

The Industrial Utilization of Rosin

Ray V. Lawrence

Two types of rosin are produced in this country, wood and gum rosin. Wood rosin, along with other constituents, is extracted by a petroleum solvent from resinous stumps and deadwood of the pine tree. Gum rosin is the residue in the still after the turpentine has been steam-distilled from the oleoresin made to flow by wounding certain species of the living pine.

Rosin is graded and sold on the basis of color, the paler colors bringing the higher prices. The color grades range from pale yellow, graded X, to dark red (almost black), graded D. The colors between these extremes increase progressively through the grades, WW, WG, N, M, K, I, H, G, F, and E. Because of improved modern methods, about 80 percent of the gum rosin produced is grade M or better. Unrefined wood rosin, as produced directly from the extracting solvent, is ruby red. It is graded FF. The highly colored material obtained in refining wood rosin is no longer classifiable as rosin. It is sold as B resin or under various trade names. (Resin, a general term, refers to a wide variety of natural and synthetic products. Rosin, a specific kind of resin, is obtained only from pine trees.)

The color of gum rosin is due almost entirely to iron contamination and oxidation products. The oleoresin as it exudes from the tree will yield a rosin that is practically colorless. The color of wood rosin is due to the presence of

oxidized resin acids and other organic compounds extracted from the wood along with the rosin. The color bodies are most commonly removed from wood rosin by means of selective solvents and by selective adsorption on solid adsorbents, such as fuller's earth.

In the selective-adsorption method, a 10- to 15-percent solution of dark wood rosin in gasoline is pumped up through a bed of fuller's earth. The dark products removed from the rosin solution remain on the fuller's earth. When the fuller's earth becomes saturated, it is washed with alcohol, which removes the colored products. The washed fuller's earth is freed from alcohol and used again. The dark material washed off by the alcohol is known as B resin. Such a method is also suitable for improving the color of gum rosin, but it is much simpler just to keep the color bodies out of gum rosin.

Rosin consists of about 90 percent resin acids and 10 percent neutral matter. Of the resin acids about 90 percent are isomeric with *l*-abietic acid, whose composition is $C_{20}H_{30}O_2$, (20 parts of carbon, 30 parts of hydrogen, and 2 parts of oxygen). The other 10 percent is dihydroabietic acid, $C_{20}H_{32}O_2$, and dehydroabietic acid, $C_{20}H_{28}O_2$. Although the ultraviolet absorption of the acid portion of pine gum and gum rosin indicates that *l*-abietic acid may be present to the extent of about 10 percent, this acid has not been isolated from the unisomerized resin acids. About half the total resin acids in rosin can be converted to *l*-abietic acid by acid or heat isomerization. The neutral portion of rosin has not been thoroughly investigated, but it has been shown to contain methyl chavicol, stilbene derivatives, terpene dimers, aldehydes, and a mixture of hydrophenanthrene hydrocarbons, all of them plasticizers for the resin acids.

The United States produces more than a billion pounds of rosin a year, or about 72 percent of the total world production. In 1949, we exported 306 million pounds of rosin, valued at 20 million dollars. Rosin for export is packaged in drums holding about 500 pounds each. Rosin for domestic consumption is packaged in 500-pound drums and in paper bags holding 100 pounds each. For many large consumers rosin is shipped in the molten state in railroad tank cars.

About three-fourths of the rosin used here goes into varnishes, lacquers, and other protective coatings, and into paper and soap. Each of several other industries—rubber, linoleum, grease, adhesive, and the foundry-supply—accounts for 1 to 3 percent of the total domestic consumption.

A varnish is usually prepared by heating a drying oil and a resin together until the desired amount of polymerization, or combining of the molecules, of the drying oil has taken place. When the mixture has reached the proper consistency it is thinned to a satisfactory viscosity with a volatile solvent. A wide variety of resins may be used, rosin being a common one. To convert rosin into a desirable varnish resin, it is necessary to raise its melting point and lower its acidity. This is usually done by converting the rosin to one of its derivatives—generally as a separate step in the process. Some rosin esters, however, may be prepared during the cooking of the varnish. In that case, the rosin, drying oil, and polyhydric alcohol are heated together until the esterification of the rosin and polymerization of the oil are complete.

The rosin derivatives most commonly used as the resin in varnish are the esters, including the malcic-modified esters; rosin phenol-formaldehyde resins; limed rosins; zinc resinates; and various combinations of these classes of derivatives. Rosin may also be hydrogenated, dehydrogenated, disproportionated, or polymerized to obtain derivatives more suitable for use in varnish than the original rosin.

