obtained by the fractionation of a number of rubber samples are summarized in table III and are represented graphically in XIII-D - figures 1 to 38. Column 4 of table III lists the areas under the histograms. The values in column 5 were obtained by multiplying the intrinsic viscosities of the original samples by 100.

(1) Reproducibility. The following tabulation shows the maximum differences between the histogram areas for duplicate experiments on a number of samples.

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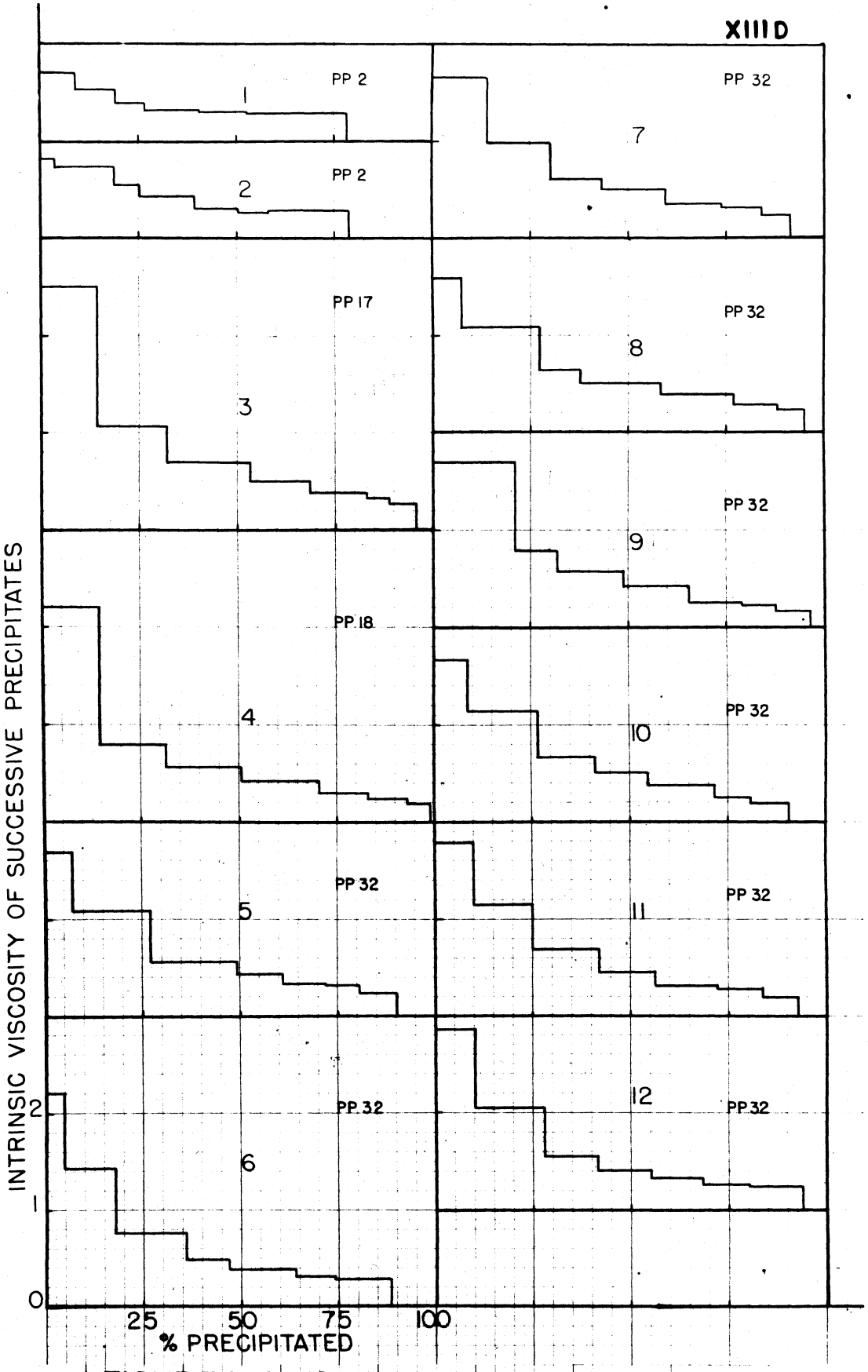
Sample	Figures	Areas	Δ	%
PP2	1 and 2	34.6, 30.6	4.0	9.6
PP17	32 and 3	88.3, 86.6	1.7	2.0
PP32	9 and 10	67.2, 61.8	5.4	8.4
PPa	13 and 14	60.1, 59.6	0.5	0.9
Hevea Crepe	17 and 24	213.3, 199.3	14.0	6.8

(2) The Shape of the Histogram. In general, the histograms are stepwise curves descending from left to right. The height of the first step for a given sample is higher if the first fraction precipitated is small. This does not affect the total area of the histogram as can be seen by XIII-D - figures 13 and 14 for a goldenrod rubber (PC-1558) whose areas are 60.1 and 59.6 respectively.

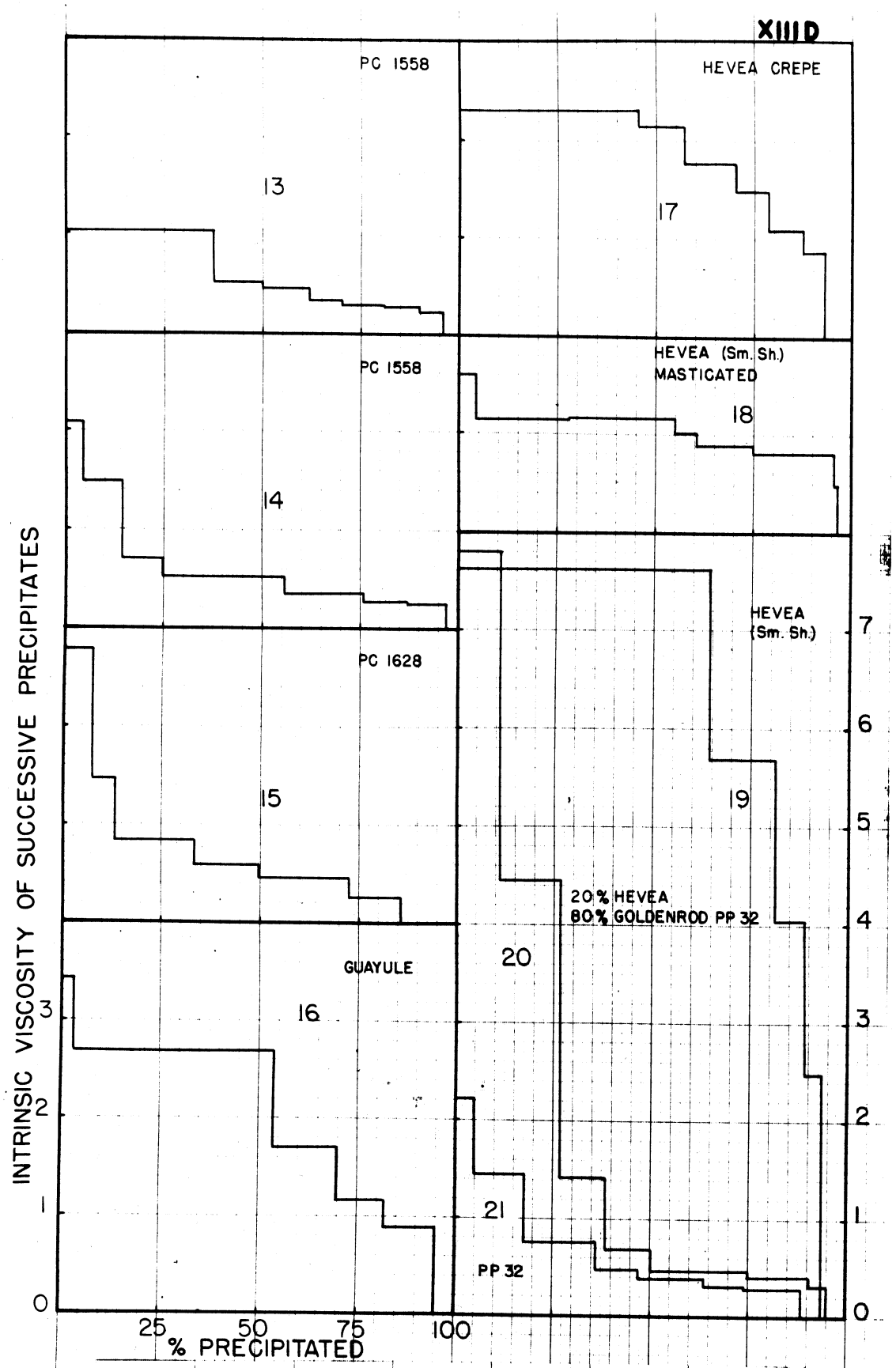
(3) Removal of Resins Not Necessary. According to the Johnson Method the sample is prepared for fractionation by soaking in acetone for 18 to 24 hours to remove the major part of the resins. Duplicate runs were made on Pilot Plant Run #32, PP32, in which the sample was prepared for fractionation (a) by acetone precipitation, XIII-D - figures 7 and 8; (b) by forming a slurry with Merck's activated charcoal and then filtering, figures 9 and 10; (c) by omitting the removal of resins altogether and taking enough sample to give 2 grams of rubber excluding resins, the proportion of the resins having been determined previously by analysis, XIII-D - figures 11 and 12. An examination of table III shows that the variations obtained by these different methods as compared to the usual method (XIII-D curves 5 and 6), are within the experimental error to be anticipated from the reproducibility. Unless otherwise mentioned in table III the resins were usually removed by soaking in acetone as suggested by Johnson.

b. Comparison of Pilot Plant Goldenrod Samples. The average histogram areas for various pilot plant runs of goldenrod rubber have been arragned in the order of their magnitude in table IV. For the most part, the areas for these pilot plant (PP) goldenrod rubbers fall between 60 and 70. Excluding PP2 and PP17, the average area is 63.2. The area for PP2 (32.4) indicates a much lower average molecular weight than usual. This sample resulted from the extraction of "goldenrod leaves from dead and field-dried stems" and was very much degraded judging from the fact that it was very sticky and semi-liquid. On the other hand, the large area (87.4) found for PP17 showed that it had an abnormally high average molecular weight. In fact, this was in a sense a partially fractionated rubber since the acetone used for the initial extraction of resins from the leaves contained some 20% of benzene and it has been shown in previous experiments that a mixture of acetone and benzene will extract some of the lower molecular fractions from the rubber leaving behind a rubber of higher average molecular weight. This fact is brought out in the discussion of XIII-D - figures 25 and 26. PP17 was obviously a harder rubber and was almost non-sticky.

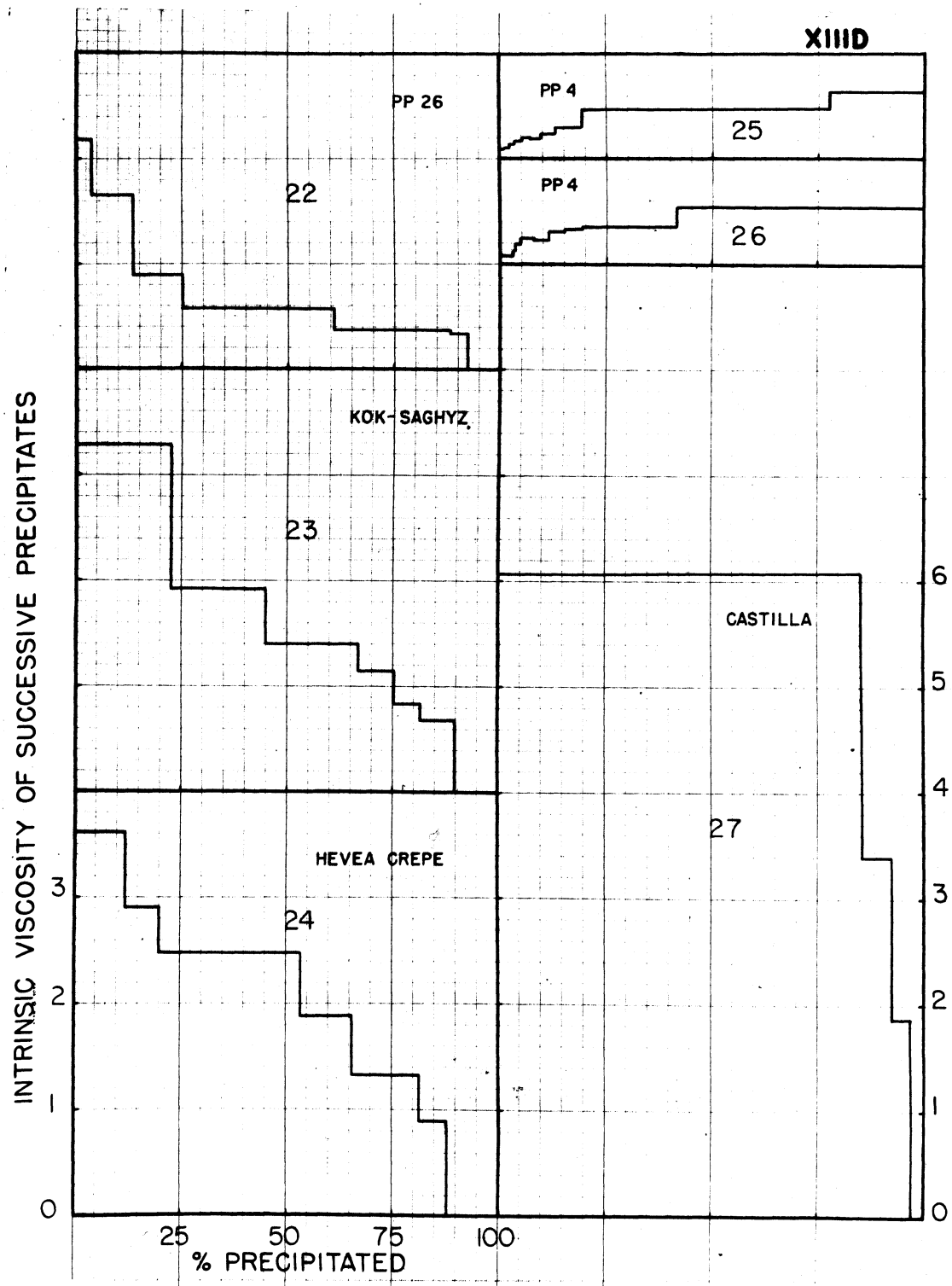
c. Comparison of Hevea Samples. Inspection of XIII-D-figures 17, 18, 19, 20 and 24 and a comparison of their areas, given in table III, indicate a marked difference between the various hevea samples. Figure 19 for hevea



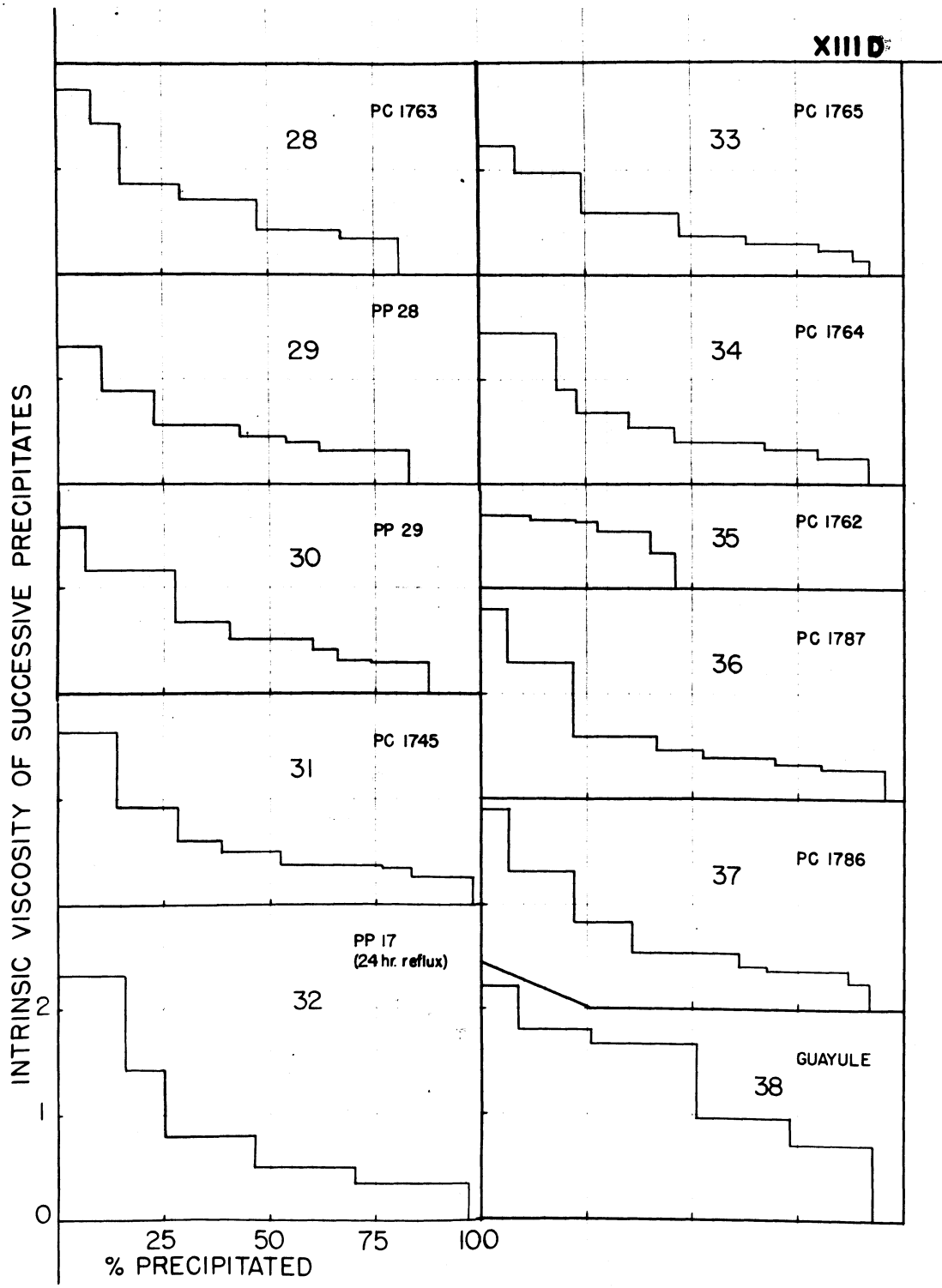
FIGURES 1-12. FRACTIONATION CURVES.



FIGURES 13-21. FRACTIONATION CURVES.



FIGURES 22-27. FRACTIONATION CURVES.



FIGURES 28-38. FRACTIONATION CURVES.

TABLE III
SUMMARY OF FRACTIONATION DATA

Figure No.	Sample	PC No.	Area (Exp.)	Area (Calc.)	Δ Area
1	PP2* a/	415	30.6	37.3	-6.7
2	PP2 a/	415	34.6	37.3	-2.7
3	PP17 (1st 10 hrs.) b/	724	86.6	87.2	-0.6
4	PP18 (1st 11 hrs.)	1351	71.8	73.7	-1.9
5	PP32	1287	59.9	63.6	-3.7
6	PP32	1287	62.2	63.6	-1.4
7	PP32 (acet. pptd.) c/	1456	65.2	63.6	+1.6
8	PP32 (acet. pptd.) c/	1456	63.8	63.6	+0.2
9	PP32 d/	1287	67.2	63.6	+3.6
10	PP32 d/	1287	61.8	63.6	-1.8
11	PP32 e/	1287	62.7	63.6	-0.9
12	PP32 e/	1287	61.8	63.6	-1.8
13	PPa	1558	60.1	59.4	+0.7
14	PPa	1558	59.6	59.4	+0.2
15	PPe	1628	69.0	67.2	+1.8
16	Guayule f/	--	199.1	--	--
17	Hevea crepe	1528	213.3	205.	+8.3
18	Hevea (S.S.)Masticated	252	104.5	102.5	+2.0
19	Hevea (S.S.) +	252	626.2	600.	+26.2
20	80% PP32	1287			
	20% Hevea (S.S.)	252	198.5	(171)**	+27.5
21	PP32	1287	62.2	63.6	-1.4
22	PP26 (1st 10 hrs.)	1352	68.8	68.8	0
23	Kok-saghyz	1665	166.3	171.5	-5.2
24	Hevea crepe	1528	199.3	205.	-5.3
25	PP-4 g/	475	44.7	(58.4)***	--
26	PP-4 g/	475	44.7	---	--
27	Castilla	473	550.7	565.0	-14.3
28		1763 h/	61.7	62.3	-0.6
29	PP28	1353	53.0	55.5	-3.0
30	PP29	1354	62.6	63.6	-1.0
31	PPd c/	1745	64.1	71.5	-7.4
32	PP17 (1st 10 hrs.)	724	88.3	87.2	+0.9
33		1765 h/	48.2	52.9	-4.7
34		1764 h/	60.3	59.7	+0.6
35		1762 h/	27.5	24.8	+2.7
36	PPb i/	1787	62.5	62.1	+0.4
37	PPc	1786	68.8	67.3	+1.5
38	Guayule	437	126.8	120.	+6.8

* PP numbers refer to pilot plant runs on goldenrod

** Calculated from PC 252 and PC 1287

*** Value by precipitation method - see Figure 4 curve F of memo of September 7, 1943.

(a)Sample very sticky and soft;(b)Sample hard and almost non-sticky;(c)Acetone-precipitated sample;(d)Carbon-treated sample;(e)Resins not removed;(f)Source of sample unknown;(g)Fractionated by "dissolution method";(h)From sun-dried goldenrod leaves extracted in laboratory;(i)Acetone precipitated in the pilot plant.

smoked sheet brings out the fact that this form has the highest molecular weight (area 626). The duplicate histograms for the sample of crepe rubber investigated, figures 17 and 24, indicate that this form has a much lower molecular weight as shown by the average area, 207. Figure 18 with an area of 105 shows the extent to which the hevea smoked sheet was broken down by mastication. This sample had been masticated approximately to the extent necessary for compounding. This histogram differs from all the others obtained in the present investigation by being nearly horizontal thus indicating that the sample was made up for the most part of rubber of approximately uniform molecular weight.

TABLE IV
COMPARISON OF PILOT PLANT GOLDENROD RUBBERS.

PP No.	Figure No.	Histogram Area	Calc. Area
2	1, 2	32.4 (av.)	37.3
28	29	53.0	55.5
a	13, 14	59.9 (av.)	59.4
32	5, 6	61.1 (av.)	63.6
b	36	62.5	62.1
29	30	62.6	63.6
d	31	64.1	71.5
26 (1st 10 hrs.)	22	68.8	68.8
c	37	68.8	67.3
e	15	69.0	67.2
18 (1st 11 hrs.)	4	71.8	73.7
17 (1st 10 hrs.)	3, 32	87.4 (av.)	87.2

XIII-D-figure 20 is the histogram of a binary mixture of 20% hevea smoked sheet (figure 19) and 80% of goldenrod PP-32 (figure 21). The presence of the hevea is quite apparent. The area 198.5 obtained for curve 20 corresponds to a calculated value of 24.1% of hevea for the mixture as based on the areas 626.2 and 62.2 for figures 19 and 21, respectively. (see table III).

d. Comparison of Samples of Various Natural Rubbers. A number of different varieties of natural rubber were subjected to the fractionation procedure. In order to make the benzene solutions, the samples extracted with acetone and dried in the usual way were allowed to stand in benzene for several days with occasional gentle swirling and then clarified. For clarification the solution was filtered through glass wool or cotton or, if not too viscous, through filter paper. That this procedure is adequate to dissolve the gel fraction is evidenced by the results obtained for hevea smoked sheet(XIII-D-figure 19) and castilla (figure 27). This procedure also gives reproducible results. This is shown (1) by the results for duplicate samples of hevea crepe (see XIII-D-figures 17 and 24 and table III, column 6) and (2) by the agreement between the experimental areas of the histograms and their areas calculated from the intrinsic viscosity of the original sample usually determined independently.

TABLE V
COMPARISON OF SPECIMENS OF DIFFERENT VARIETIES OF RUBBER OF UNKNOWN HISTORY

Variety	Figure	(Exp. Area)	(Calc. Area)
Guayule	16	199.1	---
Guayule	38	126.8	120
Hevea crepe	24	199.3	205
Hevea crepe	17	213.3	205
Hevea Smoked Sheet	19	626.2	600
Hevea (sm. sh.) masticated	18	104.5	102.5
Kok-saghyz	23	166.3	171.5
Castilla	27	550.7	565
Goldenrod	---	(32.4 - 87.2) (normally 60 - 70)	---

The conclusions which can be drawn from these fractionation results are, however, necessarily limited. In the first place, the history of the various specimens is unknown, and secondly, the samples were sometimes not completely soluble in benzene. Though the insoluble residues appeared to be foreign non-rubbery material it may have consisted partially of rubber which had become insoluble due to oxidation or some other transformation in the original sample. For this reason the results obtained and summarized in table V can be considered as representative only of the particular specimen of rubber, and not necessarily of the variety of rubber.

e. Fractionation by Dissolution. Some of the first fractionations of rubber performed in this laboratory were by the so-called dissolution method with mixed solvents as described by Bloomfield and Farmer. [Trans. Inst. Rubber Ind., 16, 69 (1940).] This method is admittedly not as reliable as the precipitation method since considerable degradation takes place before the fractions are separated. For example, it involves long periods of standing under solvents, evaporation of quantities of solvent, and considerable handling of the separate fractions before they can be evaluated. One fractionation takes two to three weeks as compared to two or three days by the precipitation method.

For the sake of comparison, a summary of the results of two fractionations of a sample of goldenrod rubber by the "dissolution" method is given in table VI and represented graphically in XIII-D-figures 25 and 26, as summarized in table III.

Briefly the procedure was as follows. A 20 gram goldenrod rubber sample was weighed into a 5-liter Erlenmeyer flask. It was covered with 1 liter of a mixture of 97% acetone-3% petroleum ether (B.P. 35-60° C.) and allowed to stand at 25°C. in the dark being gently swirled twice daily. After about 48 to 72 hours an equilibrium was reached as shown by occasional

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TABLE VI

FRACTIONATION OF GOLDENROD RUBBER PP-4 DISSOLUTION METHOD

Exp. A = Acetone-petroleum ether mixtures (XIII-D-Fig. 25)
Exp. B = Acetone-benzene mixtures (XIII-D-Fig. 26)

Solvent Mixture		Extracted %		Intrinsic Viscosity		Titration Value cc.*	
Acetone %	Other %	Exp. A	Exp. B	Exp. A	Exp. B	Exp. A	Exp. B
97	3	0.15	0.45	0	0.09	25+	25+
95	5	0.30	0.67	0.085	0.113	25+	25+
90	10	0.68	0.67	0.130	0.141	15	18
80	20	0.32	1.36	0.197	0.169	7.5	12
75	25	2.64	1.28	0.257	0.202	5.8	10.3
70	30	2.42	2.08	0.230	0.186	6.4	8.3
65	35	2.74	2.83	0.311	0.240	5.4	7.1
60	40	3.28	5.65	0.328	0.295	5.4	6.5
50	50	21.70	57.70	0.354	0.472	5.2	4.8
40	60	57.70	22.00	0.545	0.637	4.6	4.6

* cc. of methyl alcohol necessary to cause slight cloudiness when added to 10 cc. of a 0.175% benzene solution at 25° C.

total-solids determinations on 10 cc. aliquots. The solvent was then decanted carefully and evaporated to dryness in an atmosphere of nitrogen, precautions being taken against undue exposure to light. It was then weighed and redissolved in benzene, and its viscosity and precipitation values were determined. The residue left after decantation was then re-extracted in the same way with 1 liter of a mixture of 95% acetone and 5% petroleum ether. Each successive extraction was with a solvent mixture richer in petroleum ether. The results of this extraction are designated in experiment A. A similar extraction using acetone and benzene mixtures is designated as experiment B.

As shown in table III, the areas of the histograms, XIII-D. figures 25 and 26, respectively, show good agreement with each other (44.7 and 44.7) but they are much lower than the area (58.4) obtained by a preliminary version of the precipitation method applied to the same sample. This indicates that considerable degradation of the sample had occurred during the fractionation by the dissolution method.

f. Miscellaneous. The values for XIII-D-figures 3 and 32 are in very good agreement which shows that no appreciable degradation of the sample took place when the pilot plant benzene extract (PP17, 1st 10 hours) was refluxed for 24 hours in a darkened hood.

Figures 28, 33, 34 and 35 are for samples extracted in all-glass

apparatus. They were from "sun-dried goldenrod leaves" submitted to us for fractionation and evaluation by Dr. M. N. Walker of Rubber Plant Investigations, Bureau of Plant Industry. The histogram area indicates that the sample for figure 35 is very highly degraded. Figures 28 and 34 are almost equal in area to the average of pilot plant goldenrod rubbers (63.1) mentioned above and figure 33 is appreciably below this average.

Summary. The precipitation method for fractionation of rubber by successive precipitation from a benzene solution has been investigated and applied to various samples of goldenrod and other varieties of natural rubbers. The size of each successive fraction and its intrinsic viscosity are determined. These give an indication of the weight distribution. The data can best be represented in the form of a histogram, the shape of which depends on the number and size of the fractions but which for the natural rubbers investigated is always a series of descending steps. As might be expected, the area of the histogram, on the other hand, is independent of the number and size of the fractions and is characteristic of the particular sample of rubber. The higher the average molecular weight, the larger the area. This area is shown to be 100 times the intrinsic viscosity of the original sample. It might therefore be concluded that as a control method or for the evaluation of different samples of goldenrod rubber, fractionation has no advantage over the relatively simple determination of the intrinsic viscosity of the original sample, unless the information revealed by distribution of the components of variable viscosity warrants the considerable amount of work involved in obtaining the results. It should be kept in mind that the single determination will not show this distribution.

Comparison has been made of the histogram areas obtained for (1) various pilot plant runs of goldenrod rubber (table IV), (2) various hevea samples (section c, under Results), (3) specimens of various natural rubbers (table V).

Evidence is given to show that histogram areas obtained from fractionation data can be used to estimate the percentage of hevea rubber in hevea-goldenrod mixtures.

Fractionations by the dissolution method are shown to be unsatisfactory, due perhaps to degradation of the sample.

A summary of the results for all samples fractionated are tabulated in table III.

Advantages of Histograms in Representation of Fractionation Data. According to the method of graphical representation of fractionation data described to us by Dr. B. L. Johnson of the Firestone Tire and Rubber Co., a curve is constructed from the intrinsic viscosities of the successive fractions precipitated. The slope of this curve is read at various intrinsic viscosities and these values are plotted to give a weight distribution curve. XIII-D-figures 39A and B, respectively, are the curves obtained by so plotting Dr. Johnson's data for a mixture of pilot plant runs #6 and #11 of goldenrod rubber. The weight distribution curve, curve B, thus depends on the shape of curve A.

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An analysis of the method shows that the shape of curve A. depends in turn upon the number and size of the fractions precipitated. This is illustrated in XIII-D-figure 40. Here the full curve A is the histogram representing the data of table I and XIII-D-figure 3. In curve B the data are plotted essentially as in figure 39A, i.e., by connecting the inner corners of the steps of the histogram. (It should be noted that only 96% of the original rubber was accounted for as precipitated fractions; the remaining 4% was probably of too low a molecular weight to be thrown out by the total volume of precipitant used. These facts are taken into account in figure 40, curve B. That is, curve A in figure 39 should perhaps really start at the upper axis.)

If enough precipitant had been added so that the second, third, and fourth fractions had precipitated out together, the intrinsic viscosity of this large fraction would be the weighted average of the values for the three smaller fractions, as shown above. The corresponding changes in the curves are shown by the broken lines, curves A' and B' in figure 40.

It is thus apparent that curve B is itself really a fictitious curve. The true curve would be obtained by this method only if there were an infinite number of small fractions. This objection would still hold if the curve were drawn through the midpoints or the outside corners of the histogram steps, as is sometimes done in similar cases, instead of through the inside corners.

The histogram, on the other hand, is a true graphical representation of the data obtained and has the advantage of possible evaluation by means of its area. For example, an examination of curves A and A' from the point of view of area show them to be the same and this can even be observed roughly by inspection.

The advantage of the histogram over the usual weight-distribution method of representing fractionation data is again brought out by a comparison of the data for (1) hevea (smoked sheet), (2) a mixture of 20% hevea smoked sheet and 80% of goldenrod, and (3) goldenrod alone as plotted by these two methods.

The histograms of these three samples are represented in XIII-D-figures 19, 20, and 21, respectively. The weight distribution curves for the same data though rather questionable due to the personal equation involved, are shown in XIII-D-figure 41, curves C, B and A, respectively. It will be noted that the 20% of hevea shows up much more definitely in the histogram than in the weight distribution curve. Furthermore, the area of the histogram can be used to estimate the percentage of hevea. Thus, using the areas of the histograms for the hevea and goldenrod samples, 626.2 and 62.2, respectively, and for the 20% mixture, 198.5, the following equation can be set up:

$$626.2 \left(\frac{x}{100}\right) + 62.2 \left(\frac{100-x}{100}\right) = 198.5$$

where (x) is the percentage of hevea in the mixture. Solution of this equation gives (x) = 24.1%.

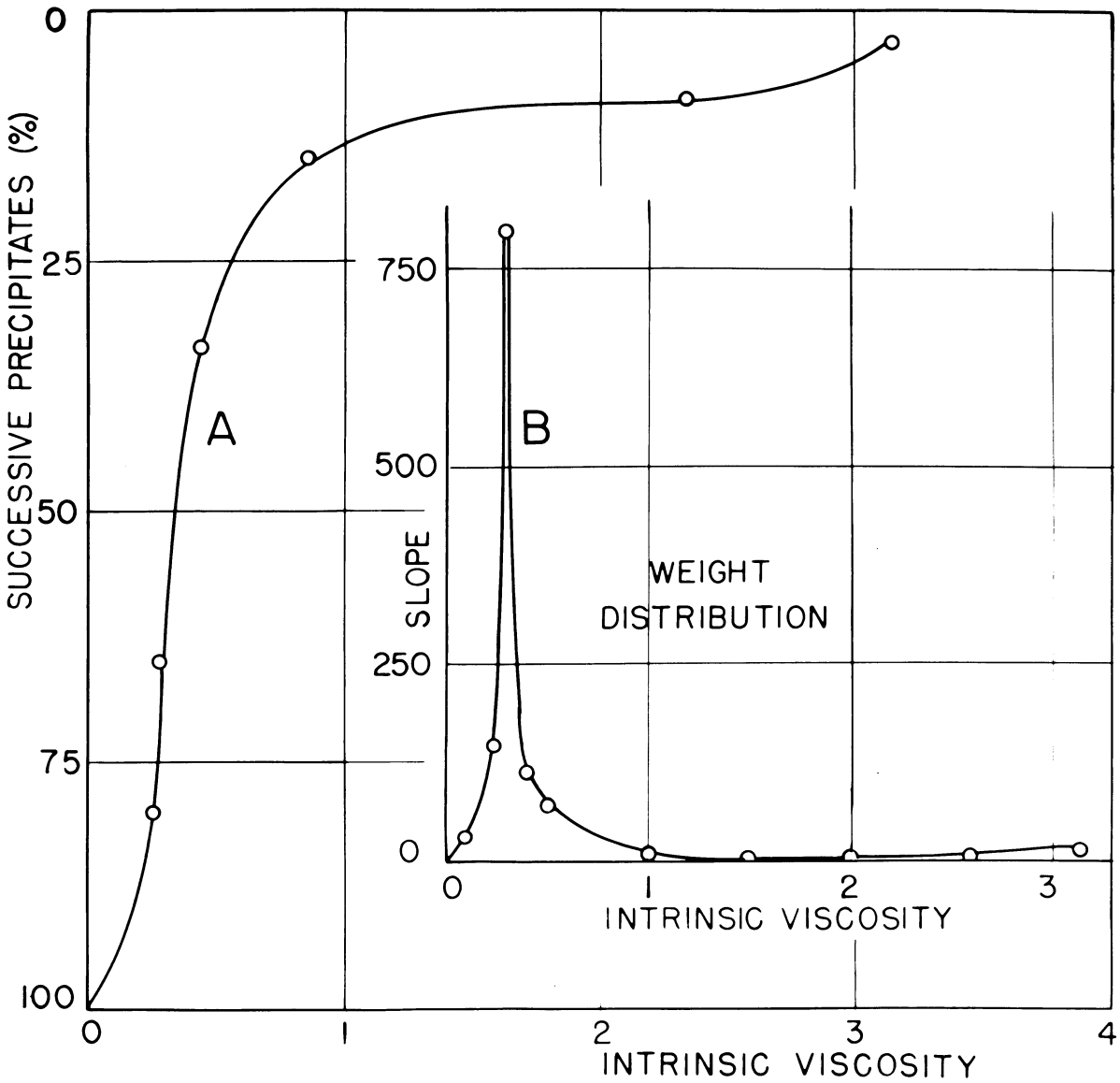

FIGURE 39. WEIGHT DISTRIBUTION METHOD OF PLOTTING.

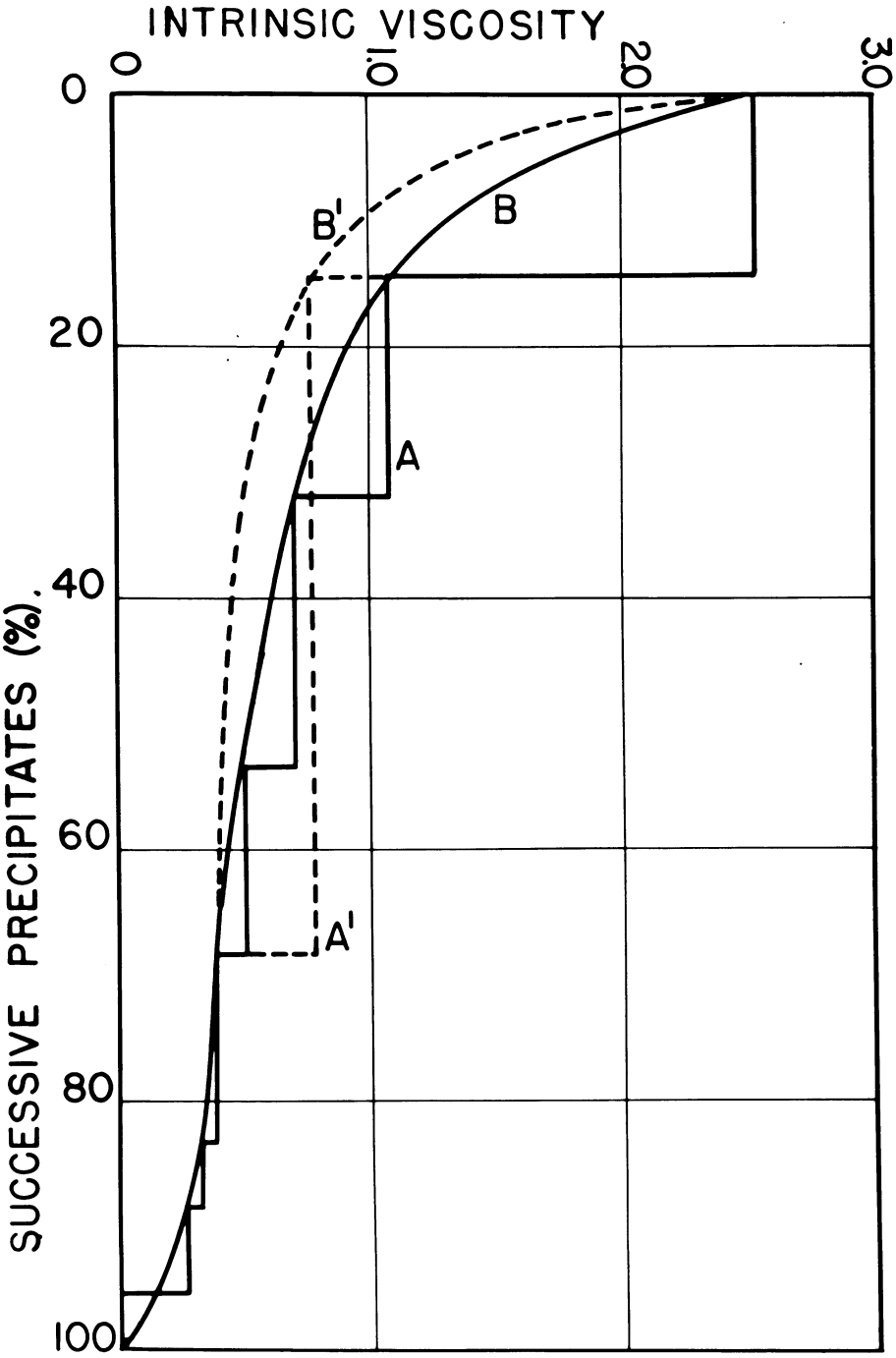

FIGURE 40. VARIATION WITH SIZE OF FRACTIONS.

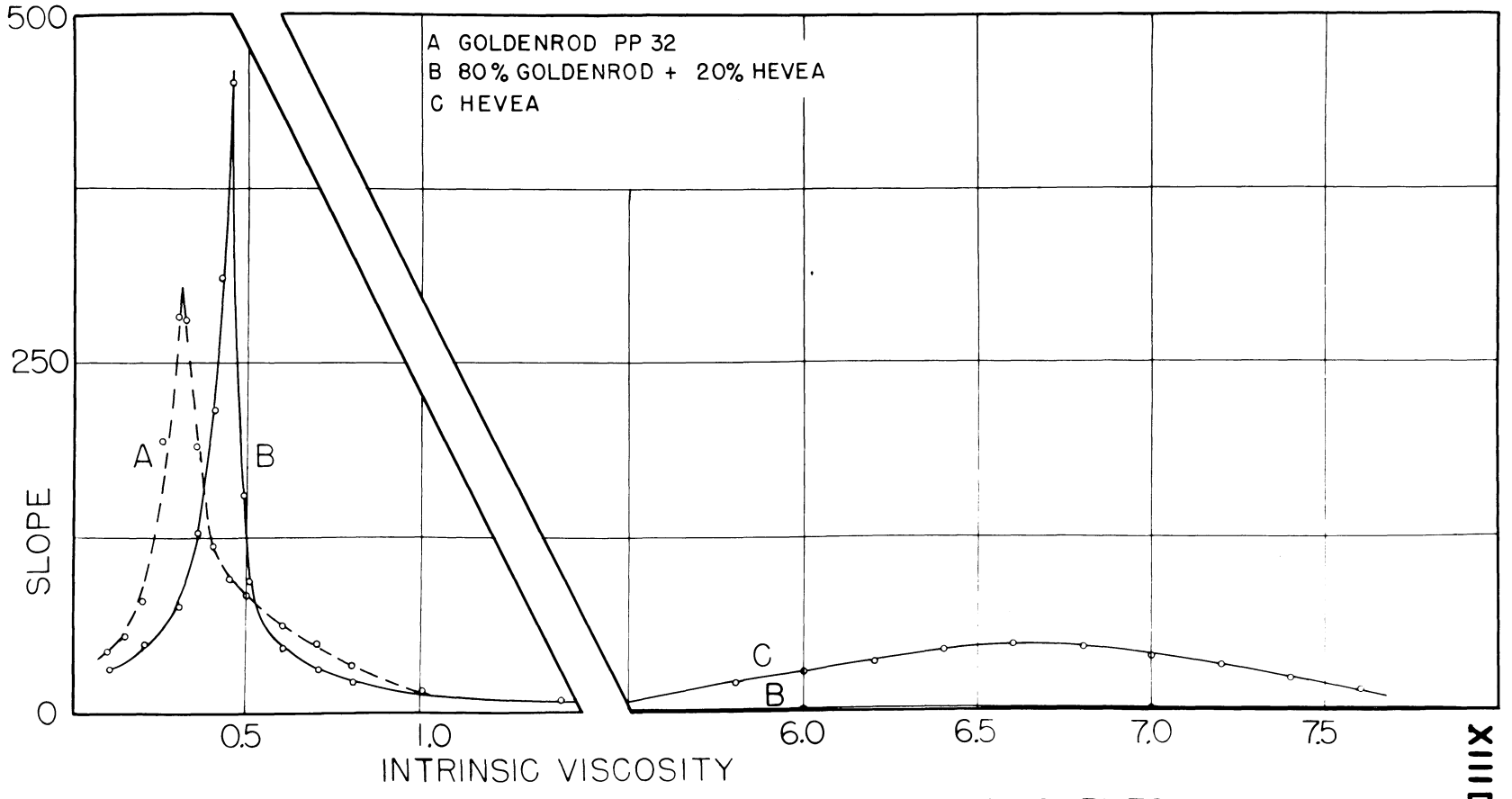

FIGURE 41. WEIGHT DISTRIBUTION CURVES.

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Summary. Analysis of the methods of plotting fractionation data shows that the usual weight-distribution curve representation is based on a more or less fictitious curve whose shape depends on the size and number of the fractions. The histogram, on the other hand, is a true graphical representation of the data whose area is characteristic of the sample. This area can be used in the evaluation of different samples of rubber and for an approximate analysis of mixtures of different rubbers.

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E-EFFECT OF LIGHT

1. Effect of Light on Benzene Solutions of Goldenrod Rubber in Pyrex in Presence of Oxygen as Influenced by Various Rubber Antioxidants and Other Reagents.

When a benzene solution of goldenrod rubber is exposed in a Pyrex vessel to the light of a Mazda lamp or to sunlight, the titration value of the solution increases, the viscosity decreases, and the rubber undergoes a "degradation" and becomes more liquid and sticky. The nature of this degradation is uncertain but the literature on hevea indicates that it involves some kind of oxidation.

That goldenrod rubber takes up oxygen under these conditions was shown by an early experiment. A benzene solution of about 1% concentration, cleaned up with carbon, was divided into two parts in Pyrex Erlenmeyer flasks and one flask was kept in the dark while the other was exposed to sunlight for six hours. The titration value for the first flask remained unchanged at 4.40 cc. and for the irradiated sample it was 21 cc. The solutions were evaporated to dryness, benzene removed in vacuo, and the samples submitted to the Analytical Section for semi-microcombustion analysis. Assuming five carbon atoms in the goldenrod rubber hydrocarbon unit the corresponding formulas were calculated from these data and are given in the last column of the following tabulation:

Analysis of Blank (In triplicate)

% C	% H	% N	Unit formula, isoprene = $(C_5H_8)n$	Average formula
86.0	11.48	less than 0.2	$C_5H_{8.02}O_{0.11}$	
86.1	11.40		$C_5H_{7.95}O_{0.11}$	
87.2	11.82		$C_5H_{8.21}O_{0.04}$	$(C_5H_{8.06}O_{0.09})n$

Analysis of Irradiated Sample (In duplicate)

78.6	10.46	less than 0.05	$C_5H_{8.0}O_{0.52}$	
78.4	10.25		$C_5H_{7.85}O_{0.54}$	$(C_5H_{7.92}O_{0.51})n$

These data show that a total of about 9% of its weight of oxygen was taken up by the goldenrod rubber during irradiation; the sum of the percentages of C, H and N was changed by irradiation from 98.0% to 88.9%; the calculated formula from $(C_5H_{8.06}O_{0.09})n$ to $(C_5H_{7.92}O_{0.51})n$. Thus six hours of irradiation resulted in an increase of oxygen content corresponding to 0.4 atom of oxygen per isoprene unit.

This oxidation, or "degradation" reaction is speeded up or activated by small amounts of chlorophyll, the presence of which has no effect if the sample be stored in the dark. Thus on exposure to sunlight for 20 minutes a hevea solution retained its original titration value, 3.90 cc., while another portion of the same solution containing a trace of chlorophyll

gave a titration value of 6.00 cc.

Early tests had shown that this light reaction could be inhibited in the various benzene solutions of goldenrod by adding about one percent of Agerite (Resin D) or Flectol H, antioxidants which are used to inhibit aging of the raw rubber as well as of vulcanizates. It seemed possible, therefore, that the efficiencies of various rubber antioxidants might be estimated by means of their relative effect on the titration value during irradiation of goldenrod rubber in benzene solution.

A series of common antioxidants and other substances were tested by adding them in very small amounts to carbon-treated goldenrod rubber solutions, irradiating the solutions, and comparing the effect on the titration values. The lower the titration value after irradiation the greater the antioxidant effect of the reagent. If the titration value after irradiation is higher than that of the irradiated blank, the reagent can be said to activate rather than inhibit the light reaction. The results of these experiments are shown in the following tables (experiments I to V). In each table the reagents tested are arranged in the order of their apparent efficiency; all above the blank are inhibitors, all below are activators.

The results given within any table are comparable but titration values in different tables are not. This is due to the fact that the intensity of irradiation differed and that different samples of goldenrod rubber solution were used in the different experiments.

Results and Discussion. The order of efficiency of the reagents tested differed only in a few instances in the different experiments. P-aminophenol acted as an antioxidant (inhibitor) and phenyl-beta-naphthylamine acted as an activator in all cases where they were tested. Some reagents, however, (e. g., JZF, Flectol H and Agerite) acted sometimes as inhibitors and sometimes as activators.

The light reaction in question takes place with light of wave lengths which pass through ordinary Pyrex glass but are held back quite effectively by low-actinic red Pyrex glass.

The titration values for the blanks differ in the different experiments for the same length of irradiation. This is due in part to the fact that the intensity of the irradiation was different and that the samples used contained different amounts of chlorophyll or pigment.

Experiment IV was performed to determine the influence of residual pigments in the sample on the effectiveness of the antioxidant, Flectol H (and incidentally to see if the old and new Flectol H were the same in the light of their behavior in experiments 1 and 2). After the usual carbon cleanup, Sample PC-549 was much less colored than PC-868 and PC-947. The results indicated that the effectiveness of Flectol H as an antioxidant decreased with decrease in pigmentation. Thus, when PC-868 and PC-947 blanks had reached 25+ cc., the Flectol H sample had reached only 9.20 and 8.50 cc., respectively, whereas in PC-549 the blank was only 10.2 when the Flectol H treated sample was 8.50 cc.

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In experiment V the sample was cleaned up by triple treatment with carbon so that it was almost water white. In this case, the sample was much less sensitive to light, as shown by the blank; and p-amino-phenol was the only antioxidant which still inhibited the light reaction.

Phenyl-beta-naphthylamine apparently activates the light reaction in all cases.

Summary. The results of the above experiments seem to show, (a) that the reaction of light on a benzene solution of goldenrod rubber in Pyrex vessels may involve the absorption of at least 9% of its weight of oxygen corresponding to 0.4 atom of oxygen per isoprene unit; (b) that this reaction is much enhanced or activated by the presence of some substance or substances such as chlorophyll or other pigments and that it may be prevented by filtering the light through low actinic red Pyrex glass; (c) that certain antioxidants commonly used in the trade to inhibit rapid aging, inhibit not the light reaction itself but rather the activity of the chlorophyll; (d) that if little or no pigment is present in the benzene solution, these antioxidants may often behave as activators; (e) that para-amino-phenol was by far the most effective of the antioxidants tested in inhibiting the light reaction investigated; and (f) that, since many of the substances tested and found to be activators are known to be good rubber antioxidants, this method of evaluation of antioxidants is therefore not applicable to vulcanizates.

TABLE I

SIXTY MINUTE SUNLIGHT IRRADIATION; 5 MG. OF REAGENT IN 10 CC. OF BENZENE SOLUTION CONTAINING 0.0175 GM. GOLDENROD RUBBER CLEANED UP WITH CARBON TITRATION VALUE ORIGINAL SAMPLE = 4.4 CC.

Reagent	Titration Value cc. sixty minutes
JZF	5.6
Old Flectol H	7.0
Agerite	8.0
Beta-naphthylamine	8.3
Pyrogallol	8.7
Catechol	8.9
Hydroquinone	9.3
Blank	9.6
Quinone	12.0
Phenyl-beta-naphthylamine	15.0
Benzophenone	over 25.0

After sixty minute irradiation in low-actinic red Pyrex glass tube, the titration value was unchanged, 4.4 cc.

TABLE II

SUNLIGHT IRRADIATION 40 TO 125 MINUTES; 5 MG. OF REAGENT IN 10 CC. OF BENZENE SOLUTION CONTAINING 0.0175 GM. GOLDENROD RUBBER CLEANED UP WITH CARBON. TITRATION VALUE OF ORIGINAL SAMPLE = 4.45 CC.

Reagent	Titration Value cc.			
	40 minutes	70 minutes	100 minutes	125 minutes
P-aminophenol	5.10	6.0	6.50	6.7
Stabilite alba	6.4	7.1	7.8	9.5
P.C.P. #5	5.7	6.9	8.5	10.5
Methylumbelliferone	6.7	7.5	9.3	10.6
Ethyl alcohol	6.2	7.5	9.8	12.5
J. Z. F.	6.3	7.7	10.0	11.8
BLE Powder	6.7	8.5	10.5	12.5
Agerite Resin D	5.2	8.5	11.0	—
Blank	6.4	8.3	11.0	13.0
Acetone	6.4	8.0	11.0	16.0
Chlorcarvacrol (crude)	7.0	10.0	12.5	13.0
Thymol cryst U.S.P.	6.3	8.9	11.0	16.0
New Flectol H	6.7	9.0	12.5	13.5
Diphenylamine	8.3	11.3	15.5	24.0
Albasan	7.7	11.0	20.0	25+
Agerite Powder	9.7	16.0	25+	25+
1,4-naphthaquinone	11.0	16.0	24.0	25+
Phenyl-beta-naphthylamine	11.0	19.0	25+	25+
M U F	12.5	20.0	25+	25+
Stabilite	23.0	25+	25+	25+
Chlorothymol N.F. VII	25+	25+	25+	25+
B L E	25+	25+	25+	25+
Carvacrol C.P.	25+	25+	25+	25+

TABLE III

SUNLIGHT IRRADIATION; 5 MG. OF REAGENT PER 10 CC. OF BENZENE SOLUTION CONTAINING 0.0175 GM. OF GOLDENROD RUBBER CLEANED UP WITH CARBON. (SAMPLE SLIGHTLY PIGMENTED.) TITRATION VALUE OF ORIGINAL SOLUTION = 4.45 CC.

Reagent added	Titration Value cc.			
	0 Minutes	40 Minutes	60 Minutes	80 Minutes
Flectol H	4.45	9.5	23.0	25+
	4.45	9.7	23.0	25+
P-aminophenol	4.45	10.0	22.0	25+
	4.45	10.0	22.5	25+
(None Blank)	4.45	25+	25+	25+

TABLE IV

SUNLIGHT IRRADIATION; 5 MG. FLECTOL H PER 10 CC. OF BENZENE SOLUTION CONTAINING 0.0175 GM. OF GOLDENROD RUBBER CLEANED UP WITH CARBON. (THREE DIFFERENT SAMPLES). PC-549 WAS LEAST COLORED.

Sample	Reagent	Titration Value cc.		
		0 Minutes	30 Minutes	70 Minutes
PC-947	Old Flectol H	4.60	8.5	15.0
	New Flectol H	4.50	8.5	14.0
	Blank	4.60	25+	25+
PC-868	Old Flectol H	4.80	9.2	17.5
	New Flectol H	4.90	9.0	15.0
	Blank	4.80	25+	25+
PC-549	Old Flectol H	4.40	6.00	8.6
	New Flectol H	4.50	6.00	8.5
	Blank	4.35	6.5	10.2

TABLE V

SUNLIGHT IRRADIATION; 5 MG. OF REAGENT PER 10 CC. OF BENZENE SOLUTION CONTAINING 0.0175 GM. OF GOLDENROD RUBBER CLEANED UP THREE TIMES WITH CARBON AND ALMOST WATER WHITE. TITRATION VALUE OF ORIGINAL SOLUTION = 4.45 CC.

Reagent	Titration Value cc.			
	13 Minutes	23 Minutes	33 Minutes	43 Minutes
P-aminophenol	4.40 4.50	4.45 4.50	4.50 4.50	4.70 4.70
Blank	4.60 4.50	4.70 4.70	4.90 4.90	5.05 5.10
P.C.P. #5	4.55 4.55	4.80 4.85	4.95 4.95	5.05 5.05
Stabilite alba	4.70 4.60	4.80 4.70	5.10 5.20	5.20 5.30
Methylumbelliferone	4.65 4.65	4.85 4.85	5.00 5.05	5.20 5.25
J.Z.F.	4.70 4.70	4.90 4.90	5.20 5.20	5.30 5.30
Agerite	5.00 4.80	5.40 —	6.70 6.60	7.25 7.35
Flectol H	5.00 5.10	5.95 5.80	7.65 7.75	8.30 8.35
Phenyl-beta-naphthylamine	5.10 5.00	6.50 6.60	8.9 8.9	11.0 11.4

2. Increasing the Viscosity of Goldenrod Rubber and the Formation of Gels by Irradiation in Absence of Oxygen.

It has been shown in the literature that when a benzene solution of raw hevea rubber is irradiated in the absence of oxygen its viscosity increases until finally a gel is formed (1, 2, 3, 4, 5, 6, 7).

This is the basis of U. S. Patent #2,234,743 assigned to the Goodrich Rubber Company. In actual practice this rise in viscosity is preceded by a slight fall in viscosity which is attributed to the presence of minute traces of oxygen which it is practically impossible to remove. The viscosity thus falls until, according to the accepted theory, all of the available oxygen has been used up in oxidation or depolymerization, and then rises due to polymerization until finally a gel forms. If the depolymerization has proceeded too far gelation does not take place.

A sample of goldenrod rubber from Pilot Plant Run #4 containing no Agerite and having a titration value of 4.30, was cleaned up with activated charcoal Merck. The concentration of the solution was 0.02864 gm./cc.

In the following experiments 9.2 cc. (257 mg.) of the cleaned up rubber solution was mixed with various activators and sealed in vacuo in Pyrex tubes. The weight of the activator used was 5 percent on the weight of the rubber except in the experiments with carbon tetrachloride and chlorophyll as the activators. When carbon tetrachloride was used an amount of the carbon tetrachloride equivalent to the amount of benzene was used. When chlorophyll was used 1 mg. of chlorophyll was added to each 250 mg. rubber (0.4%).

The samples were introduced into Pyrex exposure tubes by a capillary-tipped funnel. The solutions were frozen solid in a dry-ice-alcohol slush, evacuated to a pressure of about 0.02 mm. to eliminate most of the oxygen and sealed off with a flame under this vacuum.

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(1) Porritt, B. D., India Rubber J., 60, 1161 (1920).
(2) Pummerer, R., and Kehlen, H., Ber., 66, 1107 (1933).
(3) Smith, W. H., and Saylor, C. P., J. Res. Natl. Bur. Standards, 13, 453 (1934).
(4) Meyer, K. H., and Ferri, C., Helv. Chim. Acta, 19, 694 (1936).
(5) Spence, D. and Ferry, J. D., J. A. C. S., 59, 1648 (1937).
(6) Stevens, H. P., Trans. Inst. Rubber Ind., 16, 211 (1940).
(7) Naunton, W. J. S., Trans. Far. Soc., 38, 332 (1942).

A test run was made on each set of tubes to determine the gelling time in sunlight:

Activator	Gelling Time (hrs.)
Benzophenone	4.5
Benzaldehyde	4.5
Carbon tetrachloride	7
Benzoyl peroxide	8
Maleic anhydride	13 - 15
Quinone	108
Chlorophyll	65
None	-*

* In a previous case, using a wider tube a sample gelled within 10 hours.

A series of tubes from each set was exposed to sunlight for varying periods of time based on gelling time, one tube of each being kept in the dark as a blank. After exposure the tubes were opened, dilutions made, and titration values and viscosities, in solution 0.175 gm. per 100 cc. of benzene at 25° C., determined on the resulting solutions. The undiluted solutions were evaporated to dryness under a stream of CO_2 to compare tackiness.

The results are tabulated in table I and plotted in XIII-E-figure 1 attached. The original values for the viscosities and titration values were different due to the presence of the activators. (See Table on page 40).

In most cases, as was found in hevea, irradiation caused an initial decrease in viscosity and then the viscosity rose above the original value. The titration value would be expected to rise at first due to oxidation and would rise to different values in the different sample tubes of any one set according to the amounts of the "traces" of oxygen left in the tubes.

The abnormal value for the one-hour values for benzophenone and for benzaldehyde and the seven-hour value for maleic anhydride could be explained by the assumption that a larger amount of available oxygen was left in these three tubes so that oxidation or depolymerization proceeded to a much greater extent giving a much higher titration value, 7.60, 8.15, and 13.00, respectively, and a lower viscosity than the other tubes in the set.

In the cases where carbon tetrachloride and benzoyl peroxide were the activators, however, the titration values decreased steadily on irradiation.

For each curve in the graph the last point shown was the last point before gelation took place.

Discussion and Summary. The viscosity of goldenrod can be increased until gelation takes place by irradiation of its benzene solution in the presence of catalysts and in the absence of oxygen. Benzophenone, benzaldehyde, and carbon tetrachloride seem to be the best activators.

In general the viscosity first decreased, due to reaction with traces of oxygen as shown by an increase in the titration value, and then increased. When carbon tetrachloride, benzoyl peroxide, and benzophenone were used as

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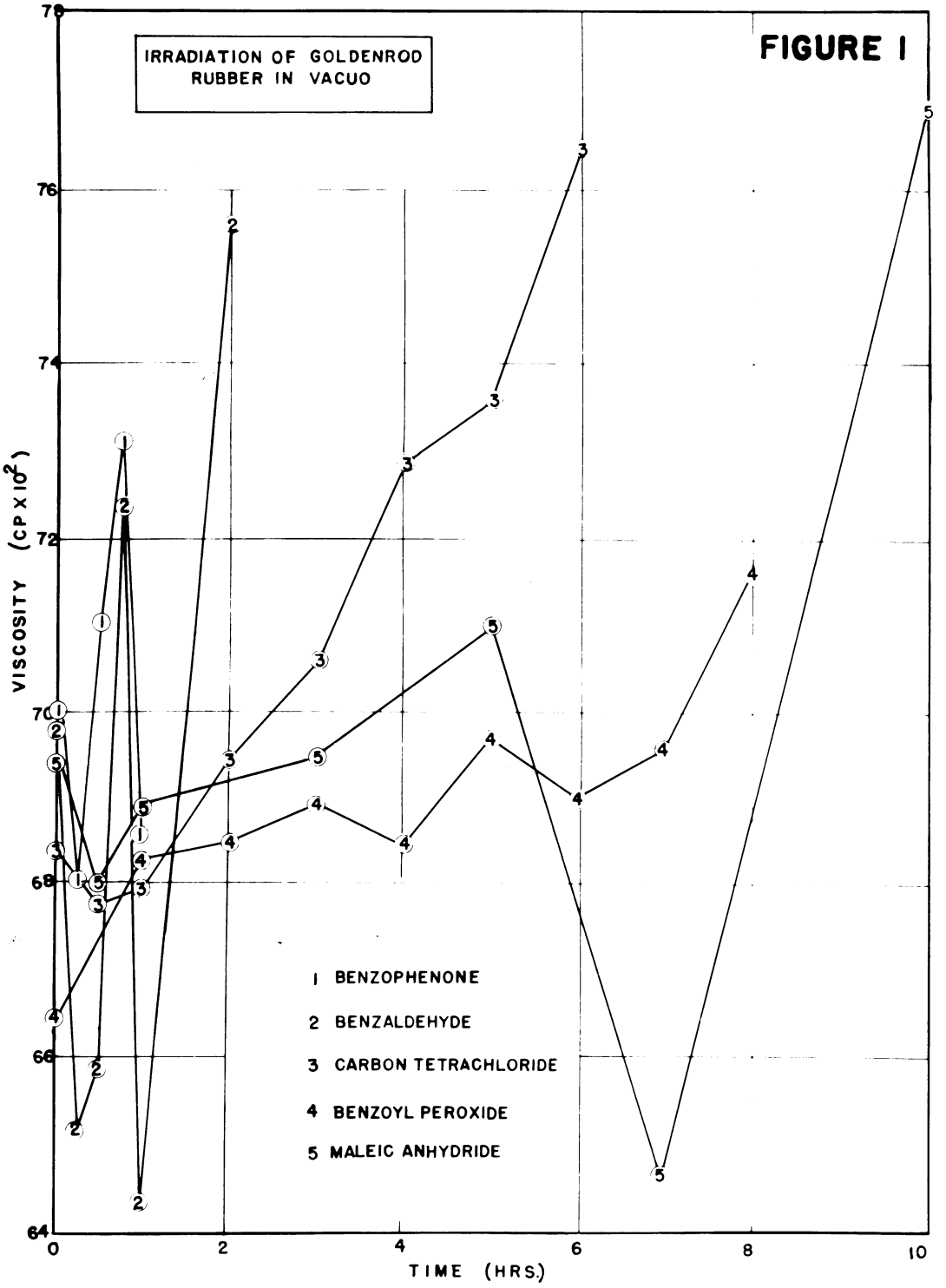
TABLE I

GOLDENROD IRRADIATION IN ABSENCE OF OXYGEN

Activator	Time Exposed (hours)	Viscosity	Titration Value at 25°C.	Stickiness No.
Benzophenone	0	0.700	4.45	1?
"	1/4	0.681	4.75	4
"	1/2	0.710	4.55	4
"	3/4	0.731	4.55	4
"	1	0.679	7.60	4
Benzaldehyde	0	0.698	4.50	2?
"	1/4	0.652	7.00	3
"	1/2	0.659	5.85	2
"	3/4	0.724	4.50	1
"	1	0.644	8.15	1
"	2	0.756	5.75	±
Carbon tetrachloride	0	0.684	4.45	2?
"	1/2	0.679	4.45	3
"	1	0.680	4.40	2
"	2	0.674	4.30	2
"	3	0.710	4.30	1
"	4	0.728	4.30	2
"	5	0.736	4.35	1
"	6	0.765	4.30	2
Benzoyl peroxide	0	0.665	5.05	4?
"	1	0.683	4.90	4
"	2	0.685	4.85	3
"	3	0.690	4.80	2
"	4	0.685	4.75	2
"	5	0.697	4.70	3
"	6	0.691	4.70	4
"	7	0.696	4.65	4
"	8	0.716	4.70	-
Maleic anhydride	0	0.694	4.40	3?
"	1/2	0.679	4.50	4
"	1	0.689	4.65	3
"	3	0.695	4.60	2
"	5	0.710	4.65	1
"	7	0.647	13.00	0
"	10	0.771	4.70	0
"	15	gel	---	-
Quinone	0	0.644	4.60	1?
"	108	0.681	8.20	-
"	208	0.684	8.35	-
Chlorophyll	0	0.694	4.65	3?
"	208	0.724	4.55	-
Blank	0	0.702	4.35	4?

XIII E


IRRADIATION OF GOLDENROD RUBBER IN VACUO
FIGURE I
VISCOSITY (CP X 10²)
TIME (HRS.)
1 BENZOPHENONE
2 BENZALDEHYDE
3 CARBON TETRACHLORIDE
4 BENZOYL PEROXIDE
5 MALEIC ANHYDRIDE

activators the titration value remained fairly constant after reaching a certain level.

When benzaldehyde and maleic anhydride were used as activators there seemed to be a decrease in stickiness as the viscosity increased.

Gelation has been obtained by this procedure in a sample of goldenrod rubber in benzene solution in ten hours without the use of an activator.

After the benzene has been removed from the gel formed by this procedure a product is obtained which is insoluble but swells extensively in benzene, which has no tack or stickiness, and which seems to have lost some of its rubber properties.

This investigation suggests the desirability of irradiating about 50 grams of goldenrod rubber by this procedure (omitting the catalyst) until the viscosity has been raised from about 0.700 to about .730 and then having it vulcanized by the solution method.

Large Scale Photogel Formation and Its Vulcanization. The following experiment was performed to test the vulcanization properties of goldenrod rubber whose viscosity had been increased by irradiation in the presence of CCl_4 and in the absence of oxygen. In order to obtain a sample of rubber containing no antioxidant (antioxidants are said to inhibit the irradiation reaction), 886 grams of goldenrod leaves ground to 30 mesh were extracted in the "dark extractor"; acetone extraction 28 hours, benzene extraction 24 hours, 6.75% yield.

The 2400 cc. of benzene solution containing about 60 grams of rubber were treated with 60 grams of activated carbon (Merck), slurried, allowed to stand overnight in the dark, and filtered through a thin layer of carbon under an atmosphere of CO_2 (except for the first 15 minutes or so of the filtration, when the solution was inadvertently exposed to air). The clear filtrate was evaporated under reduced pressure to a volume of 800 cc. at 30-35° C. under a CO_2 atmosphere. It was transferred to a special irradiation tube made of 70 mm. Pyrex tubing and an equal volume of carbon tetrachloride was added. The tube was degassed by successively freezing and evacuating to 3-4 mm. twice. Irradiation was then carried out in sunlight removing 10 cc. samples from time to time to follow the change in viscosity. The original sample removed before irradiation had an absolute viscosity of 0.663 c.p. at 25° C. in 0.175% concentration. After 8 hours of exposure the viscosity had changed to 0.690. It had been intended to raise the viscosity to about 0.72 but an accident to the apparatus necessitated the termination of the irradiation. The bulk of the solution was treated at once with antioxidants and compounding materials in a distilling pot by The Engineering and Development Division, and finally vulcanized.

They reported that the sample required a higher temperature of cure than usual. One 60-minute cure 30° higher (290° F) gave 1430 p.s.i., and the sample bloomed on standing indicating that it was still not completely cured.

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F-MODIFICATION OF GOLDENROD RUBBER

Goldenrod rubber has the undesirable quality of being sticky and soft. This makes it difficult to mill and compound on the rolls like hevea. There seem to be at least two causes for this stickiness and softness, (1) the presence of oxidative degradation products, and (2) the fact that it has a lower average molecular weight and consequently a lower melting point. A number of methods were applied to modify goldenrod rubber so as to make it non-sticky and heavier-bodied without precompounding or precuring it. These methods may be classified under the headings (1) purification by extraction of the oxidized and the lower molecular weight fraction, (2) polymerization, or copolymerization with styrene or acrylonitrile, using a catalyst such as sodium, diazoaminobenzene, or benzoyl peroxide, (3) reaction with maleic anhydride in the presence of a catalyst, (4) treatment with formaldehyde; and (5) mixture with resins and similar substances. These will be taken up in the order named.

1. Modification by Extraction with Solvents.

It was shown by Bloomfield and Farmer that the oxidized fraction and the lower molecular weight fraction of hevea rubber can be extracted by a mixture of acetone and petroleum ether. This method has been applied to goldenrod rubber and it has been shown that a rubber of higher viscosity giving a vulcanizate of higher tensile strength could be so obtained. It was evident from these experiments that a better rubber would be obtained in the pilot plant if a small percentage of benzene were present in the acetone used for extracting the resins from the goldenrod leaves prior to benzene extraction. This was verified by results of Pilot Plant Run 17. This treatment caused a substantial lowering of the yield of rubber obtained in the benzene extract. Further preliminary experiments were therefore performed to obtain information as to the solubility of goldenrod rubber in various concentrations of different solvent mixtures. The details of these preliminary solubility determinations are appended to the following description of the fundamental experiment.

<u>Extraction of Rubber to Isolate Fractions of Higher Viscosity and Greater Tensile Strength.</u> One hundred and twelve grams of benzene extract from Pilot Plant Run #4 were slurried with 112 grams of Merck activated carbon and, after standing 12 hours, it was filtered through a layer of carbon and filter cell on a Buchner funnel into a suction flask containing 1.12 grams of Agerite. The solution was evaporated to a syrup under partial vacuum and precipitated with acetone then dried by heating in a stream of oxygen-free nitrogen.

83 grams of this product were placed in a 6-liter Erlenmeyer flask and covered with 2-1/2 liters of a mixture of 60% acetone and 40% petroleum ether by volume. The air in the flask was displaced by CO_2, and, after stoppering, the flask was kept in a dark cabinet for six days with occasional tilting. The supernatant liquid was then decanted and, after adding 200 mg. of Agerite, stored in a stoppered Erlenmeyer flask under CO_2 (fraction 1).

The residue was covered with 2-1/2 liters of a 50-50 mixture of acetone and petroleum ether, 200 mg. of Agerite added, and kept under CO_2 in the

Bloomfield, C. F., and Farmer, E. H., J. Inst. Rubber Ind., <u>16</u>,69 (1940).

dark for 10 days. The supernatant liquid was decanted and a washing with acetone added to it (fraction 2).

The residue was dried by heating in a stream of oxygen-free nitrogen and labelled (fraction 3).

Fractions 1 and 2 were finally brought to dryness in a vacuo, dried in a stream of oxygen-free nitrogen, and weighed. Samples were removed from each fraction for determination of titration value, viscosity, iodine number, carbon, hydrogen, and nitrogen.

Fractions 1 and 2 combined and fraction 3 were dissolved in benzene and submitted to the Engineering and Development Division for vulcanization. The results are given in the accompanying table I.

Solubility Experiments. In the above experiment which was carried out to show the possibility of fractionating goldenrod rubber, no attention was paid to yield or speed of extraction.

A number of small-scale solubility experiments were then performed for the purpose of obtaining data for possible use in choice of solvents and temperature to obtain a high yield and rate of extraction in fractionation investigations.

(a) Solubility of Goldenrod Rubber With Acetone-Skellysolve B Mixtures at 45° C. Goldenrod rubber from Pilot Plant Run #4, was cleaned up with carbon, acetone precipitated, and dried in a stream of oxygen-free nitrogen. Ten-gram samples were placed in 500 cc. stoppered Erlenmeyer flasks, covered with 250 cc. each of various mixtures of Skellysolve B and acetone, and allowed to stand in a constant temperature bath at 45° C. in a dark room. At intervals, 5 cc. aliquots were removed, evaporated to dryness, and weighed to follow the rate of dissolution. Before taking a sample, the supernatant liquid was swirled gently to make it homogeneous. The data are represented in graph XIII-F-figure 1. The extraction was, in all cases, practically complete in 24 hours in the amounts shown in the following table:

(10 grams of samples to 250 cc. of solvent - 45°C.)

10%	Skellysolve	B - 90%	Acetone	2%	dissolved
20%	"	" - 80%	"	3%	"
30%	"	" - 70%	"	8%	"
40%	"	" - 60%	"	28%	"

(b) Solubility of Goldenrod Rubber in Acetone-Benzene Mixtures at 45° C. Goldenrod rubber from Pilot Plant Run #4 was cleaned up with carbon and then precipitated with acetone and dried in a stream of oxygen-free nitrogen. Ten-gram samples were placed in 500 cc. stoppered Erlenmeyer flasks, covered with 250 cc. of solvent, and allowed to stand in a constant temperature bath at 45° C. in the dark. Five cc. portions were removed during the course of the experiment after mixing the supernatant liquid to make homogeneous, and total solids were determined. The total amounts dissolved after equilibrium had been reached, about 28 hours, were as follows:

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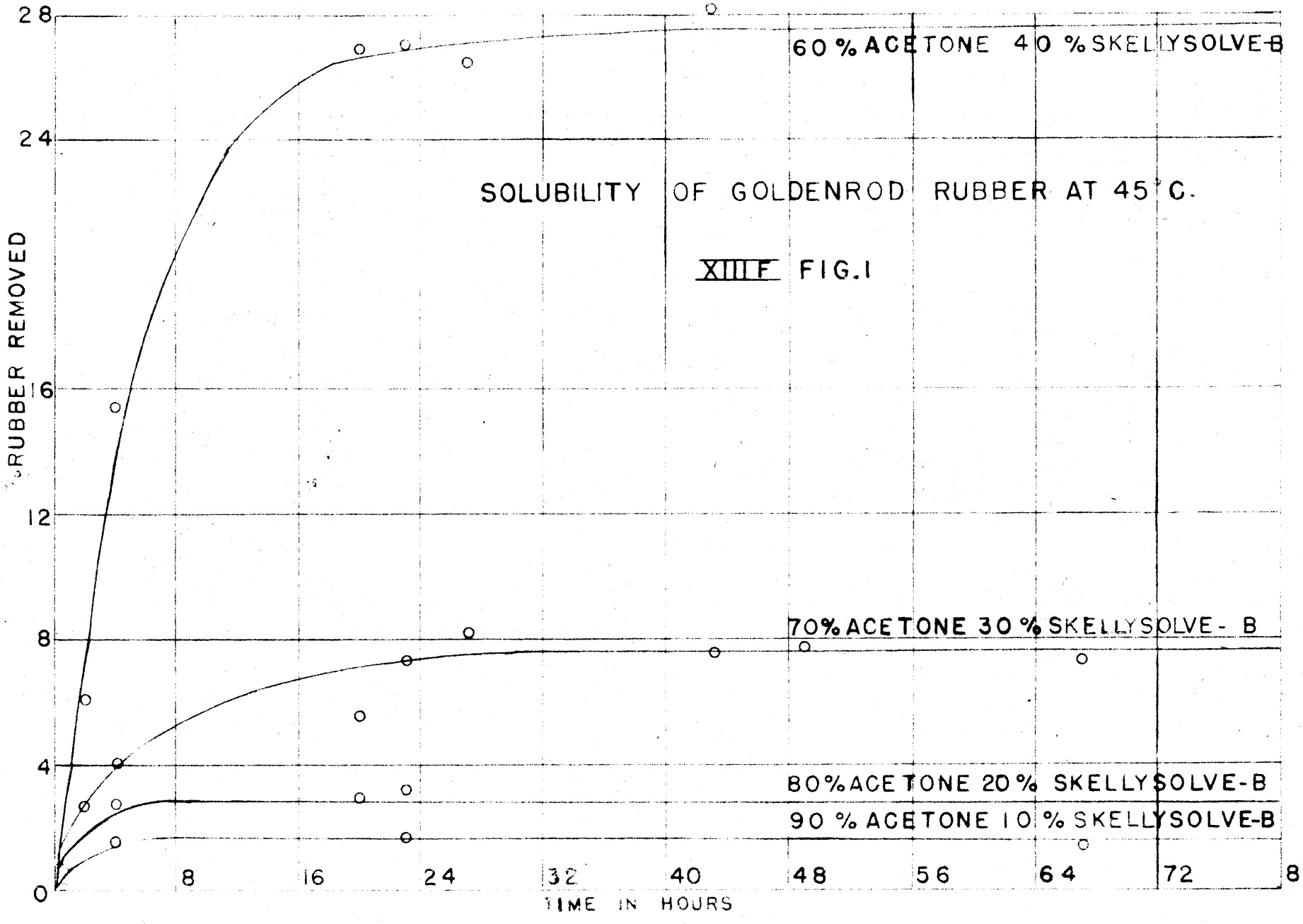
TABLE I

FRACTIONATION OF GOLDENROD RUBBER

Fraction No.	Solvent Mixture by Vol.	Sample Weight	Titration val. at 25°C. (*)	Viscosity 0.175% soln. in benzene	Iodine No.	Analysis C	Analysis H	Analysis N	Vulc. No.	Time of Cure	Tens. str.	Ult. Elongation
		gm	cc.	c.p.		%	%	%		Min.	p.s.i.	%
1	Portion soluble in 40-60 mixt. pet. ether - acetone	6	5.50	0.625	339	83.5	10.45	0.50				
					337	83.4	10.45	0.55	204A	60'	435	550
									204B	40'	540	550
2	Portion of residue from #1 soluble in 50-50 pet. ether-acetone	14	5.35	0.623	344	86.9	11.46	0.09				
					346	86.0	10.45	0.09				
3	Portion of residue from #2 insoluble in 50-50 pet. ether-acetone	52	4.45	0.722	355	84.6	11.06	0.03	203A	60'	2590	700
					354	84.4	10.95	0.03	203B	75'	2500	750
					357				203C	45'	2610	775
									203D	30'	2490	800

* Titration value original sample was 4.35 cc.


SOLUBILITY OF GOLDENROD RUBBER AT 45°C.
XIII F FIG. I
60 % ACETONE 40 % SKELLYSOLVE-B
70% ACETONE 30 % SKELLYSOLVE- B
80% ACETONE 20 % SKELLYSOLVE-B
90 % ACETONE 10 % SKELLYSOLVE-B
% RUBBER REMOVED
TIME IN HOURS
0
4
8
12
16
24
28
8
16
24
32
40
48
56
64
72
80

XIII F

(10 grams of sample to 250 cc. of solvent - 45° C.)

20%	benzene	-	80%	acetone	3% removed
30%	"	-	70%	"	10% "
40%	"	-	60%	"	44% "
50%	"	-	50%	"	80% "

(c) Solubility of Very Poor Grade of Goldenrod in 50-50 Acetone-Skellysolve B Mixtures at Room Temperatures. After cleaning up and acetone-precipitating Pilot Plant Run #2, which had a titration value of 4.85, 68% of the sample was soluble at room temperature in 20 volumes of 50-50 mixture of these solvents.

It would thus not be practicable to obtain a reasonable yield of high molecular weight rubber from this poor degraded sample of goldenrod rubber.

The soluble or oxide fraction was brought to dryness in a vacuo and used to make solubility tests with some thirty solvents, which were carried out simultaneously on a good sample of goldenrod rubber of titration value 4.3 cc. Ethyl acetate showed the biggest difference in comparison with the good rubber.

(d) Solubility of Goldenrod Rubber in Ethyl Acetate. Goldenrod Pilot Plant Rubber #3 was cleaned up with a carbon slurry and brought to dryness in vacuo; 8 grams of this material were allowed to stand under 300 cc. ethyl acetate in the dark for 24 hours at room temperature and then the turbid supernatant liquid was decanted and evaporated to dryness in vacuo, dissolved in benzene and cleaned up with carbon. The residue was dried in vacuo, dissolved in C_6H_6 and cleaned up with carbon.

(8-gram sample to 300 cc. ethyl acetate - room temperature)

	Titration Value	Absolute Viscosity 0.175% C_6H_6 soln.
Soluble fraction 18%	6.30 cc.	0.650 c.p.
Insoluble fraction 82%	4.60 cc.	0.721 c.p.

Method of Obtaining Improved Grade of Goldenrod Rubber in Pilot Plant by Use of Mixed Solvents. Pilot plant rubber can thus be fractionated with (a) acetone-benzene mixtures, (b) acetone-Skellysolve B mixtures, or (c) ethyl acetate at room temperature to obtain a rubber of a higher viscosity and therefore, probably a higher molecular weight. The lower molecular weight fraction could be recovered for other possible uses.

The above results suggest that it would be advantageous to mix a little benzene (or petroleum ether) with the acetone in the initial acetone extraction of goldenrod leaves. The "oxide" and low-molecular-weight fraction of the rubber would then be expected to be removed with the resins so that the final benzene extract would contain a smaller yield of a better grade of rubber. The optimum proportion of the solvents to be used would depend on the duration of extraction or the total volume of solvent passing over the leaves. The solvent in the boiler would, of course, be lower in acetone-percentage than that desired in the extractor. It was suggested that the

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effect of addition of various amounts of benzene to the acetone be investigated in the pilot plant. This principle was involved in Pilot Plant Run #17 in which some 20% of benzene was present in the acetone used for resin extraction from the leaves. As is evident from the data on this sample, given above in sections XIII-C and D, the product of Pilot Plant Run #17 was actually a much better grade of rubber and was relatively non-sticky and hard.

In this run, however, the amount of rubber which was extracted with the resins and therefore lost was very considerable, as is shown by the low yield of rubber (reported about 60% of the usual yield). It seemed possible that approximately the same effect could be attained with a higher yield if a smaller percentage of benzene were used in the acetone.

The "solubility" data below were therefore obtained to serve as a basis for the selection of the optimum proportion of benzene in acetone to be used for the extraction of resins by the pilot plant process at 25°C. It may be possible to obtain an improved goldenrod rubber by extracting the more soluble, less desirable fraction of the rubber with the resins in this way without an inordinate sacrifice in yield.

Pilot plant #27 goldenrod rubber extracts first 12 hours and last 12 hours were mixed in the ratio of their yields, 3.8 to 1, to give a representative mixture for the whole extraction. The rubber was acetone precipitated and dried in vacuo. Ten-gram samples of this mixture were allowed to stand at 25° C. under successive 200 cc. volumes of acetone-benzene mixtures of various ratios. The usual diffusion solubility technique used in rubber fractionation, i.e., with no stirring, was followed. After various periods ranging from 28 to 48 hours the solvent was decanted and replaced with fresh solvent of the same composition. Total solids were determined on the solutions decanted.

The total percent dissolved after six passes for the various solvent mixtures is shown in the following table. The total duration of the extraction was ten days. The amounts extracted in the sixth pass varied from 0.25% to 0.47%; this extract was probably made up in considerable proportion of oxidized or otherwise degraded rubber formed during the extraction judging from previous experience.

Volume Ratio acetone-benzene	Percent Dissolved						Total
	Pass #1	#2	#3	#4	#5	#6	
85-15	.82%	.48%	.35%	.41%	.15%	.25%	2.5%
80-20	1.32	.91	.81	.65	.44	.43	4.6
78-22	1.32	.98	.77	.66	.41	.31	4.5
75-25	1.55	1.30	1.06	.95	.40	.47	5.7

The results indicate that at 25°C. some 15% of benzene in the acetone coming from the still-pot might be tolerated without too great a loss of rubber in the resins. The loss can be expected to be greater than the 2.5% shown in the table since 24 passes at least would be used in the pilot plant and because of the lower efficiency of extraction by the diffusion method above.

Additional data should be obtained on the titration values and viscosities of fractions obtained by fractionation of pilot plant rubber with the various solvent mixtures mentioned above, with particular emphasis on mixtures which would give a good grade of rubber in high yield.

2. Modification by Polymerization and Copolymerization.

A polymerization of 200 grams of pilot plant goldenrod rubber containing antioxidant was performed by shaking the 13.5% benzene solution with 20 grams of thinly sliced sodium. The reaction was continued for two weeks, being shaken in the daytime and stationary at night (total shaking time 87 hours). The top of the rubber solution was decanted and precipitated with alcohol, washed with acetone, and dried - total weight 81 grams. It was considerably less sticky than the original rubber. The sodium was picked out of the remaining more gel-like solution, and the solution was decanted from lumps of sodium resinates and evaporated to dryness. This sample, weighing 107 grams, contained pockets of brownish resinous solid material, probably resinates, but was drier and had much body and toughness. No tests were run on these samples.

A typical small-scale copolymerization experiment with styrene was performed as follows:

A 10% solution of goldenrod rubber in benzene, 10% of sliced metallic sodium, and 20% of redistilled styrene on the rubber were shaken intermittently and after 10 days, gelling had taken place. A semi-hard product was removed by acetone precipitation and submitted for test. "The sample milled very well. It was not lacy and could be sheeted. This material was only slightly sticky and it appeared to have sufficient body so that compounding chemicals could probably be incorporated satisfactorily."

Copolymerization of goldenrod rubber with acrylonitrile was also attempted but the product showed no marked improvement.

3. Modification by Treatment with Maleic Anhydride

It has been found that the properties of goldenrod rubber can be modified over a wide range by simple treatment of the benzene solution with various proportions of maleic anhydride in the presence of a catalyst. The possibility of obtaining this effect was suggested by recent publications and patents of Bacon and Farmer and of Dickhauser.

Bacon, R. G. R., and Farmer, E. H., Rubber Chem. and Tech., 12, 200 (1939); British Patents 535,889 and 541,167 (1941) assigned to The British Rubber Producers' Research Association.

German Patent 544,326 (1932) assigned to the I. G. Farbenind.

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Bacon and Farmer made a thorough study of this reaction on hevea rubber and reported that the products obtained varied from rubberlike substances when 7% of anhydride on the rubber was used, to hard, horny substances when 100% was used.

In applying this reaction to goldenrod rubber, the general procedure was as follows:

A 10% benzene solution of goldenrod rubber containing the maleic anhydride and the benzoyl peroxide in the desired proportions was heated for about 3 hours on a steam bath or until a small sample evaporated on a watch glass gave a non-sticky product. The solution was then evaporated to a syrup and the rubber precipitated with acetone and dried in vacuo to remove the solvent.

Various ratios of maleic anhydride and benzoyl peroxide were tried and the product obtained varied accordingly. One percent of maleic anhydride and 1% of benzoyl peroxide on the rubber gave a product which was still sticky; 2%-2% gave a fair product better than 3%-1%. The product obtained with 3%-3% of anhydride and benzoyl peroxide was very similar in its appearance, body, and toughness to hevea. Higher percentages of maleic anhydride and catalyst, above about 9%, gave hard brittle resinous products. It was found that fresh maleic anhydride gives a better product.

A fifty gram sample made with 3% of maleic anhydride and 3% of benzoyl peroxide was submitted for test. It was reported to have excellent milling properties. "It worked well on the rolls, picking up carbon to form an excellent dispersion. Thus compounded it could actually be calendered in thin sheets on the rolls. A 30 minute cure with 0.5 part of D. P. G. gave a soft sticky vulcanizate which bloomed; a 30 minute cure with 0.5 part of D. P. G. and 5.5 parts of zinc stearate gave a vulcanizate which had a tensile strength of 1520 p.s.i. and an ultimate elongation of 600%. This vulcanizate bloomed." The acid value of the unvulcanized rubber was reported to be equivalent to 2400 mg. of KOH per 100 grams of rubber. This was taken into account in various compounding formulas used but the vulcanizates so obtained were very poor.

A fifty gram sample of maleic acid-benzoyl peroxide reaction product with an acid value about the same as the above-mentioned sample was dissolved in benzene and refluxed with 2% alcoholic potassium hydroxide, after which it was precipitated with alcohol, washed, and dried. The product was completely non-sticky and resembled a vulcanized gum stock of very low tensile strength. No tests were made on this sample as it had practically no tack and it was obvious that it would not mill well.

<u>Further Possible Applications of Maleic Anhydride Reaction.</u> The marked change obtained in the alcoholic KOH treatment just described suggests that a non-sticky goldenrod rubber may be obtained by so treating a maleic anhydride reaction product formed with a very low percentage of maleic anhydride and benzoyl peroxide.

Furthermore, it should be pointed out that the purpose of Farmer's patent on this reaction with hevea was not to make a non-sticky rubber, but rather

to make a resinous material which was compatible with cellulosic materials. For example, in British patent 541,167, the statement is made that "acetone solutions of cellulose acetate and of the maleic anhydride-rubber derivative are mutually compatible and by mixing acetone solutions of the two materials it is possible to incorporate the maleic anhydride-rubber derivative uniformly into cellulose acetate". It is in fact possible by the claims of this patent to cause chemical combination of the rubber and cellulose derivatives. Thus claim 1 covers "a process for the preparation of modified rubber derivatives or resins consisting in combining rubber with esters or ethers of cellulose by reaction with maleic anhydride". It seems likely from these statements that a solution of goldenrod rubber subjected to these reactions with a fairly large percentage of maleic anhydride could be applied to tire cord to improve its adhesion to rubber since the derivative would be expected to be compatible with both rubber and cellulose.

Diazoaminobenzene Instead of Benzoyl Peroxide as a Catalyst. A preliminary experiment showed that diazoaminobenzene can be substiuted for benzoyl peroxide as a catalyst for the maleic anhydride reaction with goldenrod rubber. The product obtained with 2% of maleic anhydride and 1% of diazoaminobenzene at 80° C. for three hours was slightly sticky. It was submitted to the Engineering and Development Division who reported as follows: "It resembled nervy reclaim on the rolls, and would not sheet well as it was extremely lacy. It was only slightly sticky and appeared to have sufficient body so that compounding chemicals could be incorporated satisfactorily on the rolls". It seems probable that better products could be obtained by trying various modifications of the percentages used.

4. Modification by Treatment with Formaldehyde.

This treatment was suggested by a step in the preparation of "U.S.F., a New Crude Rubber" described by McGavack in a recent article of that title.

McGavack, J. M., Ind. Eng. Chem., 34, 1335 (1942).

In that process, hevea latex is treated with formaldehyde as soon after tapping as possible. It prevents bacterial and enzymatic changes and acts as a stabilizer, especially against oxidation. When a sample of sticky goldenrod rubber sticking firmly to a glass or iron vessel was covered with 37% formalin, it could be scraped away from the walls with a spatula after about an hour. By drying in a stream of nitrogen and then in vacuo a product was obtained which was definitely much less sticky and which had more body than the original.

Since this treatment seemed more or less superficial, various other methods were tried to obtain a good mixture of the rubber with formaldehyde. These included (a) precipitation of the rubber from a benzene solution with acetone containing paraformaldehyde and formaldehyde and (b) soaking the ground goldenrod leaves in formalin before extracting the rubber. The products obtained however showed no improvement.

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5. Modification by Addition of Resins.

Various coumarone and indene resins were mixed with the rubber in benzene solution but the products obtained were still very sticky.

Summary of Investigation of Modification of Goldenrod Rubber. Goldenrod rubber can be improved by extraction with suitable mixtures of a solvent and non-solvent. The lower molecular weight fraction and the oxidized or degraded fraction can thus be removed leaving a much less sticky product with a higher viscosity and giving a vulcanizate of much higher tensile strength. On the basis of these experiments it was predicted that addition of benzene (solvent for rubber) to the acetone (non-solvent for rubber) used in extracting the resins from goldenrod leaves would result in a rubber which on subsequent benzene extraction of the leaves would be harder and non-sticky and which would give a vulcanizate of a much higher tensile strength. Pilot Plant Run #17 showed this to be true. Additional solubility data have been obtained to assist in a choice of solvent mixture to accomplish this effect with less loss in yield.

The purpose of the remainder of this series of experiments was to obtain a goldenrod rubber in a non-sticky form which could be compounded on the rolls. Therefore, unless the products obtained by the various methods milled well, no vulcanization was carried out.

Sodium polymerization does not look promising. In the first preparation by this method two fractions were obtained, a lighter top fraction of the reaction mixture still slightly sticky, and a heavier fraction much less sticky. In a second preparation, the yield was collected as a whole and was still too sticky to mill. A non-sticky product can perhaps be obtained by collecting only the gelled product, but this would entail a loss in yield. The fact that the sodium polymerization even with catalysts is time-consuming also argues against its use.

The product with the best milling properties was perhaps a reaction product with 3% maleic anhydride and 3% benzoyl peroxide. It had an extremely high acid value and this may have contributed to its poor vulcanization properties. The sample obtained by subsequent treatment with alcoholic KOH was so non-sticky and non-tacky that it behaved like a vulcanized gum stock and, therefore did not mill well. It is possible that if this KOH treatment is used on a sample prepared with much smaller percentages of maleic anhydride and benzoyl peroxide, a suitable degree of non-stickiness may be attained without impairing the vulcanizability.

Treatment of solid pilot plant rubber with formalin solution was shown to reduce stickiness and increase hardness superficially. Mixing pilot plant rubber on the rolls with carbon containing formaldehyde or paraformaldehyde might perhaps give good results.

These experiments were discontinued because of the success of the method of precompounding described elsewhere in this report.

G-CONTROL DETERMINATIONS

In the course of the program a large number of measurements were made for the purpose of pilot plant control. These included over 1800 samples as summarized below and involved over 4000 separate determinations.

Titration values	247
Viscosities	170
Analysis of acetone-benzene-water mixtures	1292
Density of Abrasion blocks	86
Fractionation to show distribution	38
Miscellaneous including molecular weights, pH, solubilities, preparation of rubber solutions, ASTM solvent tests, thermometer calibrations and fractionation of 324 liters of solvents	111
	2044

XIV - ANALYTICAL INVESTIGATIONS

METHODS FOR THE ESTIMATION OF RUBBER CONTENT OF GOLDENROD MATERIAL

The method used during the first part of the work was as follows:

Moisture. Weigh accurately duplicate two gram samples into American Oil Chemists' Society aluminum moisture dishes. Place the uncovered dishes in a forced-draft oven at 105° C. for 2.5 hours, keeping draft at a minimum. Cover the dishes, remove from oven, cool in a desiccator for 30 minutes, weigh and calculate loss of weight as moisture.

Acetone Extractible Material (so-called resins). The extractions were made in Smalley type extractors with ground ₮ 24/40 joints at bottom and ₮ 45/50 joints at top, equipped with Hopkins condensers with drip tips. The flasks were 100 ml. in capacity with ₮ 24/40 joints. The acetone extraction may be made on either a variable controlled hot plate or on a steam bath. Blanks should be conducted on the acetone.

Weigh accurately duplicate samples of about 5 g. of the ground goldenrod material and fold in two filter papers in the conventional cottonseed wrapping manner, using C. S. and S. No. 597 15-cm. paper or equal. To distribute the solvent place a piece of absorbent cotton at the top of the second paper which serves as a thimble. See A.O.A.C. 5th edition, page 446. Place 50 ml. of acetone into each tared flask and extract for exactly 6 hours at a rapid, constant rate of drip. Evaporate almost to dryness, collecting the acetone in a small glass tube which replaces the thimble when the evaporation process takes place. Place the flasks in a vacuum oven at 65° for 2.5 hours, cool in a desiccator for at least 1/2 hour and weigh. Correct for blank.

Benzene Extractible Material (rubber). Remove the wrapped samples from the acetone extractions and leave in open beakers over night. Then replace in the extractors equipped with tared flasks containing 50 ml. benzene. Extract for exactly six hours at a rapid, steady rate, heating on a variable controlled hot plate. Remove most of the benzene and place in a vacuum oven for 2.5 hours at 65° C. Cool in desiccator for at least 1/2 hour and weigh. Correct for blank on the benzene.

Fineness of Grinding in Relation to Efficiency of Extraction. It soon became evident that when the above method was used, fineness of grinding had a marked influence on the results. In one particular sample, acetone and benzene extracts were conducted on portions A and B of the sample, A being the sample as it was received and B being the sample after milling in a "micro" Wiley mill using the 20 mesh screen. As shown in the table below, a large difference was found:

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	% Moisture		% Acetone Extract		% Benzene Extract	
	Independent	Avg.	As rec'd	MFB	As rec'd	MFB
A	7.38	7.41	12.4	13.3	5.7	6.1
	7.43		13.5	14.6	5.6	6.0
B	6.62	6.60	18.7	20.0	7.7	8.2
	6.58		17.8	19.0	8.0	8.5

To show what effect an intermediate particle size would have, some of the same lot (GRG 70) was ground in a large Wiley using a 10 mesh screen. The results follow:

% Moisture		% Acetone Extract		% Benzene Extract	
Independent	Avg.	As rec'd	MFB	As rec'd	MFB
8.13	8.11	16.9	18.5	6.03	6.56
8.08		15.9	17.3	6.28	6.83

It can, therefore, be deduced that even at this fineness (which is approximately 99% at 30 mesh), a greater yield is extracted than without milling. It is clear that the extra fine milling makes possible the extraction of a good deal more rubber.

The same lot, not ground in the Wiley, was extracted in the Pilot Plant in two different runs of twenty-four hours each, with following results:

Run No.	9	10
Benzene extract (as is basis)	4.77	4.94

The residues from these runs were milled in the large Wiley using a 10 mesh screen and much benzene-extractable material was found:

Run No.	9	10
Benzene extract (as is basis)	3.07	2.51

The sums of the Pilot Plant extract and Pilot Plant unextracted "rubber" add to approximately the "rubber content" as determined on the very fine basis:

Run No.	9	10
Benzene extract	7.84	7.45

The effect of fineness of grinding was studied in greater detail on a number of original samples of miscellaneous unextracted and pilot plant extracted goldenrod. Each sample was coned and quartered and divided in half. One-half was not altered in any way, but the other half was milled in a micro Wiley mill using a 20-mesh screen. The samples which were not reground varied in particle size from very coarse to fine. One sample of unextracted goldenrod and one of extracted goldenrod, both milled in the micro Wiley with 20 mesh screen, were given screen analyses. The results, which are a good indication of the general trend followed

throughout the samples, follow:

	% passing thru 40 mesh	% passing thru 60 mesh
Unextracted	93.7	46.7
Extracted	93.8	41.5

Duplicate determinations were conducted on each unground sample as well as on each ground sample. These included moistures run at 105° C. for 2-1/2 hours, 6-hour acetone extractions, and, on the acetone-extracted samples, 6-hour benzene extractions.

As regards moisture values, it was never quite predictable whether the material would gain or lose moisture during milling. Some few samples varied from 0.2% to as much as 1% between milled and unmilled portions.

The true extent of the differences in extraction can be gained by studying the data on some paired samples. For example, coarsely ground samples in this group averaged 5.4% rubber when analyzed as received. These same samples, finely ground, averaged 6.5% rubber. The relative increase of effect of fine grinding on the same material, after partial extraction of rubber in the pilot plant, is also noted. The average value for these partially extracted samples when analyzed as received was 1.3% rubber and when analyzed finely ground, 1.9% rubber, as per Table I.

Residues from the analytical extractions were submitted for microscopic examination. Although the results do not all show the same trend, the great majority of residues from the extractions of fine material showed less rubber than those from coarse material. Also, in most cases, the amount of rubber left in a residue from the extraction of fine material was little or none at all.

In an effort to determine whether or not fineness of grinding had any effect on the quality of the rubber extracted, all the benzene extracts were carefully redissolved in benzene and collected as the analyses proceeded. Collection was conducted under two main groupings, ground and unground, each of which was subdivided into two more groupings...rubber extracted from original goldenrod leaves and rubber extracted from pilot plant extracted residues. To determine what percentages of the four rubbers were "resins", two methods were employed:

1. Acetone extraction for 6 hours.
2. Double throw down method, the essentials of which are:
   (a) Dissolve in benzene, precipitate with acetone KSCN and centrifuge.
   (b) Decant supernatant and evaporate off solvent.
   (c) Add acetone, mix and centrifuge.
   (d) Decant supernatant, evaporate off solvent and weigh residue as "resins" after correcting for blank.

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XIV - TABLE I
SOME PAIRED ANALYSES SHOWING EFFECT OF FINE GRINDING

% ACETONE EXTRACTS (MFB)						% BENZENE EXTRACTS (MFB)					
Original Material			Corresponding Residue			Original Material			Corresponding Residue		
Anal. No.	As Rec'd	Finely ground	Anal. No.	As Rec'd	Finely ground	Anal. No.	As Rec'd	Finely ground	Anal. No.	As Rec'd	Finely ground
AF-923	16.5	18.7	AF-926	6.07	7.40	AF-923	5.77	7.40	AF-926	0.57	0.92
AF-950	15.2	19.6	AF-949	0.84	1.05	AF-950	5.61	8.29	AF-949	3.72	4.45
AF-951	14.6	17.5	AG-74	0.58	1.09	AF-951	5.07	5.57	AG-74	0.98	1.71
AF-952	13.8	17.4	AG-75	0.93	2.02	AF-952	7.73	7.88	AG-75	1.04	1.45
AG-442	14.7	16.4	AG-443	2.35	3.24	AG-442	5.27	6.12	AG-443	1.60	2.31
AG-444	14.7	18.4	AG-445	1.34	2.71	AG-444	5.10	4.91	AG-445	1.53	2.34
AG-446	13.3	16.0	AG-447	0.56	1.88	AG-446	-	-	AG-447	0.54*	1.53*
AG-448	16.5	17.6	AG-449	1.77	1.21	AG-448	4.13	4.84	AG-449	0.37	1.14
AF-928	13.4	15.6	AF-927	0.94	0.94	AF-928	4.76	5.89	AF-927	0.59	0.88
Avg.	14.7	17.5		1.71	2.39	Avg.	5.43	6.46		1.30	1.90

* These figures not included in average.

A comparison of the values obtained by each method follows:

Method of determination of "resin" content of rubber	"Resin" content of: Rubber from original goldenrod material: Extracted from fine samples	Extracted from coarse samples	Rubber from pilot plant residues: Extracted from fine samples	Extracted from coarse samples
	%	%	%	%
6 hour acetone extraction of rubber	5.4	16.4	9.4	18.0
Double throw down method	7.4	19.4	13.2	21.1

These results show that regardless of the method used for estimating the "resin" content of the analytically extracted rubber fractions, the rubber extracted from finely ground samples contains much less "resins" than that extracted from coarsely ground samples.

Moisture Content of Samples in Relation to Efficiency of Extraction. Since experiments described in another section of this report showed that rubber could be extracted more rapidly and completely from completely dry goldenrod material, the effect of moisture was investigated in relation to the analytical extraction. In conjunction with these investigations, the relative rubber extraction qualities of Skellysolve B and benzene were studied side by side. The goldenrod used throughout GRG-43(AE-454) was finely ground in a micro Wiley mill using a 20 mesh screen. The standard analytical sample was exactly 5 grams of this raw material and all percentages given in this report are on the basis of this standard analytical sample.

All of the solvents employed were dehydrated prior to extraction. The acetone was dehydrated with calcium chloride and the benzene and Skellysolve B with calcium oxide. These anhydrous solvents were employed exclusively, regardless of pre-extraction treatments of the goldenrod. Also, in order to minimize the variables, every determination was conducted in Smalley extractors equipped with calcium chloride tubes. All extractions were conducted for exactly 6 hours.

Whenever a drying operation was called for, this consisted of overnight drying (ca. 16 hours) in a 50° C. vacuum oven. The term "de - acetone", refers to the removal of acetone from the samples by allowing the acetone to evaporate overnight under atmospheric conditions.

After the rubber extractions were concluded, all the residues were dehydrated and extracted with dry benzene (operation No. 5) to determine the amounts of rubber which had not been extracted in operation No. 4.

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An outline of the drying and extraction procedures followed and the average results obtained are presented schematically in Table II.

Summarizing some of the high points of the data given in the table it may be concluded that:

1. In order to accomplish rather complete "resins" removal, there must be some moisture present during acetone extraction. This is probably due to the presence of some water-soluble material which is insoluble in anhydrous acetone.

2. Regardless of the pre-treatment of the goldenrod, more material is extracted from it by benzene than by Skellysolve B. Whether or not this extra material is rubber has not been proven. However, some microscopic investigations indicate that Skellysolve B performs as thorough a job of extraction of rubber per se as does benzene.

3. Even when Skelly B extracted residues are dried out and then extracted with benzene, the total of these extracts is not as great as when this operation is conducted on benzene-extracted residues.

4. When goldenrod is acetone-extracted in an anhydrous condition, then the method of rubber extraction must also include anhydrous conditions, or else the "rubber" values will be abnormally high. This increase in "rubber" values is probably due to some of the water solubles (which had not been removed in the anhydrous acetone extraction) being extracted by the moist benzene.

5. Of the method examined, it would appear that the most nearly correct and most practical would be the second method indicated in the table. This consists in extracting with acetone in the air-dry condition, then dehydrating the residue and extracting it with benzene, under dry conditions.

6. Combining of the rubbers obtained from re-extracting the residues gave a mass of very rubber-like material, in physical appearance. As a matter of fact, this "residual" rubber appears to possess marked snap and non-stickiness. This would indicate that a longer rubber extraction time, in any case, is to be desired.

<u>Improved Method for Analysis of Goldenrod Material.</u> The method for analysis of goldenrod material was modified to take advantage of the observations that fine grinding was essential and that rubber could be extracted better if the samples were dehydrated prior to benzene extraction. Additional improvements were the introduction of a regrind of the sample between two stages of the benzene extraction and the extension of the time of both the acetone and benzene extractions.

XIV - TABLE II

EFFECT OF DRYING ON THE ANALYTICAL EXTRACTION OF GOLDENROD MATERIAL

Operation No. 1	Operation No. 2	Operation No. 3	Operation No. 4		Operation No. 5	Summary	
Pre-extraction treatment	% acetone extract (resins)	Post acetone-extraction treatment	% Skelly B extract ("rubber")	% benzene extract ("rubber")	% rubber in residue (by benzene extraction after drying	Total % "rubber" (4 5)	Total % extractibles (2 4 5)
Did not dry	14.3	dry	5.2		1.0	6.2	20.5
	14.8			6.0	0.5	6.5	20.3
	14.4	de-acetone	4.6		0.6	5.2	19.6
	14.2			5.1	1.1	6.2	20.4
Exposed 48 hrs.	13.6	dry	5.3		1.2	6.5	20.1
	13.8			6.0	0.4	6.4	20.2
	13.9	de-acetone	4.7		0.9	5.6	19.5
	13.9			5.1	0.8	5.9	19.8
Dry	12.9	dry	5.4		0.8	6.2	19.1
	13.2			6.3	0.3	6.6	19.8
Did not expose	13.1	de-acetone	5.8		0.5	6.3	19.4
	12.6			6.6	0.4	7.0	19.6

Note: All determinations were conducted in duplicate.

The full details of the method now being used are given in the following description:

A. Preparation of Sample. The goldenrod sample is ground in a large Wiley mill using a 1/32-inch screen, being careful to collect all the material which does not pass through the screen and mixing this in with the finely ground material. Store in a tightly capped container so that the moisture content will not vary.

B. Moisture. Weigh out exactly 2 g. of the sample into a tared small dish (preferably an A.O.C.S. moisture dish). Dry in a forced draft oven at 105° C. for two and one-half hours, cap, cool in a desiccator and reweigh.

$$\% \text{ moisture} = \frac{\text{loss in weight}}{2} \times 100$$

C. Acetone Extraction. Weigh out exactly 5 g. of the sample and wrap according to the method of the American Oil Chemists' Society, 1941, for the extraction of oilseeds (C. S. & S. filter paper No. 597, 15 cm. size, is recommended.) Extract with 50 ml. acetone for 16 hours in a Smalley extraction apparatus. Evaporate the acetone extract in the tared extraction flask on the steam bath and remove the last traces of acetone by drying in a 75° C. vacuum oven for about two hours.

$$\% \text{ acetone extract} = \frac{\text{wt. acetone extract}}{5} \times 100$$

D. Benzol Extract. Place the wrapped residue from above into a 75° C. vacuum oven for about 5-6 hours. Transfer the wrapped sample directly from the vacuum drying operation to the Smalley extractor provided with a calcium chloride guard tube and extract for 16 hours with 50 ml. of dry benzol (dried over CaO and filtered). Stopper the extract in its flask and set aside for the continuation of extraction later.

Remove the benzol from the wrapped residues by heating in a vented steam cabinet or in a vacuum oven (this is merely a health-protection step). Remove the sample to a mortar, add enough Ottawa sea sand to insure cell rupture (about 1-2 g.) and grind exactly two minutes, using a firm, thorough, reproducible pestle motion. Regrinding can also be done with a micro Wiley mill using a 20 mesh screen. Replace the sample and sand into the original filter paper, being very careful not to allow any "fines" to fall on the outside of the paper, where they could be washed down and

give an erroneous value in the ensuing extraction.

Dry the reground sample in a 75° C. vacuum oven (this should be at least 5-6 hours but can be run as long as overnight). Transfer the wrapped sample directly from the vacuum drying operation to the Smalley extractor provided with a calcium chloride guard tube. Extract for 6 additional hours into the same tared extraction flask used in the primary benzol extraction, adding more benzol if necessary.

Evaporate the benzol on a steam bath and then dry to constant weight (about 2 hours) in a 75° C. vacuum oven.

$$\% \text{ benzol extract} = \frac{\text{wt. benzol extract}}{5} \times 100$$

E. Rubber Content of Extract*. Redissolve the above benzol extract in ordinary, pure benzol. Transfer to a volumetric flask (50 ml. if extract weight is 100 to 200 mg. and 100 ml. if greater) and make to volume. Remove an aliquot containing 30-50 mg. crude rubber and transfer to a 150 ml. beaker. This volume is adjusted to some standard, constant volume, never more than 25 ml. (20 ml. is recommended). If concentration of the solution is necessary, it can be done by evaporation.

Add the brominating solution (made by dissolving 2 g. iodine in 100 ml. carbon tetrachloride, filtering and adding 5 ml. bromine to filtrate) in the ratio of 1 ml. bromine solution to every 10 ml. benzol-rubber solution. Let stand for one hour, stirring intermittently. Add 95 percent alcohol to the solution to precipitate the rubber "tetrabromide." Use about 40 ml. alcohol for every 10 ml. brominated rubber solution. Let the mixture stand at room temperature for two hours to insure complete precipitation.

Filter the solution through a tared Gooch crucible of either the asbestos pad or the fritted glass type. Collect the first portion of filtrate in a clean vessel and if this filtrate is not clear, repass until the pores of the filter have attained complete retentivity of the precipitate. A rubber policeman may be used to affect quantitative transfer of the precipitate since rubber is insoluble in this solution.

Wash the precipitate with at least three 10 ml. portions of alcohol. Dry the crucible and contents in a 75° C. vacuum oven to constant weight (about 1 hour). Cool and reweigh.

*Not determined on routine samples.

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$$\% \text{ rubber} = \frac{\text{wt. of rubber "tetrabromide" X 0.285* X 100}}{\text{wt. of crude rubber in aliquot}}$$

*The gravimetric factor of 0.285 for the amount of rubber in rubber "Tetrabromide" is an empirical factor. This value has been substantiated by carbon and hydrogen analysis of rubber "tetrabromide" from various sources.

NOTE: This bromination procedure is a modification of the Edison bromination procedure and was developed at the Eastern Regional Research Laboratory.

Comparison of Methods. The modified method described above was compared with that used during the first part of the work. The results are given in the following tables. The data show that the benzene extract is greater, on the average, by the modified method than by the older method. The material extracted by the modified method contains a higher percentage of rubber on bromination. The duplicate values, showed an average deviation for the benzene extract of 0.15 with the old method and 0.08 with the modified method. After bromination the average deviations between duplicates were 0.07 and 0.09. Further data on the comparison of methods is given in the second of the tables. A composite of the analytical benzene extracts from goldenrod stems contained only 19 percent "rubber" by bromination.

Attempts to Shorten the Method. Although the modified procedure is believed to give the rubber content more accurately than the method previously used and has proved efficient from the standpoint of man hours per determination due to the fact that with the available equipment 30 determinations may be started each day, it is true that four days normally elapse before the results are obtained. Since in exceptional cases it may be desirable to have results in a shorter time, attempts have been made to work out a procedure that would accomplish this even at sacrifice of efficiency in terms of man-hours per determination. A procedure that cuts the lapsed time to two days at the sacrifice of the so-called resin value and which requires considerable manipulation due to the incorporation of a bromination step is as follows:

Weigh samples containing 35 to 75 mg. of rubber, wrap in filter paper and extract for 5.5 hours with a mixture of 90 parts Skellysolve B and 10 parts of benzene. Remove the greater portion of solvent from the residues by heating in a flat pan on the steam bath. Grind with sand in a mortar for two minutes, wrap again in the filter paper and extract for 16 to 18 hours into the same extraction flask. Transfer the extract to a 150 ml. beaker with Skellysolve B-benzene mixture and adjust to about 25 ml. Add slowly with stirring three ml. bromination solution and allow to stand for one hour. Add 80 to 100 ml. ethyl alcohol with stirring and allow to stand for two hours. Filter through a tared fritted glass crucible of medium porosity, mash the lumps of rubber tetrabromide and wash thoroughly with acetone. Dry for two hours at 70° C. in a vacuum oven. Weigh and calculate the results by use of the factor 0.285 for conversion of rubber tetrabromide to rubber. The addition of carbon disulfide, 1.5

XIV - TABLE III
COMPARISON OF SIMPLE EXTRACTION METHOD FIRST USED (OLD METHOD) WITH MODIFIED DRY-REGRIND PROCEDURE (NEW METHOD).

Sample No.	Benzene extract percent as rec'd		Rubber in extract by bromination, percent		Net rubber content percent	
	Old method	New method	Old method	New method	Old method	New method
AG 629	5.38	5.35	93.2	92.8	5.01	4.97
AI 109	2.21	2.94	86.8	91.0	1.91	2.68
AI 110	2.28	2.85	83.3	90.1	1.90	2.57
AI 111	2.50	2.80	83.9	92.3	2.09	2.52
AI 112	2.52	2.97	85.5	90.3	2.15	2.68
AI 113	2.26	2.79	85.2	90.8	1.93	2.53
AI 114	2.23	3.25	82.0	88.8	1.85	2.88
AI 115	2.86	3.68	84.4	90.1	2.41	3.31
AI 116	2.66	3.37	87.3	94.8	2.32	3.19
AI 117	2.40	3.20	83.7	88.8	2.01	2.84
AI 118	2.30	3.14	85.0	86.0	1.95	2.70
AI 119	2.35	3.12	83.3	91.1	1.95	2.84
AI 120	2.24	2.83	76.7	86.7	1.72	2.40
AI 121	2.20	2.79	85.0	89.9	1.87	2.51
AI 122	2.60	3.23	86.4	93.4	2.25	3.11
AI 123	2.59	3.08	78.3	89.6	2.02	2.76
AI 124	2.30	2.67	78.3	89.0	1.80	2.37
Average	2.58	3.18	84.0	90.3	2.18	2.87

XIV - TABLE IV
FURTHER COMPARISON OF METHODS ON STEMS, LEAVES AND RESIDUES

Type of sample	Sample No.	Acetone extract percent as rec'd		Benzene extract percent as rec'd	
		Old method	New method	Old method	New method
Stems, av. of 21		3.84	4.97	0.14	0.16
Leaves	AI 175	13.7	18.1	2.30	2.81
	AI 176	14.4	19.5	2.68	2.83
	AI 177	13.3	17.1	2.39	3.04
	AI 178	13.6	17.6	2.64	2.45
	AI 268	13.5	16.8	2.36	2.77
	AI 54	11.2	13.0	1.78	2.38
Pilot-plant residues	AI 306	1.1	1.4	0.57	1.16
	AI 267	1.8	2.6	0.34	0.82

ml., prior to the alcohol, as suggested by the Eastern Regional Research Laboratory might be tried.

The above procedure gave rubber values of 4.65, 3.02 and 0.97 on three different samples, while the regular method gave values of 4.65, 2.90 and 1.00 respectively. The procedure seems worthy of further investigation.

A STUDY OF THE COX METHOD FOR THE ESTIMATION OF RUBBER IN PLANTS

The Cox method for the estimation of rubber in plants is based on the precipitation of rubber from a benzene extract by addition of acetone. The rubber precipitates as a colloidal suspension and is estimated by measuring the apparent transmission in a photoelectric colorimeter. A blank prepared from the same benzene extract diluted with a mixture of benzene and ethyl ether serves to compensate for the absorption of light by chlorophyll, carotenoids, and other pigments in the extract. Although there are theoretical reasons against the use of a colorimeter rather than a nephelometer for estimation of the turbidity of a suspension, this part of the method appears to be satisfactory from a practical standpoint. However, the method in its present form does not even approximately estimate rubber added to rubber free plant material. This shows that substances present in plant material interfere. Chlorophyll and carotene, which are always present in green parts of plants interfere with the method, apparently by affecting the precipitation of the rubber. In the case of chlorophyll, this interference is much greater after the extracts have stood for some time and may be due to the photochemical action on rubber of the light absorbed by the chlorophyll. Should some way be found to eliminate this effect of chlorophyll, carotene and perhaps other plant constituents, the method might prove useful.

EXPERIMENTAL RESULTS

Method as now used. A 5 g. sample of the dried, ground plant material is placed in a Waring blendor provided with a neoprene gasket and mixed with about 50 ml. of benzene for five minutes. The sides of the mixer are washed down with about 40 ml. benzene, mixing continued for 10 minutes, the wash down repeated, and the mixing continued for 5 minutes. The contents of the mixer are washed into a 200 ml. volumetric flask, made to volume and a portion centrifuged in capped centrifuge tubes. Three 5 ml. portions of the supernatant liquid are pipetted into test tubes. Carbon tetrachloride, 2 ml. is pipetted into each tube. Twenty ml. of a mixture of benzene and ethyl ether of the same density as acetone is pipetted into one of the tubes. This serves as a blank. Exactly 20 ml. of acetone is slowly pipetted down the side of the other two tubes, care being taken that it forms a layer and does not mix with the benzene extract and carbon tetrachloride. The tubes are stoppered with tinfoil covered corks and mixed by slowly inverting several times. Shaking or violent agitation must be avoided. Transmission is then determined in the Evelyn colorimeter with the corresponding benzene-ether blank set at 100 using the 520 filter. Readings are taken at 15 minute intervals until minimum transmission values are obtained. The logarithms of these values are used to estimate the mg. of rubber in the aliquot by use of a standard curve made by dissolving crepe rubber in benzene and precipitating with acetone by the same procedure as used with the plant extracts.

Results with Standard Rubber Solutions. When crepe rubber is used and no other substance is added except as called for in the method outlined

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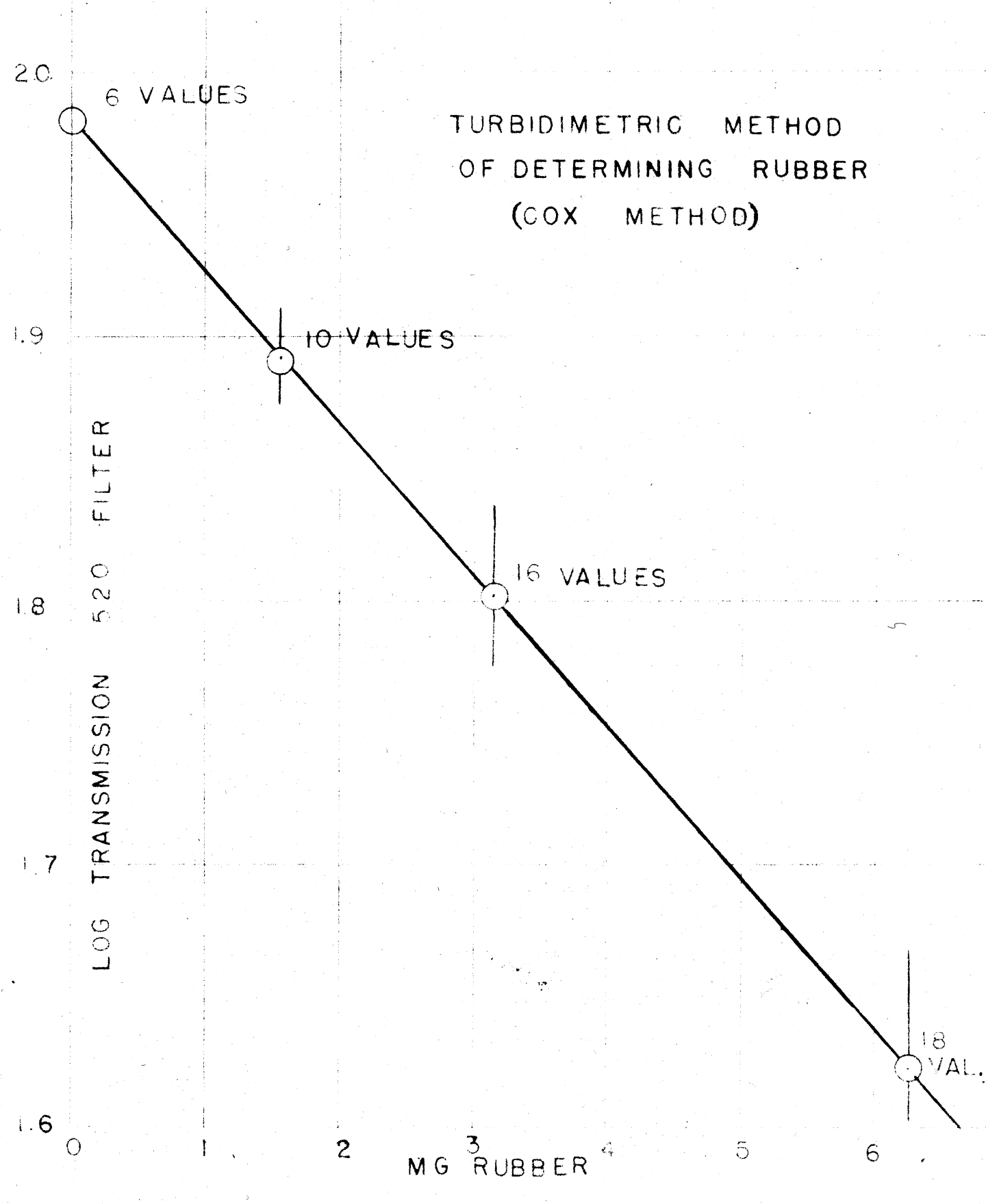
above, the values obtained are fairly reproducible. Duplicates agree quite well when run on the same rubber solutions at the same time. The day to day and solution to solution variation is quite large. This is probably due to temperature variations and difficulties in the preparation of standard rubber solutions. The rubber values were of necessity based on the amounts of crepe rubber actually weighed out. Although a small amount of insoluble material was centrifuged out prior to use, the residue found on evaporation of the benzene solution was usually greater than the rubber added, even after heating for several hours at 65° C. in a vacuum oven. Analysis of the residue for oxygen should show whether this increase in weight is due to incomplete removal of the benzene or to oxidation of the rubber. Results with various solutions of rubber are summarized in Figure 1. In this figure the circles represent the average transmission for each rubber concentration and the lines the maximum and minimum values observed. The average values fall on a straight line, but deviations equivalent to 10 to 15 percent of the rubber present occur quite frequently.

Effect of Added Chlorophyll. In experiment No. 1, 1.250 g. of 98 percent crepe rubber was dissolved in a Waring blendor in benzene. About 3 hours was required. The solution was centrifuged to remove a little insoluble material and diluted to 500 ml. with benzene. Two 100 ml. portions were measured into 200 ml. volumetric flasks. Chlorophyll, 6 mg., was added to one flask and both were made to volume with benzene. Dilution of one-half and one-fourth were made from this solution using benzene. Benzene alone, with and without chlorophyll, served to give 0 values (no rubber). Aliquots of these solutions, 5 ml., were analyzed by the Cox method as described above. After 5 and 7 days some of these solutions were analyzed again. The results will be found in Table V. It will be noted that addition of chlorophyll increased the transmission of the rubber solutions. This effect was greater after the solutions had stood several days and after 7 days standing no rubber precipitated even though 3.13 mg. had been added.

Experiment No. 2 was similar to experiment No. 1, except that 12.1 mg. of chlorophyll were used. In experiment No. 3, 1.67 mg. of chlorophyll were used. In experiment No. 4, 2.5 mg. of chlorophyll were used. The amounts of rubber found in the presence of chlorophyll were about 85 percent of those found in its absence, even when the determinations were made soon after the addition of chlorophyll. After the solutions had stood 4 or 5 days, only about half of the rubber was found and after 6 or 7 days the rubber values had fallen to zero.

Effect of Added Carotene. In experiment No. 6, 1.25 g. of crepe rubber were dissolved in 500 ml. of benzene. Carotene, 7 mg., was added to 100 ml. of this and the solution made up to 200 ml., with benzene. Likewise, 100 ml. of the same rubber solution was made up to 200 ml. One-half and one-fourth dilutions of these solutions were made. Rubber was estimated on 5 ml. aliquots of these solutions by the Cox method. The results will be found in Table VI. The addition of carotene increased the transmission of the rubber solutions. Experiment No. 6 was similar to No. 5, except


TURBIDIMETRIC METHOD
OF DETERMINING RUBBER
(COX METHOD)
6 VALUES
10 VALUES
16 VALUES
18 VAL.
2.0
1.9
1.8
1.7
1.6
LOG TRANSMISSION 520 FILTER
0
1
2
3
4
5
6
MG RUBBER

XIV FIG. I

that 4 mg. of carotene were used and the transmission measured with the 660 filter. In experiment No. 7, the same solutions as used in experiment No. 6 were used seven days later. The readings were taken with the 520 filter. The effect of carotene does not appear to increase with aging of the solutions. In general, addition of carotene lowers the amount of rubber found.

Effect of Added Vegetable Oil. In order to see if vegetable oil interfered with the method, 4 drops of peanut oil were added per 200 ml. of a benzene solution containing 125 mg. of rubber. The peanut oil had no significant effect.

Addition of Known Amounts of Rubber to Plant Extracts. The recovery of rubber added to various plant extracts was investigated in order to see if substances commonly found in plants interfered with the method. In all cases 5 g. samples of the dried, ground plant material was dispersed in a Waring blendor as called for in the method. A benzene solution of known rubber content was then added, the mixture made up to 200 ml., centrifuged and rubber determined on 5 ml. aliquots of the supernatant liquid undiluted and diluted with an equal volume of benzene.

Determinations were also made on the plant material without added rubber and on the standard rubber solution. Giant ragweed was used as a plant low in rubber and two of the grasses, Spartinia cynosuroides and Sorghym halpense, L (Johnson's grass) were used as plants which apparently contain no rubber. The results are given in Table VII. In no case was satisfactory recovery of the added rubber obtained. With giant ragweed significantly less than the amount added was found. Spartinia cynosuroides extract appears to increase the amount of rubber found, but in line with previous results with chlorophyll, less was found after the extracts had stood for 3 days. Sorghym halpense L. extracts reduced the amounts of rubber found to about half of amounts added.

Other Experiments. Attempts to improve the method by removal of chlorophyll, carotene, and other interfering substances from these extracts by use of alumina, magnesium carbonate, and other adsorbents have been unsuccessful, since such treatment appears to remove some of the rubber.

Absolute alcohol has been tried in place of acetone in the method. With pure rubber solutions a much more stable suspension was obtained. However, when used with rubber added to extracts of Sorghum halpense L., the rubber quickly coagulated and settled so that a constant reading could not be obtained on the colorimeter. This was also true when alcohol was tried in place of acetone in rubber determinations on goldenrod.

Analyses were made by the Cox method and by the acetone-benzene extraction method on various samples. The results are given in Table VIII. They show that the Cox method usually gives higher values than the extraction method.

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SUMMARY

Chlorophyll, carotene, and perhaps other plant constituents interfere with the determination of rubber by the Cox method. Until some way is found to eliminate the effect of various plant constituents, rubber values determined by this method are open to question.

XIV - TABLE V

EFFECT OF CHLOROPHYLL ON THE COX METHOD FOR THE DETERMINATION OF RUBBER.

Experiment No.	Days after preparation of solns.	Rubber per 5 cc aliquot mg.	Rubber only: Transmission 520 filter, Percent	Rubber only: Transmission 520 filter, Log.	Chlorophyll added: Transmission 520 filter, Percent	Chlorophyll added: Transmission 520 filter, Log.	Rubber Found mg.
1	0	6.25	46.7	1.669	53.9	1.732	5.0
			46.2	1.665	55.8	1.747	4.7
		3.13	67.8	1.831	74.3	1.871	2.3
			68.5	1.836	72.2	1.859	2.5
		1.56	81.5	1.911	84.8	1.928	1.0
			78.0	1.892	83.5	1.922	1.1
		0.00	96.0	1.982	95.3	1.979	0.0
			95.8	1.981	95.0	1.978	0.0
	5	6.25	42.0	1.623	63.5	1.803	3.1
			41.0	1.613	88.7	1.824	2.7
	7	3.13			95.0	1.978	0.0
					94.9	1.977	0.0
2	0	6.25	42.5	1.628	45.5	1.658	5.6
			42.0	1.623	45.0	1.653	5.7
		3.13	65.4	1.816	65.0	1.813	3.2
			65.5	1.816	64.6	1.810	3.2
		1.56	78.4	1.894	78.8	1.897	1.6
			81.0	1.909	81.0	1.909	1.5
		0.00	95.5	1.980	95.0	1.978	0.0
			95.5	1.980	95.0	1.978	0.0
	4	6.25	42.0	1.623	57.5	1.760	3.8
			41.5	1.618	60.0	1.778	3.5
	6	3.13			95.2	1.979	0.0
					95.5	1.980	0.0
3	0	6.25	40.7	1.610	46.3	1.666	5.2
			41.0	1.613	49.0	1.690	4.8
		3.13	61.0	1.785	66.5	1.823	2.5
			61.3	1.788	68.0	1.833	2.4
4	0	6.25	40.0	1.602	44.5	1.648	5.5
			40.5	1.608	43.2	1.636	5.7

XIV - TABLE VI

EFFECT OF CAROTENE ON THE COX METHOD FOR THE DETERMINATION OF RUBBER

Experiment No.	Days after preparation of solns.	Rubber per 5 cc aliquot mg.	Rubber only: Transmission 520 Filter: Percent	Rubber only: Transmission 520 Filter: Log.	Carotene added: Transmission 520 Filter: Percent	Carotene added: Transmission 520 Filter: Log.	Rubber Found mg.
		6.25	41.3	1.616	47.7	1.679	5.0
			41.6	1.619	49.7	1.696	4.7
	0	3.13	59.6	1.775	70.7	1.849	2.0
5			61.0	1.785	70.8	1.850	2.0
		1.56	75.0	1.875	80.5	1.906	1.1
			75.5	1.878	80.2	1.904	1.1
		0.00	95.3	1.979	95.5	1.980	0.0
			94.8	1.977	96.5	1.985	0.0
			Transmission 660 Filter: Percent	Transmission 660 Filter: Log.	Transmission 660 Filter: Percent	Transmission 660 Filter: Log.	
		6.25	50.0	1.699	67.5	1.829	3.2
			50.0	1.699	67.5	1.829	3.2
	0	3.13	67.8	1.831	72.8	1.862	2.5
6			68.7	1.837	71.3	1.853	2.7
		1.56	80.3	1.905	80.7	1.907	1.6
			80.5	1.906	81.3	1.910	1.5
		0.00	95.5	1.980	85.5	1.980	0.0
			95.6	1.981	95.4	1.980	0.0
			Transmission 520 Filter: Percent	Transmission 520 Filter: Log.	Transmission 520 Filter: Percent	Transmission 520 Filter: Log.	
7	7	6.25	40.5	1.608	44.7	1.650	5.6
			41.7	1.620	43.7	1.641	5.7
		3.13	62.5	1.796	63.0	1.799	3.1
			64.5	1.810	62.7	1.797	3.1

XIV - TABLE VII

RECOVERY OF RUBBER ADDED TO EXTRACTS OF VARIOUS PLANTS

Extract used	Rubber content of 5 ml. aliquot mg.	Rubber added per 5 ml. aliquot mg.	Total Rubber in aliquot mg.	Transmission 520 Filter Percent	Transmission 520 Filter Log.	Rubber found mg.	Standard Rubber only Transmission Percent	Standard Rubber only Transmission Log.
	1.50	6.25	7.75	42.5	1.628	6.3	43.6	1.640
				43.7	1.641	6.0	41.7	1.620
Giant Ragweed	0.80	3.13	3.93	68.5	1.836	2.3	60.0	1.778
				66.5	1.823	2.5	60.8	1.784
	0.00	3.13	3.13	59.5	1.775	3.7		
Spartinia				59.0	1.771	3.7		
cynosuroides	0.00	1.56	1.56	74.7	1.873	1.8		
				74.0	1.869	1.8		
Spartinia	0.00	3.13	3.13	67.0	1.826	2.8	64.3	1.808
cynosuroides				63.0	1.799	3.4	65.5	1.816
extract	0.00	1.56	1.56	79.7	1.902	1.3	76.7	1.885
3 days old				79.5	1.900	1.3	77.3	1.888
	0.00	3.13	3.13	78.0	1.892	1.5	63.7	1.804
Sorghum				77.0	1.887	1.5	64.3	1.808
halpense, L	0.00	1.56	1.56	86.0	1.935	0.8	76.0	1.881
				85.3	1.931	0.8	76.7	1.885

XIV - TABLE VIII

COMPARISON OF THE COX METHOD WITH THE ACETONE-BENZENE EXTRACTION METHOD FOR RUBBER

Material Analyzed	Rubber Percent of Dry Weight			
	Cox Method		Extraction Method	
Goldenrod leaves, dried and ground	2.3	2.4	1.4	1.6
Goldenrod leaves, dried and ground	6.7	6.8	5.2	5.2
Goldenrod leaves, dried and ground	7.2	7.2	6.8	6.8
Goldenrod leaves, dried and ground	12.5	12.9	7.9	7.9
Goldenrod leaves, partly extracted	4.0	4.2	4.7	4.6
Goldenrod leaves, digested in alkali and acid	32.4	33.4	30.9	29.2
Cryptostegia leaves, extracted	0.5	0.6	0.2	0.2

Table X summarizes the number of analytical determinations made on almost 2000 samples, in control of the pilot plant operations and in connection with the varied lines of experimental work on goldenrod, and the rubber and other products produced therefrom.

XIV - TABLE X
SUMMARY OF ANALYTICAL SERVICE WORK ON THE RUBBER PROJECT
UP TO APRIL 29, 1944

Type of Sample	Number of Samples	Kind of Analysis	Number of Analyses
Goldenrod material	1418	Moisture	2791
		Acetone solubles	2616
		Benzene solubles (rubber)	2604
		Total nitrogen	65
		Non-protein nitrogen	4
		Total sugars	8
		Pentosans	4
Rubber and extracts from goldenrod material	503	Residue on evaporation	334
		"Resins"	433
		Acid No. of "resins"	248
		Acid No. of rubber	26
		Total sulfur	168
		Free sulfur	179
		Rubber by bromination	14
		Saponification number	12
		Total nitrogen	10
		Total chlorine	17
		Semi-micro C and H	30
		Miscellaneous	123
Fractions and substances isolated from goldenrod	23	Micro C and H	56
		Micro Dumas N	4
		Micro Kjeldahl nitrogen	6
		Micro weighings	29
		Moisture	27
		Ash	12
		Iodine number	4
		Saponification number	4
Total	1944		10,325

XV - MICROSCOPICAL STUDIES OF RUBBER IN GOLDENROD

Introduction. The extraction of rubber from goldenrod (Solidago, Sp.) is a part of the Emergency Rubber Project. Microscopical techniques have been used to demonstrate the location of rubber in the plant tissues and to study the effectiveness of various methods for its removal.

A method has been devised for staining rubber and resin *in situ* in the tissue of the plant. The structure of rubber-bearing cells in the mesophyll tissues of the solidago leaf has been studied; the location of resiniferous ducts has been demonstrated (Fig. 1). Microscopical observations at intervals during ball mill, laboratory extraction and pilot plant procedures have served as a control in estimating the efficiency or completeness of these methods.

Losses in cooking, retting, ball-milling and screening procedures were checked and residues from these processes were examined periodically to detect the presence of unextracted rubber. Photomicrographs in color were made to show rubber-bearing structures, and a series of photomicrographs of microtome sections of the goldenrod leaf were made to show the effect of successive steps in the extraction process.

Microscopical Techniques. Standard histological techniques such as paraffin and celloidin embedding for microtome sectioning were found to be unsuitable for the study of rubber-bearing plants. The solvents required to remove the embedding medium will in every case also remove the rubber (Fig. 3).

Various other embedding techniques were tried for microtome sectioning. Glycol-stearate, though recommended as a water soluble wax was not satisfactory. The only solvents which would satisfactorily remove it, also affected both rubber and resin.

Gelatin sections were also tried without success. Cellulose acetate, and ethyl cellulose when used as embedding media, were found too difficult to remove. Frozen sections and free hand sections were found to be the most satisfactory preparations for showing rubber and resin *in situ*. Permanent mounts were not attempted but colored photomicrographs were made for purposes of record. Some 50 microscopical staining techniques were tried out in an attempt to color the resin in the ducts an entirely different color from the rubber in the cells. This was unsuccessful as both substances dye similarly and are affected only by spirit soluble dyes. However, because of their localized occurrence and difference in refractive index the two substances can be differentiated. Furthermore the "resins" dissolve rather readily in alcohol or acetone, while the rubber is only coagulated. Stains which will color rubber are limited. Sudan IV, which is a general stain for vegetable oils, was found to be most satisfactory. Other fat dyes which can be used are Sudan III, Drug and Cosmetic Red 18, Celliton Blue and Calco Oil Blue. The red stains are preferable since blue is very transparent in thin section or dilute solution, and photographs less satisfactorily than red.

In order to increase the contrast between the rubber and surrounding

Over

leaf tissues a complementary color was used for the cellulose. Iodine green was chosen, although methylene blue, hematoxylin, malachite green, gentian violet, or a number of other stains could have been used equally well.

The following staining technique was adopted as generally satisfactory for either dried or fresh material:

1. Section leaves without embedding.
2. Wash in water.
3. Wash in 10% alcohol.
4. Wash in 20% alcohol.
5. Wash in 35% alcohol.
6. Stain with Sudan IV (1% solution in 50% alcohol); 10 minutes or until good color appears.
7. Stain in iodine green (0.5% aequeous) for several minutes.
8. Mount in water, glycerin, or Karo syrup.

Rubber particles are bright scarlet red and translucent. Resin globules are orange red to amber and more opaque in appearance.

Leaf Structure. By means of these staining techniques the leaf structure of goldenrod was studied. The leaf is an almost typical herbaceous leaf with a heavy midrib (Figs. 2 and 3). The only unusual structures are the "resin ducts" which occur at the anastomosis of the veins and seem rather to be reservoirs than continuous ducts. They are filled with a complex mixture of oils and waxes which have not yet been identified. These "resins" will dissolve out readily with alcohol or acetone.

The cuticular waxes of the epidermal cells, however, are much more resistant and still remain after complete pilot plant extraction with both acetone and benzene. The upper and lower epidermises seem to be identical except for a greater number of hairs on the lower epidermis. The hairs are of two kinds:

(1) pluricellular uniserial trichomes which are particularly numerous along the veins and midrib (Fig. 8); and (2) glandular hairs which are uniformly tricellular and much finer and more sparsely scattered on the epidermal surface. The prominent stomata are equally numerous and uniform on both upper and lower epidermises (Fig. 7). The diagram in Fig. 1 illustratesthe typical leaf structure of the rubber-bearing goldenrod.

There are usually 2 or 3 rows of cells in the palisade parenchyma. These cells are small, measuring about 40 microns by 7, and are usually closely packed together (Fig. 4). The cells of the spongy parenchyma are normal but rather closely packed. There exists between the palisades and the spongy parenchyma an unusual row of large empty cells similar to the epidermal cells. These occur about equidistant from upper and lower surfaces of the leaf, and more or less in horizontal line with the resin ducts.

The rubber occurs in the form of isolated globules floating free among the plastids in the protoplasm of both palisade and spongy parenchyma cells

(Fig. 5). Occasionally as many as three or five globules can be found in a single cell; usually they occur singly, and average about 2 microns in diameter. Whether this rubber is in a solid or liquid state has not been determined. It coagulates and swells with acetone; dissolves with benzene, xylol, toluene, or ether.

Stem Structure. In response to inquiry as to the rubber content of the goldenrod stem, cross-sections were made on fresh plants of *Solidago altissima*.

Most of the stem is composed of thin-walled pith cells, many of which are packed with colorless needle-like crystals presumed to be raphides of calcium oxalate. The vascular system is confined to the outer one-third of the cross-sectional area. In older stems it is quite woody, and occupies a much narrower area.

Near the green end of the stem where growth is rapid there are many small ducts associated with the young fibrovascular bundles near the edge of the stem. Each of the ducts is surrounded by a single layer of rubber-bearing cells. The ducts themselves contain " resin" which readily dissolves in the alcohol of the stain. The resin ducts do not appear to be continuous in the stem; and although scattered in the pith and cortex they are rather regularly spaced on either side of the fibrovascular cylinder.

Lower down in the woody base of the stem no ducts are apparent. Red-staining areas in the bark region indicate that the resin ducts and surrounding cells were crushed in the phloem as growth pressure compressed the outer portion of the stem.

Extractions of stem material showed negligible amounts of rubber.

Sample	Wt. sample grams	Acetone extractables, %	Benzene extractables %
Tender stem tips (top 6 in)	13.52	4.89	0.50
Woody stem bases (Lowest 6 in)	9.38	2.36	0.24

Photomicrographs were made to show the location of the ducts and the character of the rubber-bearing cells (Figs. 9 and 10).

Residues. Somewhat more than 500 samples of residues from extraction processes submitted at intervals by the Engineering and Development Division have been tested microscopically for rubber content. It must be emphasized that the microscopical estimation of rubber in these residues cannot be accepted as an analysis. The estimate is obtained by comparing visually at a magnification of 200 X the rubber-containing cells which are red-staining material, with those rubber-containing cells which show red-staining material after the slide has been dyed with a solution of Sudan IV. Results are reproducible to perhaps the nearest 5 or 10 percent. They represent an estimate of the percent of the ori-

Over

ginal rubber of the leaves which is retained in the residues. The percentage as determined microscopically is based on the premise that if all leaf cells were "empty" (free from rubber) 100 percent of the rubber would have been extracted. Stem and flower fragments, and the epidermal and fibrovascular tissues of the leaf are discounted in this estimation. The results should not be considered comparable with those of analytical procedures since it is impossible to break up this material sufficiently to make particle size measurements or area counts of rubber particles mixed with the non-rubber fragments of the leaf. The sampling error is unavoidably great and reported results are relative rather than absolute. Early pilot plant residues sometimes contained 20%to 30% of unextracted rubber cells; final pilot plant residuos were all virtually free of rubber. Examination of laboratory and pilot plant extractions showed consistently that residues from finely ground material retained not more than 5 percent of the original rubber and that in many of these samples extraction was virtually complete while in the coarsely ground and unground samples from 20%to 50% of the cells of the residue still contained rubber.

In connection with the developmental features of the emergency rubber program other investigations were conducted from time to time and various microscopical tests were made as the occasion occurred. These miscellaneous activities are briefly appended.

Air Separation of Plant Parts. The 1943 crop of goldenrod was not harvested until after blooming had set in. The ground raw material as received from Georgia was a mixture of fragments of leaf, stem and flower. A device for winnowing this material was set up by the Engineering Division.

In connection with this air separation of goldenrod leaf and blossom fragments from material sent from Waynesboro, Georgia, thirteen samples were examined and separated manually under the stereoscopic microscope.

After separation the respective fractions were weighed. Eight samples representing the "leaf fraction" recovered after one run through the air separator averaged 40 percent leaf, 36 percent flowers and,24 percent stems. Four samples representing the "blossom fraction" recovered after one run through the separator averaged approximately,10 percent leaf 89 percent flowers and,1 percent stems. The "leaf fraction" from the third re-run through the air separator contained 47 percent leaf, 38 percent flower and,15 percent stems.

Retting Experiments. Microscopical examination of leaves retted for 21 days by both aerobic and anaerobic action indicated that the anaerobic retting produces a cleaner cell with less trash and dirt, and smaller amounts of protoplasmic residue surrounding the rubber mass in the cell.

A sample of the whole leaves, which had been ensiled in Waynesboro, Georgia,was examined by the cross-sectioning technique. The resin ducts were empty, the rubber cells packed with rubber. The rubber particles seemed to be swollen considerably and occupied a greater proportion of the cell than is normally true in untreated material; the cell walls

seemed not at all disturbed, and the cell contents only slightly reduced in quantity. Except for absence of resin, and the swollen condition of the rubber, the effects of ensilage were not apparent.

Cooking Experiments. Samples of goldenrod were examined in the "wet mash" state after cooking in 0.1% H_2SO_4 and 0.5% Na OH solutions respectively. The individual cells were "freer" and cell groups less compact after the alkali cook than after the acid cook.

Waste liquors were examined after screening, and it was revealed that considerable rubber was being lost in cells which washed through the screen. To determine fineness of the mesh required to prevent this, dimensions of the cells were measured. The rubber bearing cell of the goldenrod leaf is about 7 x 40 microns.

Miscellaneous Experiments. (1) Ball Milling: A series of microscopical observations were made at intervals during ball mill experiments to study size and distribution of rubber particles in respect to time of milling. Color photomicrographs were made to show changes during the ball milling process, and size and distribution of fibrous materials in the ball mill liquor. Pre-treatment of powdered goldenrod leaves with enzymes was studied with the idea of releasing the rubber through enzymatic destruction of protoplasmic residues and of cellulose leaf tissues before ball milling. Three enzymes, cellulase, pepsin, and pancreatin were used separately. The sample treated with pepsin balled out after 298 hrs., but no balling out of rubber occurred in the other samples. This approach was abandoned as impracticable.

(2) Cytolysis: In connection with suggestions made by Mr. Wildman experiments were tried with a view to removing protoplasmic contents from the cells by cytolysis.

Leaves were subjected to ether fumes for different lengths of time from 7 to 17 hours and then pressed in a Carver press under a pressure of 3000 lbs. per square inch.

Sections of leaves after cytolysis but before crushing showed resin ducts completely empty, cell contents completely coagulated, and rubber globules numerous. Sections of leaves after crushing showed little difference from those before crushing. Microscopical examination of the plant juices extracted by crushing showed granular cell fragments, and globules of resin, but no detectable rubber. The pressed leaves when dried and extracted by regular procedures showed normal percentages of resin and rubber. The cytolysis experiments were abandoned as unpromising.

A similar cytolysis with water had been previously tried without any significant results.

(3) Extraction: Various preliminary extractions were run on a small scale in the early period of the rubber investigation. They may be briefly listed as follows:

(1) Cold extraction with acetone and benzene by shaking for 24 hours.

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(2) Hot extraction by acetone-benzene method after pre-treatments with 10%, 25%, 50%, and 100% Clorox solution. The rubber was chlorinated.
(3) Hot acetone-benzene extraction after 2% NaOH cook followed by 50% Clorox bleach.
(4) Hot acetone-benzene extraction after pre-treatment with cold H_2SO_4.
(5) Hot alcohol-benzene extraction after hot water extraction.
(6) Hot alcohol-benzene extraction after 12 hours water cook.
(7) Comparison of alcohol-benzene method with acetone-benzene method to obtain lighter-colored rubber.
(8) Comparison of benzene with toluene and xylene as solvents for rubber.
(9) Extraction of ball mill waste liquor to remove residue of rubber after balling-out phenomenon.
(10) Cold extraction of resin-rubber complex from the ball mill to separate the resin from the rubber.

(4) Harvesting Series: A study of multiple harvesting on a small plot of the local goldenrod (Solidago altissima) was conducted over a series of months in 1943. Plants in the plot were allowed to grow for only 30 days at a time before being cut back to the ground. Each harvest was compared with native material which was not disturbed by any previous cutting. Comparison of results with those obtained in 1942 at the end of the season indicated that more than one harvest per year might be advantageous.

Year	Date	Acetone extractables %		Benzene extractables %	
1942	Aug. 13	9.1		0.49	
	Aug. 24	8.7		1.5	
	Aug. 31	7.9		1.2	
1942	Nov. 11	10.5		1.9	
	Nov. 11	11.2		1.6	
		Cut	Uncut	Cut	Uncut
1943	March 15	---	7.5	---	1.5
	April 1	7.39	6.53	1.18	1.36
	April 1	7.56	6.03	0.92	1.74
	May 4	9.10	6.85	0.59	0.94
	May 4	9.55	6.99	0.55	1.2
	June 10	9.5	10.7	0.78	1.04
	June 10	9.3	10.2	0.84	1.05

Subsequent large scale experiments on the 1943 acreage by the Forest Service disproved this idea that multiple harvesting would increase the total rubber yield.

Rubber Plants Other Than Goldenrod. For purposes of comparison with goldenrod, sections of cryptostegia, kok-saghyz, and guayule plants were examined microscopically and photographed in color.

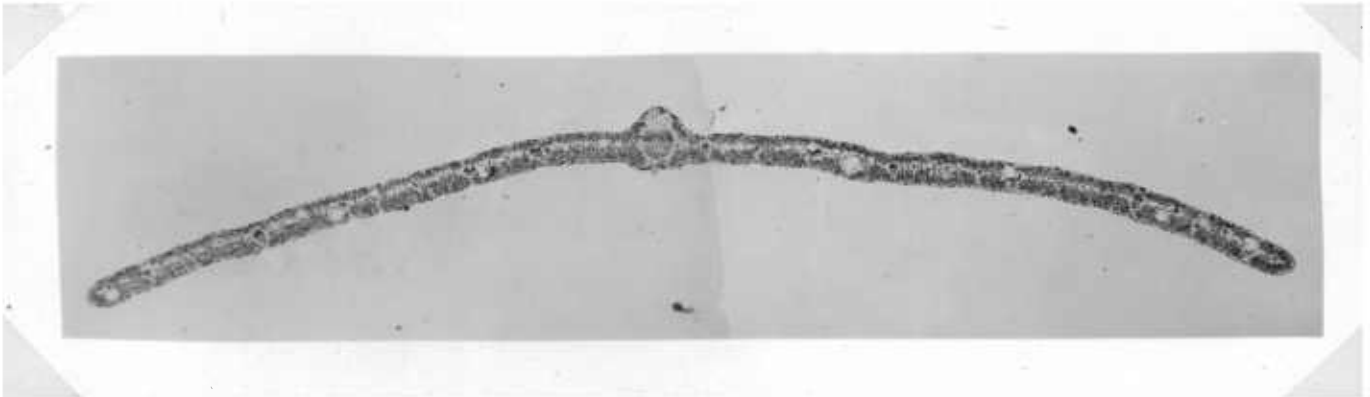
Cryptostegia was shown to have a continuous latex system occurring

on either side of the midrib in the leaf, and in the central meristem of the twig. In fresh leaves globules of rubber were also observed in the palisade parenchyma of the cryptostegia leaf, similar to those seen in goldenrod leaf tissue.

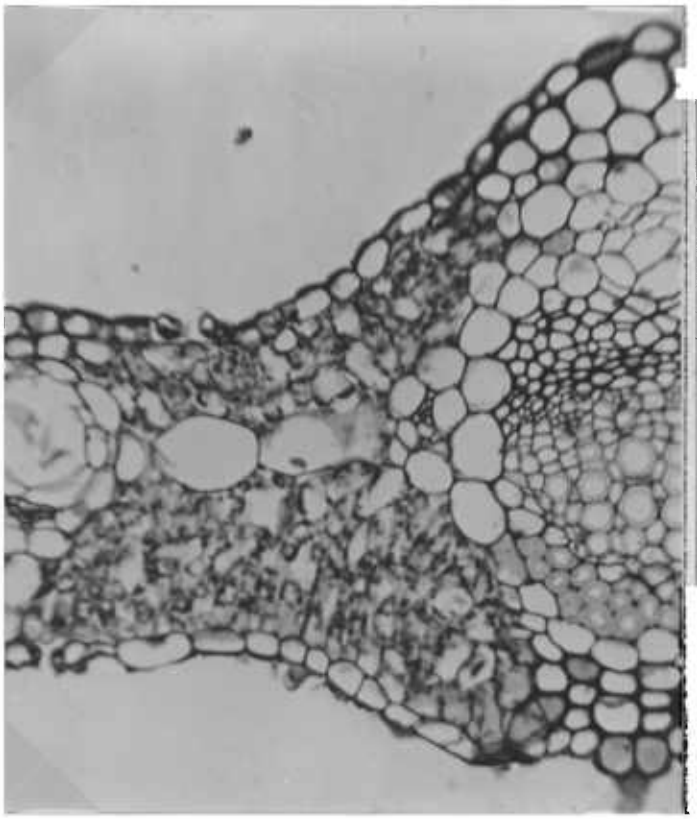
Guayule stems show rubber deposited in the cells of the pith, the ray cells of the woody area, and in the cortex. Large resin ducts occur in the central pith and in the inner cortex area near the prominent fiber bundles.

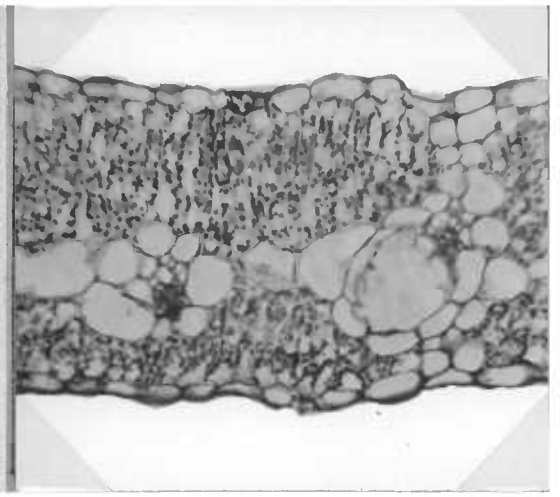
Kok-saghyz roots have anastomosing latex ducts arranged concentrically around the central stele. The cells of the protoxylem surrounding the vessels contain many small globules of rubber.

Conclusion. Microscopical examinations of raw materials and processed residues have shown that the rubber in the leaf of the goldenrod plant (Solidago leavenworthii) can be completely removed by the acetone-benzene extraction process, if the raw material is finely ground before extraction.



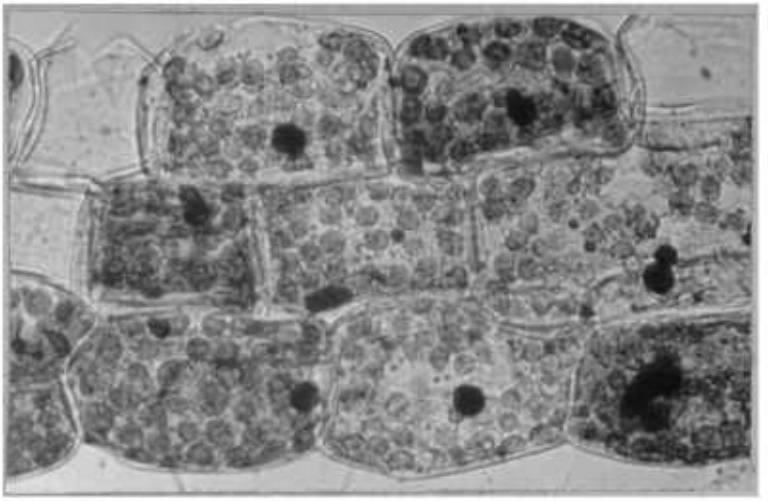
XV-Fig. 2
Cross-section of entire leaf. Mag. approx. 15x.





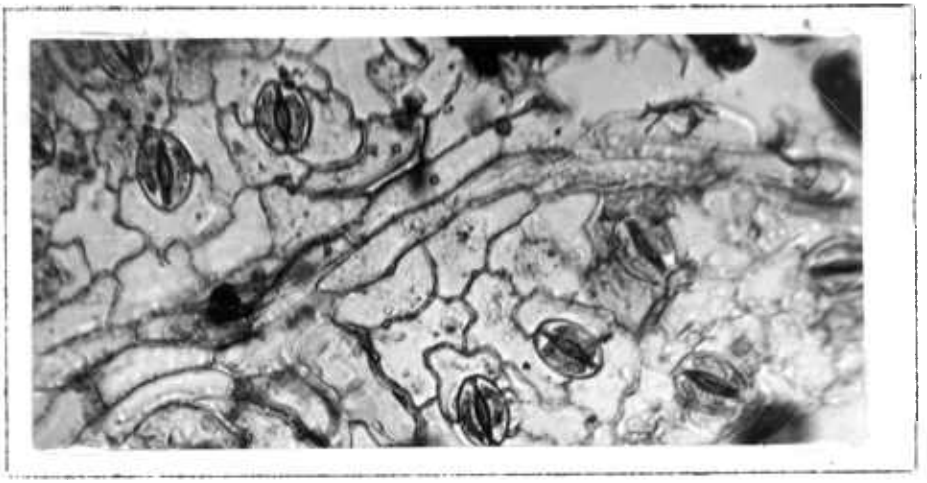
XV-Fig. 3
Cross-section of leaf prepared by standard histological techniques. Note vacancies in rubber-bearing cells where rubber has dissolved out. Mag. 250x.

XV-Fig. 4
Isolated cells from palisade parenchyma showing rubber and plastids.
Mag. 1200x

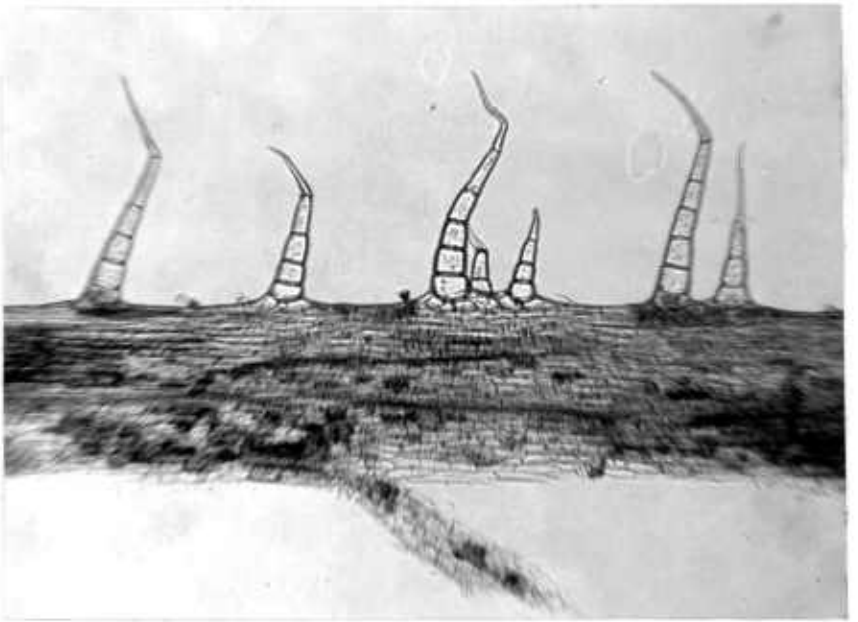


XV-Fig. 5
Group of cells from above a vein showing relation of plastids to rubber in the cell.
Mag. 600x

XV-Fig. 6
Progressive plasmolysis of cell contents during drying of leaf.
Mag. 600x

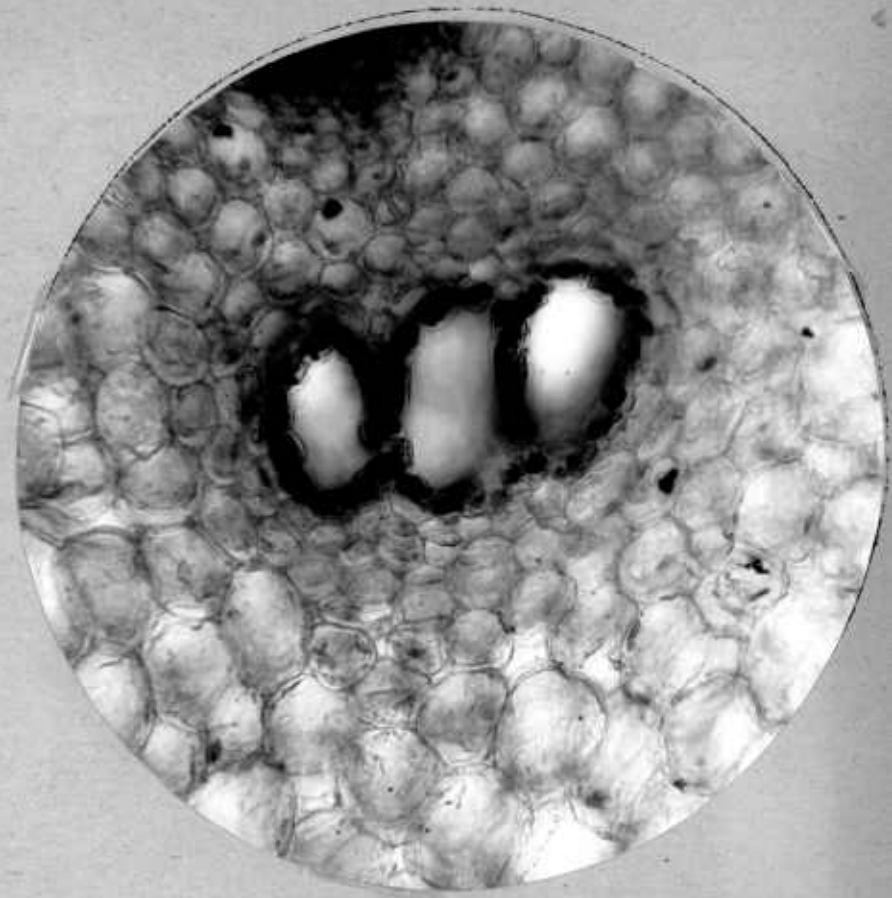


XV Fig. 7. Epidermal cells and stomata. Mag. 125x.



XV Fig. 8. Trichomes from epidermis above a vein. Mag. 125x.

XV-Fig. 9
Cross section of goldenrod stem, showing resin ducts. Mag. 125x.



XV-Fig. 10
Resin ducts from stem, showing rubber-bearing cells in rim of duct. Mag. 500x.

XVI - X-RAY, SPECTROSCOPIC, AND ABSORPTION MEASUREMENTS

X-ray Diffraction. As was expected, the X-ray diffraction patterns from crude and vulcanized hevea, guayule, chilte, and kok-saghyz were identical, the vulcanizates all showing the characteristic "spot" pattern upon elongation. This is also true of goldenrod rubber, although the extension required to produce a high degree of orientation is considerably greater than is necessary for hevea. In addition, however, goldenrod (and one of our guayule samples) gives the powder diffraction of a crystalline material reminiscent of Balata or Gutta-percha. This, we found, had been identified as Gutta-percha in unpublished work by Drs. G. L. Clark and W. H. Smith. The diffraction of interest is indicated by arrows on the reproduction in Figure 1. The spacing, in Angstroms, of these maxima (for four different goldenrod specimens) is compared with Gutta-percha and Balata in Table I. The differences in spacing, between goldenrod and Gutta-percha are too great for experimental error. The amount of this material present in goldenrod is rather small, estimated as less than 10%.

TABLE I. SPACING OF "CRYSTALLINE" DIFFRACTION MAXIMA

	Gutta-percha	Balata	Goldenrod A	Goldenrod B*	Goldenrod C	Goldenrod D	Guayule
Outer (weak)	4.48	4.40	3.76	3.72	3.75	3.76	3.81
Inner	4.97	4.76	4.14	4.17	4.12	4.20	4.35
Literature	4.9						

*Vulcanized Sample

Spectroscopic Observation. Emission Analyses, Qualitative - At the request of the Physical Chemistry Section, qualitative spectrochemical analyses were run on samples of goldenrod from dried leaves to vulcanized product as well as on the materials used in curing the rubber and on the benzol insoluble portion of several pilot plant runs. Copper, manganese, iron, and boron were found in all samples in amounts varying from insignificant traces to concentrations definitely greater than trace amounts. These and quantitative analyses to determine whether or not the amounts present are sufficiently great to seriously affect the aging properties of the rubber have been reported by the Physical Chemistry Section.

Absorption, Ultra-Violet. In connection with work on the formation and properties of "photogels" in the Physical Chemistry Section absorption studies in the region of 2400 Å to 3400 Å were made on samples of goldenrod rubber in 2,2,4 tri-methyl pentane (iso-octane) after varying intervals of irradiation.

A. Absorption curve of the rubber in the hydrocarbon solvent. Curve No. H-1, Figure 2. This curve is typical of the ultra-violet absorption curves described in the literature for other types of rubber,

over

characterized by "very small absorption in the visible region, appreciably below 2700 Å and tends towards a maximum at about 2000 Å," and that "throughout, absorption is of a general nature and not selective." The curve agrees approximately with curves published by:

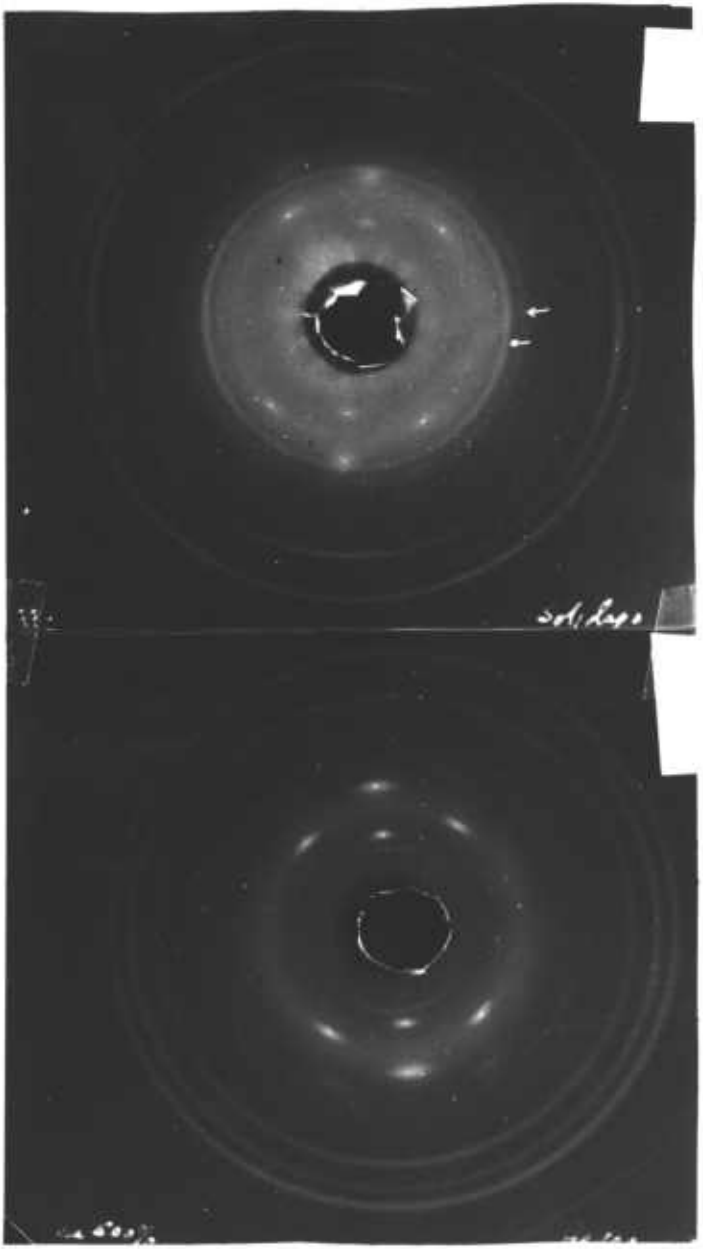
Lewis and Porritt - J. Soc. Chem. Ind. 40, 18T (1921)
Srinevasan, P. S. - Rubber Chem. Tech. 13, 549 (1940)
and
Scheibe and Pummerer - Ber. deut. Chem. Gesell 60, 2163 (1927).

The solution was entirely free of benzol and any other aromatic hydrocarbon impurities.

B. Spectral absorption of a sample of the goldenrod rubber in 2,2,4 trimethyl pentane, 425 mg/100 cc., shortly after the rubber was dissolved (solution having been kept in darkness until absorption measurements were made) compared with the absorption of the same solution after irradiation by approximately mid-day sunlight for four hours. The solution was contained in a sealed Pyrex volumetric flask. Curves Nos. H-7 and H-10, Figure 3, illustrate the great increase in absorption by such irradiation. The circles in the curve of the irradiated sample represent data obtained from the original concentration, the triangles represent data from a tenfold dilution. As, (see below), absorption increases even when the solution is in the dark, the former values were increased by a constant factor alpha = 0.09 in order to obtain a smooth curve. This value may be considered as representing the increase in absorption while the first set of data was being obtained. The increase in absorption by irradiation of the rubber solution in a closed Pyrex flask in sunlight is shown by these curves to be rather uniform throughout the spectral range studied, a four-hour period of sunlight producing about a tenfold increase in absorption. The rate of increase is somewhat greater at the shorter wave lengths. The character of the curve is unchanged with the increased magnitude of absorption and little or no bathochromic effect is observed. This might be interpreted as an increase in an absorbing medium originally present rather than a change in the nature of the material causing the absorption.

C. Absorption of the 2,2,4 tri-methyl petane solution after one and after four hours of irradiation by mid-day sun, through sealed Pyrex flasks. Curves Nos. H-8 and H-10, Figure 4, show that the increase in absorption is somewhat proportional to the time of irradiation. As before, two concentrations have been used in obtaining the curves and an adjustment, alpha = 0.03, has been made to account for the increase in absorption while the first concentration was being measured. There is no evidence of any change in the character of the absorbing medium as the increase in its quantity continues.

D. As evidence that the solution increased in absorption even when not being irradiated was noticed, a sample of the rubber solution was irradiated for one hour, the absorption of a portion of it charted while another portion was kept in complete darkness for four hours.



Stretched Goldenrod Rubber (Top)
Stretched Hevea Rubber (Bottom)

XVI - Figure 1

Curves H-8 and H-9, Figure 5, show that increased absorption results even in the dark, the nature of the increased absorption appears to be the same as that obtained upon irradiation, but the magnitude of the increase is considerably less.

These studies from a standpoint of the effect of light on rubber solution suffer from the fact that, (1) the Pyrex container cuts out most of the ultra-violet light which would be expected to be more effective in producing a photochemical result, (2) in the closed flask, the sunlight greatly raises the temperature causing some doubt as to whether the observed effect might not be due to increased temperature rather than to light, (3) the flask contains a considerable proportion of oxygen and especially considering the elevated temperatures the effect observed may be due to oxidation, and (4) even if studies were made through ultra-violet transparent flasks, a source of ultra-violet light with radiations at least to 2000 Å should be used rather than sunlight.

The absorption curves agree rather well with the one published by Lewis and Porritt - J. Soc. Chem. Ind. 40, 18T (1921).

Srinevasan - Rubber Chem. Tech. 13, 549 (1940) found that "irradiation with ultra-violet light makes rubber more transparent when in non-polar solvents due to depolymerization." However, his experiments were carried on in the absence of air and with light of shorter wave lengths.

Van Rossem - India Rubber J. 48, 172 (1914) finds that rubber is depolymerized under the action of light, while Doyadkin and Pantschenfov - Kolloid Z. 65, 350 (1933) conclude that "light is able to cause polymerization," and Asano - India Rubber J. 70, 307 (1925) finds that "ultra-violet light is able to bring about either polymerization or depolymerization according to its wave lengths."

Meyer and Ferri - Rubber Chem. Tech. 9, 570 (1936) show that in the absence of oxygen the action of ultra-violet light produced a gel resembling gel rubber, identical in properties to the original except in solubility, while the presence of oxygen resulted in a sticky viscous product which has no longer any characteristics of rubber.

From these conflicting results, it can be concluded that probably at least two independent reactions have been described, (1) the oxidation of rubber accelerated by heat and/or light, and (2) the equilibrium between polymerized and non-polymerized rubber in solution, the effect of ultra-violet light being to cause a shift in this equilibrium, the direction of the shift depending upon the nature of the solvent.

From the curves obtained as a result of these studies, it is our conclusion that the reaction studied is the first type described above, that this oxidation is slowly proceeding in the 2,2,4 tri-methyl pentane solution and that the effect of sunlight is but to accelerate the rate of this reaction.

over

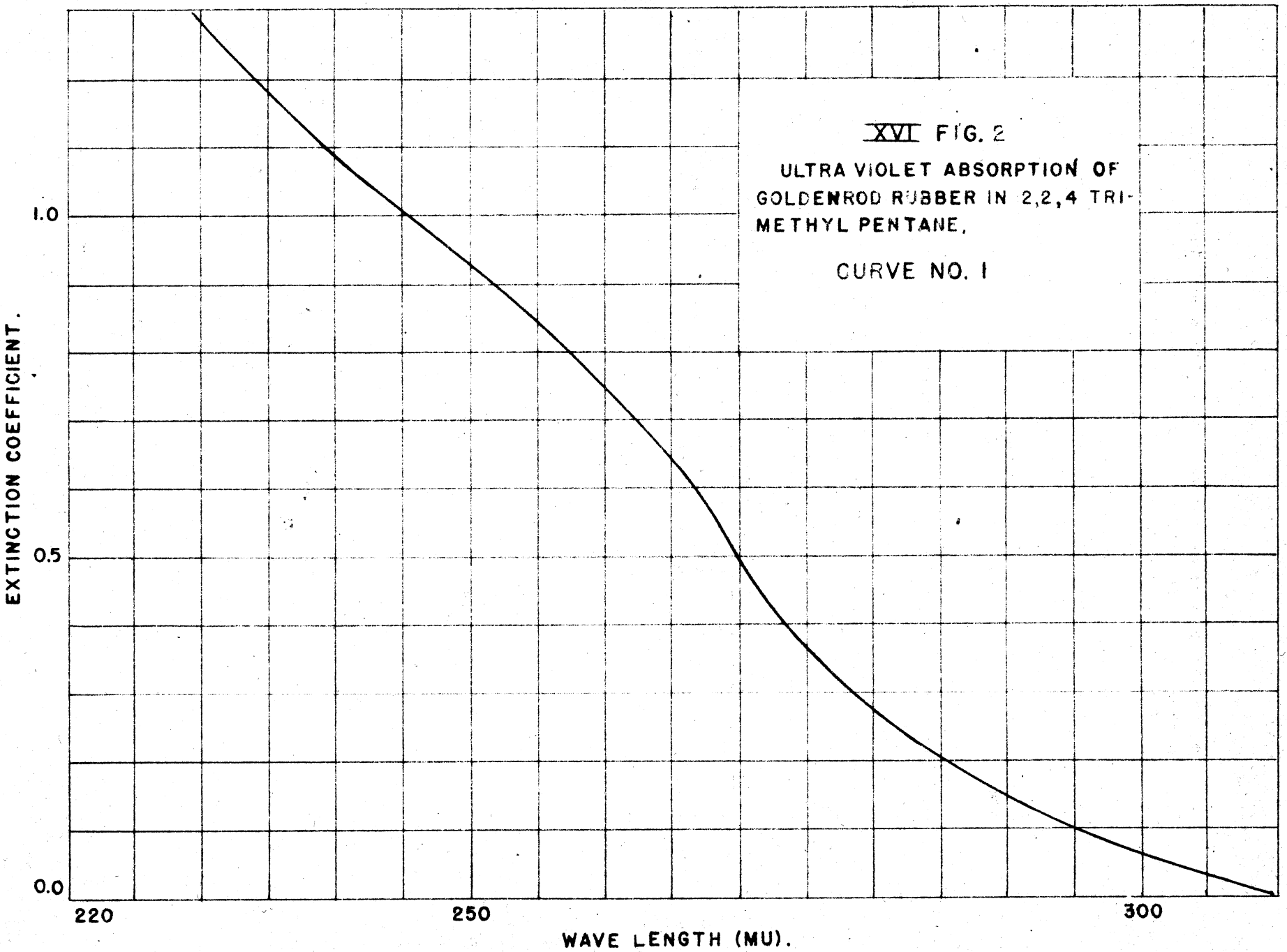
Study of the change of absorption of these solutions when held in total darkness, and the effect of ultra-violet light in the absence of heating effect might shed further light on the nature of the reaction.

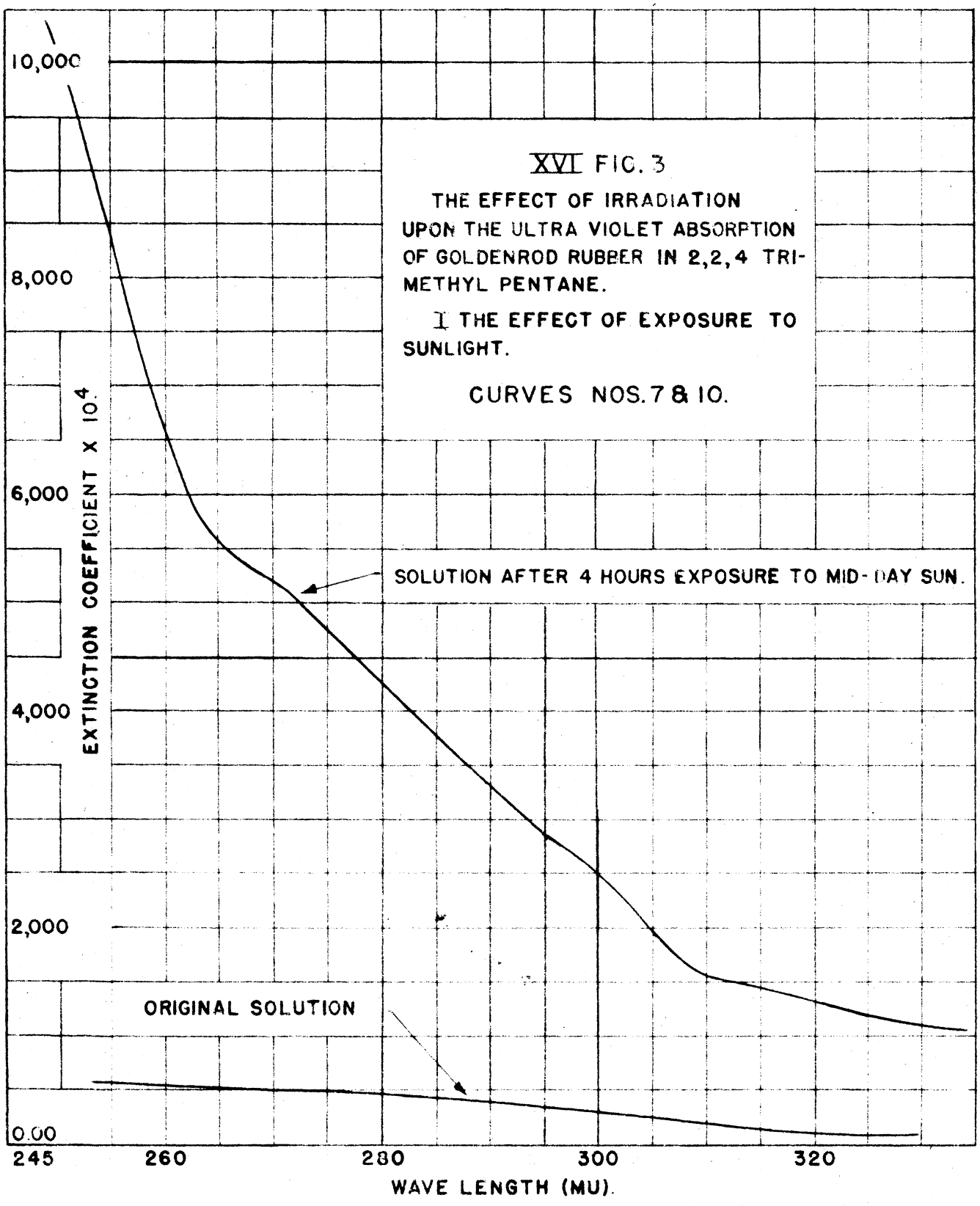
For these studies, flasks which permit ultra-violet to reach the solution would have to be used and they would have to be shielded from the far red (heat) rays. Precautions to avoid any increase in temperature and complete removal of any oxygen would have to be achieved prior to the irradiation. A source of light rich in ultra-violet rays down to 2000 Å would also be required.

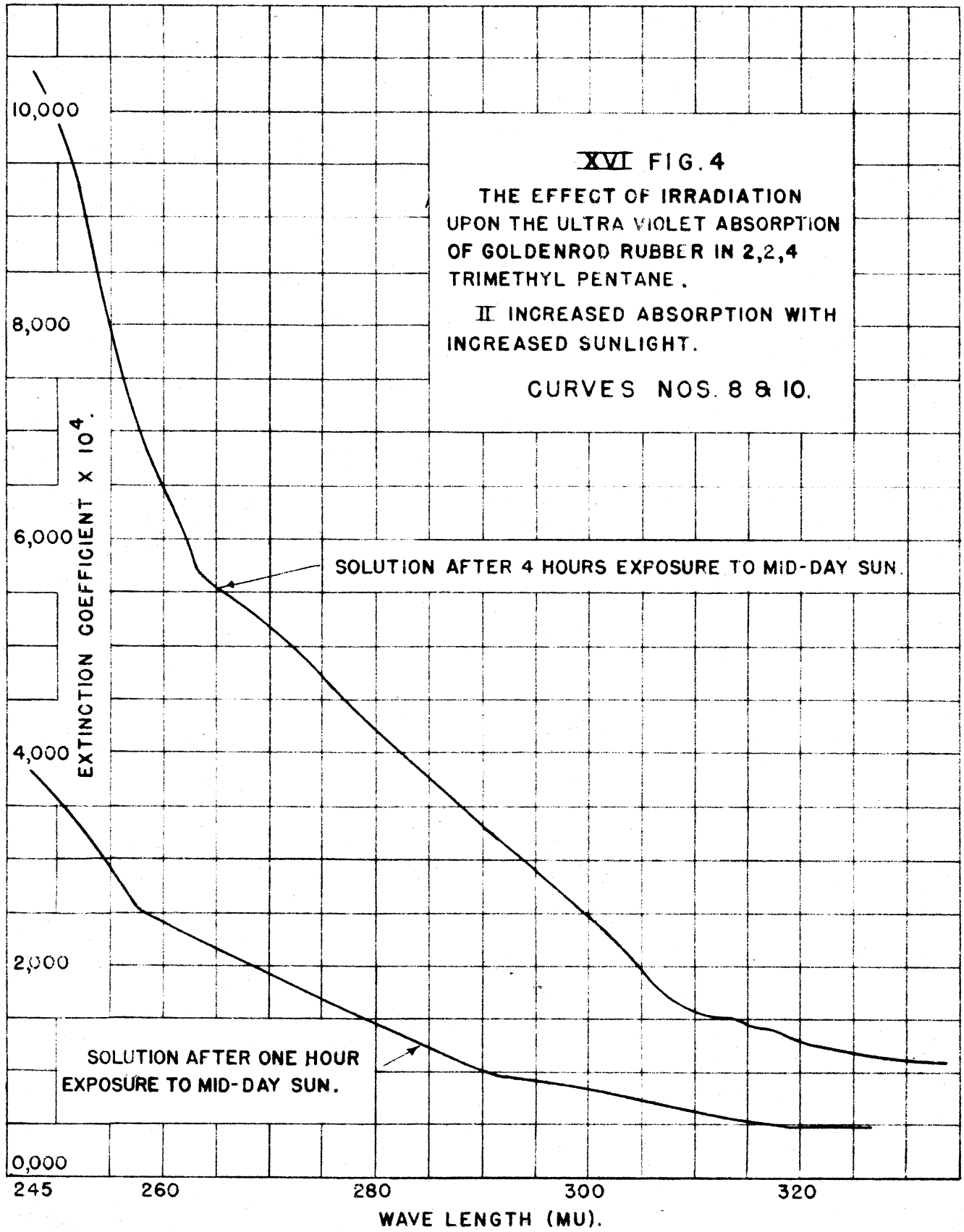
The correlation of these data and conclusions with the formation and properties of photogels have been reported by the Physical Chemistry Section.

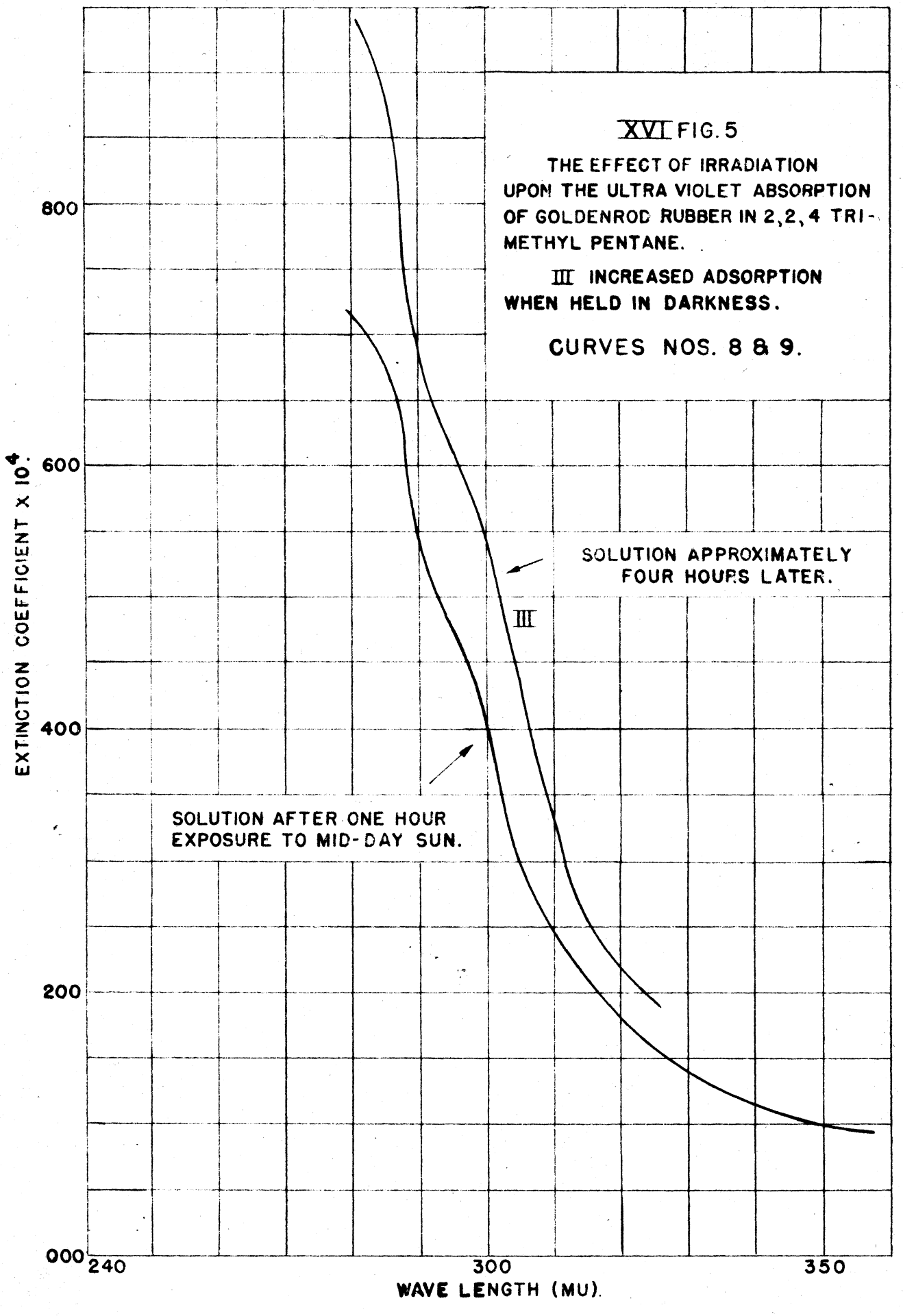
Spectrophotometric measurements in the ultra-violet of solutions of crystalline material isolated, purified, and modified by the Analytical Section and the data directly relating to the identification of this material as quercetin is included in the report of that section.

Absorption, Visible. Spectrophotometric measurements were reported on various solutions of pigment fractions from goldenrod. Carotene and chlorophyll were identified by this means. The significance of these pigments is reported by the Physical Chemistry Section.


XVI FIG. 2
ULTRA VIOLET ABSORPTION OF GOLDENROD RUBBER IN 2,2,4 TRI-METHYL PENTANE.
CURVE NO. I
EXTINCTION COEFFICIENT.
1.0
0.5
0.0
220
250
300
WAVE LENGTH (MU).


XVI FIG. 3
THE EFFECT OF IRRADIATION UPON THE ULTRA VIOLET ABSORPTION OF GOLDENROD RUBBER IN 2,2,4 TRI-METHYL PENTANE.
I THE EFFECT OF EXPOSURE TO SUNLIGHT.
CURVES NOS. 7 & 10.
SOLUTION AFTER 4 HOURS EXPOSURE TO MID-DAY SUN.
ORIGINAL SOLUTION
EXTINCTION COEFFICIENT X 10^4
10,000
8,000
6,000
4,000
2,000
0.00
245
260
280
300
320
WAVE LENGTH (MU).


XVI FIG. 4
THE EFFECT OF IRRADIATION UPON THE ULTRA VIOLET ABSORPTION OF GOLDENROD RUBBER IN 2,2,4 TRIMETHYL PENTANE.
II INCREASED ABSORPTION WITH INCREASED SUNLIGHT.
CURVES NOS. 8 & 10.
SOLUTION AFTER 4 HOURS EXPOSURE TO MID-DAY SUN.
SOLUTION AFTER ONE HOUR EXPOSURE TO MID-DAY SUN.
EXTINCTION COEFFICIENT X 10^4.
10,000
8,000
6,000
4,000
2,000
0,000
245
260
280
300
320
WAVE LENGTH (MU).


XVI FIG. 5
THE EFFECT OF IRRADIATION UPON THE ULTRA VIOLET ABSORPTION OF GOLDENROD RUBBER IN 2,2,4 TRI-METHYL PENTANE.
III INCREASED ADSORPTION WHEN HELD IN DARKNESS.
CURVES NOS. 8 & 9.
SOLUTION APPROXIMATELY FOUR HOURS LATER.
III
SOLUTION AFTER ONE HOUR EXPOSURE TO MID-DAY SUN.
EXTINCTION COEFFICIENT X 10^4.
800
600
400
200
000
240
300
350
WAVE LENGTH (MU).

XVII BY-PRODUCTS: ACETONE SOLUBLE CONSTITUENTS

The urgency of the problem of producing the rubber was such that only limited attention could be devoted to the by-products incidentally obtained. These were principally in the acetone extract removed prior to extraction of the rubber, or separated in acetone solution by reprecipitation of crude rubber for purification. When only leaves were harvested, the raw material contained two and a half to three times as much of these acetone soluble materials as rubber, and when blossoms and stems were included, the proportion was higher. The residue after distillation and recovery of acetone is a greenish black, semi-solid mass, fluid at 140°C., rather more pasty than sticky; the designation "resins" is inaccurate, although it had become established by usage in previous work on goldenrod rubber and has been employed throughout this report with qualification of its definition, for want of a better concise term.

It is probable that the material contains a minor proportion of substances that might be classed as resins in the loosely accepted sense of any natural or synthetic substance characterized by hardness, brittleness, fusibility, conchoidal fracture, "resinous" luster, etc. It is equally probable that it does not contain any substance that is a true resin, definable as the product of exudation or sap of certain plants or trees, consisting chemically of oxidation or polymerization products of the terpenes.

The material, remaining after evaporation of the acetone extract, is not completely soluble in any of the solvents tried. Cold acetone dissolves about 80 percent of the substance, leaving behind a yellowish, friable product which is partially soluble in hot water. This fraction appears to contain flavone substances and give some of the tests for tannin, but has not been investigated further. About one-third of the acetone extractives of goldenrod material is soluble in hot water. Present evidence indicates that the water soluble fraction is composed chiefly of glycosides including some tannins. Other components are sugars and organic acids. The glycoside present in the largest amount is quercitrin. Good yields of its aglucon, quercetin, can be obtained by hydrolysis of the hot water extract. This is dealt with in detail in another section of this report. Little has been learned about the composition of the water insoluble portion. Presumably it contains cuticle wax and fatty substances. Crystalline, wax-like preparations have been obtained from it, but lack of time and clear cut methods for the characterization of substances of this type has prevented the acquisition of definite information about them. The dark-green color of the acetone extractives indicated the presence of much chlorophyll. However, an analysis of a typical sample showed only 0.44 percent. This is surprising in view of the source and history of the material. Nevertheless, the value is probably correct, since the magnesium content places an upper limit of 1.4 percent on the chlorophyll content, and the water-insoluble nitrogen content puts an upper limit of 2 percent on the content of chlorophyll plus chlorophyll derivatives.

The larger part of the work on the acetone extractives was done on the sample from the evaporation of the acetone extract of laboratory extraction

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No. 11. Some of the analytical values obtained on this sample were as follows:

	Percent
Loss of weight when heated 5 hr. at 65°C. in vacuo	7.3
Ash	0.31
Magnesium	0.037
Calcium	0.005
Phosphorus, total	0.1
Sulfur, total	0.075
Nitrogen, total	0.16
Nitrogen, water soluble	0.04
Chlorophyll, estimated from absorption curve	0.44
Carotene, estimated from absorption curve	0.07
Water soluble material	38.0
Quercetin, crude, by hydrolysis of water soluble material	11.0
Organic acids estimated from titration curve of water extract	5.0
Reducing sugars and easily hydrolyzable carbohydrates, including sucrose	2.3
Sugars by complete acid hydrolysis of sample	11.9
Sugars by complete acid hydrolysis of water soluble material	11.4

It was frequently suggested that the "resins" obtained might be useful as a softener, plasticizer, or modifier of synthetic rubbers, particularly GR-S; however, it was evident early in the study of vulcanization of goldenrod rubber that amounts of this material in excess of 5% had a marked adverse effect upon the quality of the vulcanized product. Samples of the material were furnished laboratories interested in this possibility, as well as in the possible applications of the material in plastics, but no developments of practical value have been reported. It is evident that the crude material produced in the pilot plant process is a very complex mixture, a major portion of which consists of water soluble substances including carbohydrates, and that any applications would necessarily depend upon a partial separation into fractions of at least greater chemical compatibility, if not chemical homogeneity.

A single experiment was performed on the separation of the crude mater into fractions, particularly to separate the water-soluble from the insoluble portions. Steam was passed into the mass allowing condensate to accumulate so that the agitation by steaming thoroughly removed water soluble material while any volatile substances steam distilled. A preliminary trial of this procedure showed that the amount of steam volatile oil was negligible, and that much of the water insoluble material remained dispersed in the hot solution and was decanted. The experiment was made with 618.6 g. of the crude product into which steam was passed for two hours when 600 ml. of condensed aqueous solution had accumulated. On cooling to room temperature (23°C.) the insoluble material floated and was separated and again steamed for two hours. After the second steaming and cooling the insoluble residue was denser than the solution which was readily decanted. The steaming was repeated in all five times, and resulted in the removal of a total of 209.5 g. of water soluble substances equal to 33.9% of the original weight; in addition each decanted aqueous solution yielded a water insoluble fraction which settled on standing 48

hours at room temperature, the total of these fractions, 146.2 g., accounting for 23.6% of the original material.

In the last steaming operation advantage was taken of the observed dispersion of the water insoluble material at elevated temperatures to effect a separation of four distinct fractions aggregating 206.2 g. or 33.4% of the original weight. By holding the temperature for 30 mins. a successively decreasing temperatures, a partial separation occurred at each temperature, and the aqueous dispersion was separated from the insoluble precipitate. The fractions were all black, the one separated at the highest temperature being hard and brittle while those at lower temperatures were progressively softer. Fractions from the first steaming operations were either hard and brittle or waxy; all were black in color. About 9% of the original material was lost in handling or as a small amount of volatile oil in the first distillates. Table I shows the amounts of the fractions obtained, but time permitted no further work upon their properties and composition.

XVII TABLE I

Fract.	Settling Temp. °C.	Settling Time hrs.	Vol. Decanted ml.	Wgt. of Mtrl. In Sol. Grams	Wgt. of Mtrl. In Ppt. Grams	Ppt. % orig. mtrl.	Sapon. No.
A	23	48	600	171.2	10.5	1.7	--
B	23	48	175	4.1	1.0	0.2	--
C	23	48	725	18.7	46.0	7.4	90-93
D	23	48	225	6.9	83.7	13.5	92-97
E	95	0.5	400	---	40.0	6.5	97-98
F	70	0.5	---	---	115.0	18.6	88-90
G	50	0.5	---	---	36.2	5.9	75-80
H	30	0.5	---	---	15.0	2.4	89-98
I	23	48	---	8.6	5.0	0.8	-----
tal				209.5	352.4	57.0	

solation of Quercitrin and Quercetin from the Acetone Extract of rod Material. Since preliminary experiments indicated that the ace- xtract of goldenrod material (chiefly leaves) contained a consider- a quantity of flavone-like substances, steps were taken to isolate the chief flavone component.

Approximately 25 g. of the green, gummy residue from the evaporation of the acetone extract of laboratory extraction No. 11 was ground in a mortar with 200 ml. 0.25 N sodium hydroxide, filtered through a fluted paper. the residue ground with 100 ml. more 0.25 N sodium hydroxide and filtered. The filtrate was made acid with acetic acid, allowed to stand several hours and the precipitate which formed centrifuged out. The supernatant was neutralized with 10 percent sodium hydroxide, 25 ml. saturated lead acetate added, the copious precipitate which separated centrifuged out and washed well with water. The precipitate was suspended in water and the lead removed by treatment with hydrogen sulfide for three days with frequent shaking. The lead sulfide was filtered out,

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washed with hot water and the hydrogen sulfide removed from the filtrate by aeration with nitrogen. The lead sulfide was saved since it retained adsorbed material. The filtrate was evaporated almost to dryness in vacuo in a 45°C. bath and the brown sirup washed from the flask with about 100 ml. acetone after standing several hours, a small precipitate was removed by filtration, the filtrate evaporated in vacuo, taken up in 20 ml. acetone and mixed with 100 ml. ethyl ether. After standing overnight a copious precipitate was separated by filtration, washed with ether and dried. It weighed 0.6 g., tasted bitter and gave a strong test for "tannin" with ferric alum. It was not investigated further. The filtrate was allowed to evaporate to dryness. The light-yellow residue weighed 1.2 g. It was taken up in 5 ml. water and washed well with water. The residue was dissolved in 15 ml. acetone and water added to incipient turbidity. After several days a crystalline precipitate was filtered out on hardened paper, washed with water and dried in vacuo over phosphorus pentoxide. It weighed 0.69 g. and was designated AH406. It was proved to be quercitrin by the evidence given later. The lead sulfide precipitate saved from the above experiment was eluted with 250 ml. acetone. This elutriate on evaporation yielded 1.0 g. of a product similar to that obtained from the filtrate. It was not investigated further.

In an experiment similar to that just described, approximately 53 g. of the same acetone extract was processed for the flavone-like substance. In this experiment, most of the product was found adsorbed on the lead sulfide precipitate, from which it was eluted with acetone. The yield from this experiment was about 3 g. A photomicrograph of the crystals from this experiment is shown in Fig. 1. About 10 g. of the material was obtained from various experiments and combined in one lot designated as AH405. All of this was eluted from the lead sulfide precipitate. A smaller lot designated as AH407 was obtained from the lead sulfide filtrate.

The results of microcarbon and hydrogen determinations were as follows:

	% Carbon	%Hydrogen	%Ash
AH405	52.1	5.0	
AH406	53.9	5.0	0.
AH407	54.2	5.3	
Calculated for quercitrin $C_{21}H_{20}O_{11} \cdot 2H_2O$	52.0	5.0	
AH406 dried at 170°C. (loss 5.6%)	56.3	4.7	
Calculated for quercitrin, dry, $C_{21}H_{20}O_{11}$	56.2	4.5	

The absorption curves of the preparations yielded the following data:

	Max.	Ext. Coef.*	Min.	Ext. Coef.*	Max.	Ext. Coef.*
AH405	2600Å	48	3000Å	16	3500Å	35
406	"	49	"	19	3450Å	36
407	"	48	"	19	3450Å	35

*($E^{g/l}_{1cm}$)

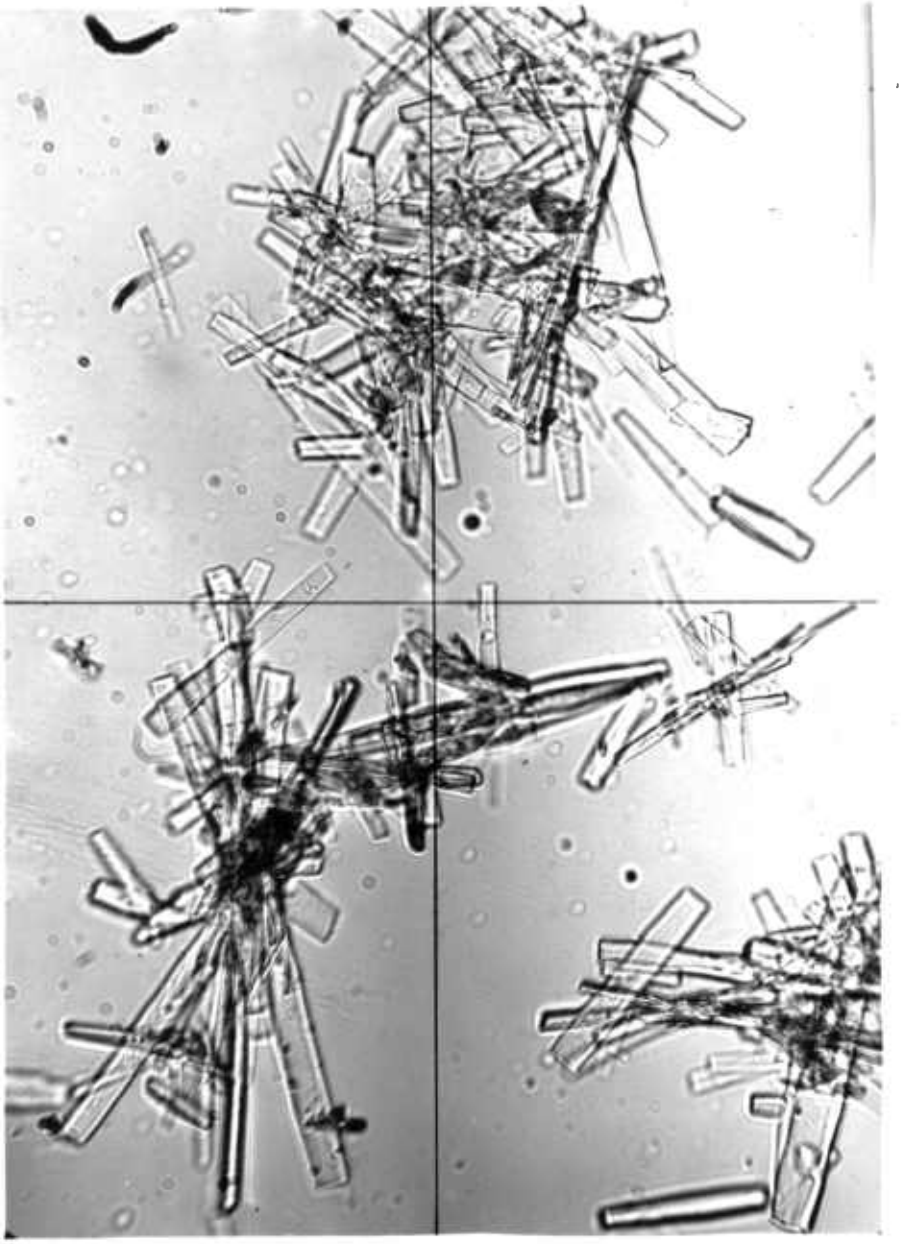

Fig. 1. Crystals of Quercitrin from Goldenrod Material

The absorption curve of AH406 in 95 percent ethanol is given in Fig. 2. This curve is based on the undried product which lost 5.6 percent on drying at 170°C. Marchlewski, L. and B. Skarzynskii, Bioch. Z. 297 56-9, 1938, C. A. 32 8931 give the absorption manima for quercitrin at 2612 A and 3560 A.

A positive Rosenthaler test for rhamnose (Morrow and Sandstrom, 2nd Ed., page 168) was given by the substance after acid hydrolysis.

Since the above data showed that the substance was quercitrin (3,5,7, 3',4' pentahydroxyflavone-3-rhamnoside) or a closely related substance, positive identification was sought by hydrolysis to the aglucon and sugar, each of which was identified.

The preparation designated as AH406 was hydrolyzed by refluxing one hour with 25 ml. water plus 2 ml. concentrated sulfuric acid. The yield of aglucon from 200 mg. was 125 mg. The sulfuric acid was removed from the filtrate with barium carbonate and the filtrate was evaporated to about 3 ml. A small precipitate was removed by centrifugation in a 15 ml. conical tube and 5 ml. of phenylhydrazine reagent added (Morrow and Sandstrom, 2nd Ed., page 161). The tube was then heated at 95°C. for 0.5 hr. and the osazone centrifuged out. Heating for an additional 2 hours brought down more osazone precipitate was recrystallized twice from dilute pyridine and twice from 50 percent methanol. After drying in vacuo over phosphorus pentoxide, the osazone melted at 184°-185° (corr.) when heated rapidly as recommended by Morrow and Sandstrom, 2nd Ed., page 161. An osazone prepared from a known sample of rhamnose melted at 185°-186°C. (corr.); mixed melting point 184°-185°C. (corr.). The osazone from the preparation AH406 was dried at 120°C. and analysed for nitrogen by the micro Dumas method. Found, nitrogen 16.28, 16.37 percent; calculated for the osazone of rhamnose 16.36 percent. The aglucon was prepared from the preparations designated as AH405 and AH406. After recrystallization from dilute alcohol and drying at 125°C., the following results were obtained by micro-combustion.

	% Carbon	% Hydrogen	% Ash
AH405 a glucon	58.5	3.4	1.4
AH406 a glucon	59.1	3.4	0.9
Calculated for quercetin $C_{15}H_{10}O_7$	59.6	3.3	

The absorption curves of the aglucon preparations yielded the following data:

	Max.	Ext. Coef.	Min.	Ext. Coef.	Max.	Ext. Coef.
AH405 aglucon	2560Å	74	3000Å	20	3740Å	74
AH406 aglucon	2560Å	74	3000Å	20	3720Å	74

Grinbaumowna, R. and L. Marchlewski, Bioch. Z. 290 261-8, 1937, C. A. 31 6968 give the maxima for quercetin at 2555A and 3755A.

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From the above evidence, it may be concluded that the chief flavone substance in the acetone extract of the goldenrod material is quercitrin (3,5,7,3',4' pentahydroxyflavone-3-rhamnoside).

Since it seemed likely that the aglucon, quercetin, could be isolated much more simply than the glycoside, quercitrin, the isolation of quercetin directly from the acetone extract was undertaken. In a preliminary experiment, 5 g. of the green, gummy residue from the acetone extract of laboratory extraction No. 11 was extracted with portions of boiling water until about 500 ml. was used. The hot water extract was filtered and evaporated to dryness. The yield of material soluble in hot water was 1.9 g. or 38 percent. This material was re-extracted with six 25 ml. portions of hot water, 4 ml. concentrated sulfuric acid in 25 ml. water were added to the filtrate which was refluxed for one hour and placed in a refrigerator overnight. The crude quercetin that precipitated weighed 0.552 g., a yield of 11 percent based on the acetone extractives. The crude quercetin was recrystallized twice from dilute alcohol and dried at 125°C.

Microcarbon and hydrogen determinations gave C, 59.7 percent, H, 3.7 percent, ash 0.4 percent. An absorption curve showed maxima at 2560A and 3780A with extinction coefficients of 67 and 68, respectively.

Because of some interest in derivatives of quercetin from a therapeutic standpoint, its isolation from the acetone extractives of goldenrod material was undertaken on a larger scale. After a number of experiments on 50 g. lots of the acetone extractives, the following large scale experiment was made.

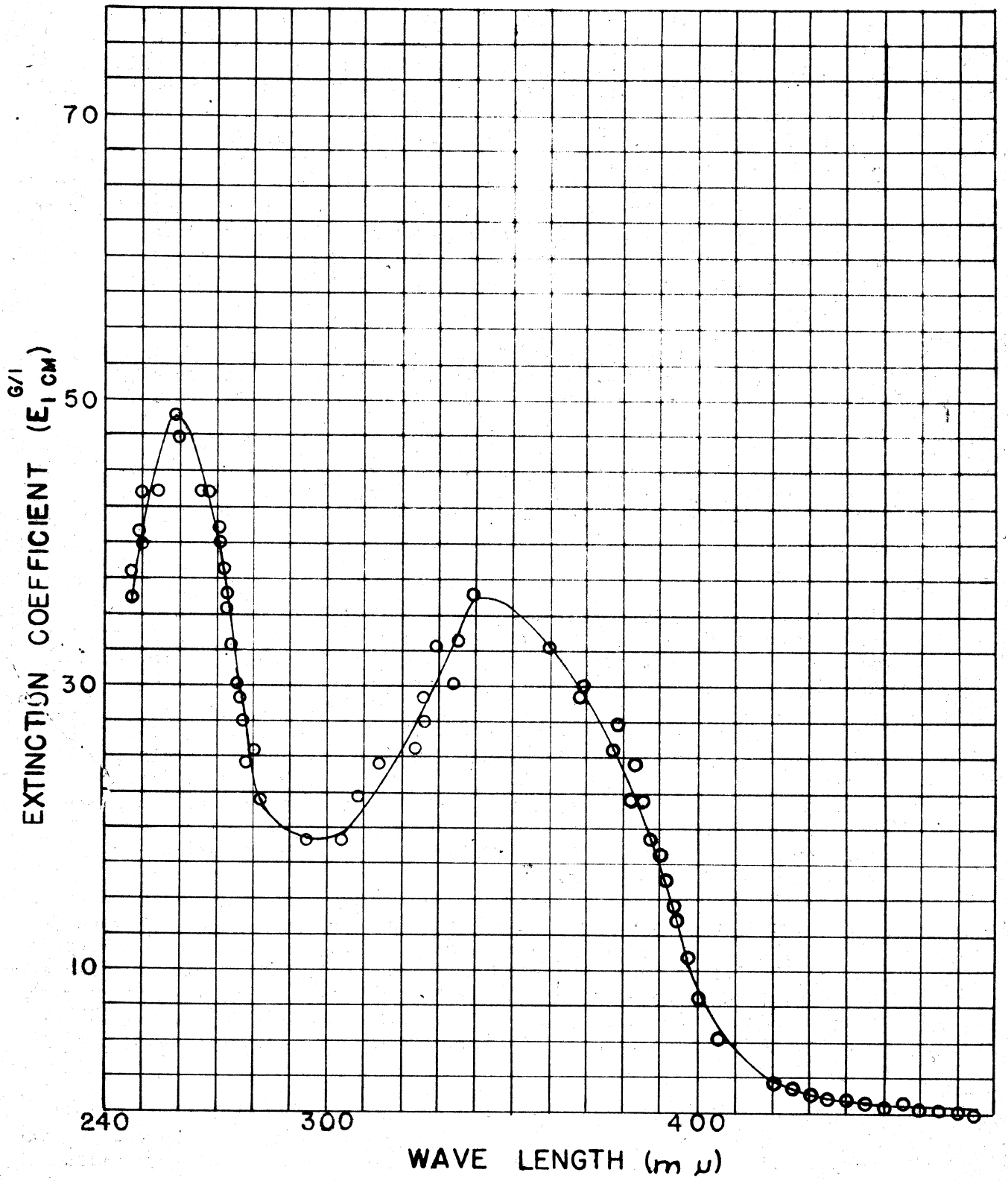
A total of 47 kg. of the evaporated acetone extracts from the 1942 pilot plant runs nos. 1,2,3,4,5,9,10,11, and 12 was mixed for 3 hours in three approximately equal batches with a total of 70 gallons of hot tap water at 98°to 100°C. The mixture was allowed to cool overnight and the supernatant liquid was siphoned from the cake of undissolved material. The combined supernatant liquid was divided into three approximately equal batches, each of which was mixed with 1.5 liters of concentrated sulfuric acid and heated at the boiling point for 2 hours. This hydrolyzed the flavone glycosides to quercetin. The mixture was allowed to cool for 2 hours and the crude product which settled to the bottom was separated by siphoning and decantation of the supernatant liquid. All the above operations were carried out in a steam-jacketed copper kettle equipped with a motor-driven stirrer.

The crude quercetin was washed with distilled water on a large Buchner funnel until free of acid, dried in a steam cabinet followed by 7 hours in an oven at 105°C., and ground through a coffee mill. The yield of crude product was 4.3 kg. An absorption curve of this crude material gave maxima at 2580A and 3700A. The extinction coefficient at 3700A was 44. This gives an upper value of about 58 percent for the quercetin content of the crude product.

The product was dissolved in hot 95 percent ethyl alcohol, precipitated with an equal volume of water and washed with 50 percent alcohol. After recrystallization from 80 percent alcohol (at this stage an absorption

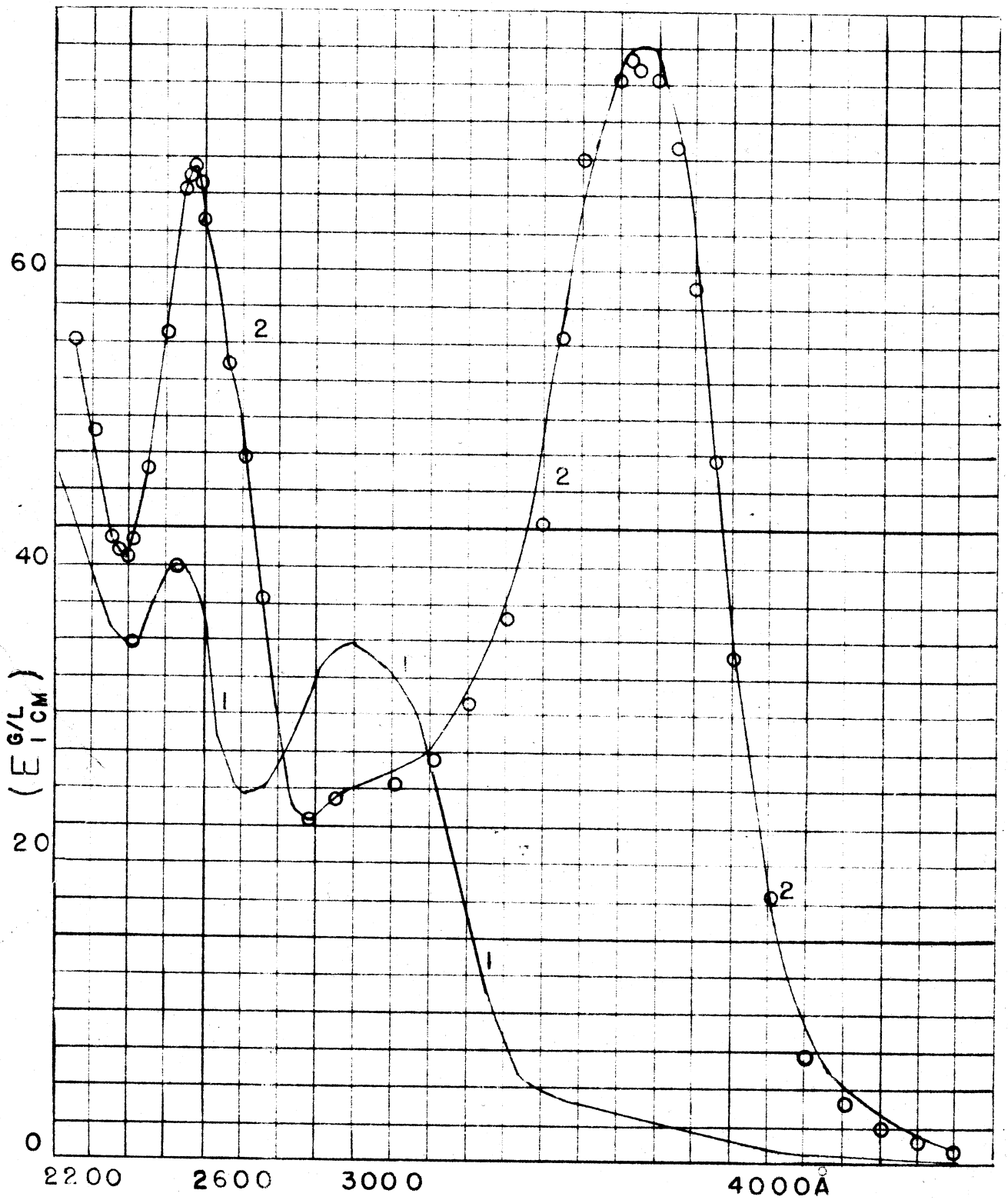
ABSORPTION CURVE OF QUERCITRIN
SAMPLE AH406

XVII FIG. 2



CURVE 1, PENTA-ACETATE OF QUERCETIN. CURVE 2, QUERCETIN REGENERATED FROM THE PENTA-ACETATE POINTS ARE VALUES FOR PURIFIED QUERCETIN FROM THE LARGE SCALE EXPERIMENT

XVII FIG. 3



curve indicated a purity of 82 percent), it was dissolved in hot acetone and fractionally precipitated with Skellysolve F. About 2.5 liters of acetone was required for each 200 g. of quercetin. On addition of an equal volume of Skellysolve F a black, gummy material separated in a few minutes. The filtrate from this material was diluted with an additional 2 liters of Skellysolve F and the red, oily material which precipitated was separated after decantation of the supernatant liquid. Quercetin was precipitated from the supernatant liquid as a bright yellow product by an addition of 2 liters of Skellysolve F. The red, oily material also yielded some quercetin when dissolved in acetone and fractionally precipitated with Skellysolve F. The total yield of purified quercetin was 780 g. The yield could be increased by working over various impure fractions.

Micro C and H determinations on the purified product dried at 170°C. gave 59.1, 59.3 percent carbon and 3.8, 3.7 percent hydrogen. The calculated values for quercetin, $C_{15}H_{10}O_7$ are 59.6 percent carbon and 3.3 percent hydrogen. A small portion of the product was further purified by recrystallization and dried at 170°C. It gave 59.7, 59.7 percent carbon and 3.6, 3.5 percent hydrogen. A portion of the main lot of purified product was converted to the penta-acetate according to the procedure described by Morrow and Sandstrom, 2nd Ed., p. 295. The recrystallized penta-acetate melted at 200°C. (corr.). A preparation made from a sample of quercetin from Eastman Kodak Co. melted at 200° C. (corr.). Mixed melting point was 200°C. (corr.). Quercetin was regenerated from the penta-acetate and recrystallized. The absorption curves for the quercetin penta-acetate from goldenrod and the quercetin regenerated from it are shown as smooth curves in Fig. 3. For comparison, the points taken from the absorption curve of the main batch of purified product are also plotted in the same figure. All values are based on the dried sample weight. It will be noted that the main product was essentially pure quercetin. The absorption curves of the penta-acetate from goldenrod and the penta-acetate from Eastman Kodak quercetin were identical. This was also true of the absorption curves of the preparations of quercetin regenerated from the penta-acetates. The curves show that the absorption maxima for quercetin in 95 percent ethanol are at 2570A and 3750A with extinction coefficients, ($E^{g/l}_{1cm}$) of 67 and 75.5 respectively. The extinction coefficient at 3750A appears to be the more reproducible of the two.

The quercetin from both goldenrod and Eastman Kodak Company was found to have a marked antioxidant action on peanut oil, cottonseed oil, and lard when added in amounts of about 0.02 percent. The antioxidant action of quercetin has been previously noted by Greenbank, Oil and Soap 13 140-44, 1936.

Note on the Waxy Impurity Spontaneously Separated from Concentrated Benzene Extracts. As noted in Section III it was observed that on storage a precipitate settled from the pilot plant benzol extracts which had been concentrated to about 15% rubber. Some of this precipitated material was collected, purified by recrystallizing from Skellysolve B followed by washing with ether and hot alcohol. The purified material was a fine white

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crystaline substance having a molecular weight of 480 $\pm$ 30 and a sharp melting point at 87°C. The elementary analysis is as follows:

C	82.05%	N	none
H	13.60%	S	none
O	4.35%	P	none

Iodine No. (Wijs) 19.10

The substance could possibly be 18-penta-triacontanone (Stearone) $(C_{17}H_{35})_2CO$ although positive identification was not attempted because of lack of time.