The rosin esters most commonly used in varnish are the glycerol and the pentaerythritol esters. The glycerol ester, commonly called ester gum, has the better solubility characteristics; the pentaerythritol has the higher melting point. If maleic anhydride is reacted with the rosin before esterification, the modified rosin will have a higher melting point and will react more rapidly with the glycerol or pentaerythritol. While rosin will react with 25 percent of its weight of malcic anhydride, 10 to 15 percent is much more commonly used.

Rosin is combined with a heat-reactive phenol-formaldehyde resin to give a widely used varnish resin having much more desirable properties than either the rosin or the phenol-formaldehyde alone. The properties of these resins vary with the ratio of phenol and formaldehyde to rosin and with the type of phenol derivative used. The resin obtained by this reaction is usually esterified with glycerol to give a varnish resin with a low acid number and high melting point. The development of these resins has made possible the rapid-drying (4-hour) varnishes.

One of the simplest methods of forming a derivative suitable for use in varnish is to combine the rosin with a small amount of lime. The melting point and acid number of this limed rosin can be controlled (within certain limits) by varying the amount of lime used. The rosin may be limed in the presence of drying oil, so that the varnish is prepared in a single step.

Zinc resinate resembles limed rosin in that the rosin has been reacted with a metal oxide or salt to reduce the acidity and raise the melting point. Zinc resinates are more difficult to prepare, but they have several advantages, including greater resistance to water.

Some rosin derivatives have uses in paints and varnishes other than serving as a resin. Certain metal resinates are used as driers, which act as catalysts. For a drying-oil film to harden within a reasonable time, a small amount of

drier has to be present. The most commonly used driers are the oil-soluble salts of cobalt, lead, and manganese, generally the resinate, naphthenate, and linoleate salts. The resinates may be prepared by the addition of the metal oxide, hydroxide, or acetate to molten rosin, or by the precipitation of the metal resinate from an aqueous solution of sodium resinate with a water-soluble salt of the desired metal. The products prepared by the first method are known as fused resinates; those prepared by the second, as precipitated resinates. The fused resinates contain less metal but have better solubilities in the varnish solvents. The precipitated resinates, being in a fine state of subdivision, are more difficult to store since they are readily damaged by oxidation.

Unmodified rosin is preferred for other uses. Because of its excellent solubility it may be mixed with poorly soluble resins to make possible their use in formulations in which they would not otherwise be satisfactory.

Another use for rosin in varnish is to retard gelation of certain highly reactive drying oils. For example, one difficulty in preparing varnishes from tung oil is the rapidity with which this oil polymerizes into an insoluble gel. The use of rosin as the resin greatly retards the rate of gelation of tung oil, thus facilitating processing and improving the quality of the varnish. If the tung oil has already gelled, rosin may also serve as a peptizing, or solubilizing, agent.

The use of rosin and a wide variety of its derivatives in printing ink closely parallels their use in ordinary varnish, since a printing ink is essentially a varnish having a high resin and a high pigment content with little or no thinner.

Present-day lacquers consist largely of cellulose derivatives, resins, plasticizers, and solvents. The cellulose derivatives, usually cellulose nitrate or acetate, are the film-forming materials, but they lack adhesion, gloss, and workable viscosity. For instance, the viscos-

ity of a solution containing 20 percent nitrocellulose would be so great that it would be unworkable for application purposes. Viscosity characteristics are improved by use of various natural and synthetic resins, rosin esters, rosin-modified phenolics, and maleic-modified rosin esters. A 20-percent solution of ester gum has a very low viscosity in lacquer solvents and when mixed with a like concentration of nitrocellulose in similar solvents it gives satisfactory viscosity. Because both the nitrocellulose and the resin are usually too brittle to form satisfactory films, a plasticizer is required. The methyl ester of rosin and other low-melting rosin esters are often used for that purpose.

Paper is sized to reduce its penetration by liquids. Numerous sizing agents are used, of which rosin is one of the most important. Rosin size represents the greatest use of a single derivative of rosin—the greater amount consumed by the protective-coating industry is in the form of numerous derivatives whose end uses are difficult to trace. The size is usually added to the pulp in the beater. Here rosin size is precipitated by adding 1 to 2 parts of alum for each part of rosin. The amount of rosin required for sizing varies with the type of pulp and grade of paper manufactured, from as little as 0.2 to 2 percent on regular grades up to 8 percent on special types of paper.

Combinations of rosin with wax, with casein or soy protein, or with glue are also used for sizing. Maleic-modified rosin is said to have much greater sizing power than rosin. One pound of modified-rosin size can do the work of about 4 pounds of ordinary rosin size.

In preparing rosin size, the rosin is usually cooked for a few hours with a sodium carbonate solution. Ordinarily only enough alkali to neutralize from one-third to three-fourths of the rosin is used, so as to yield a product that will remain emulsified when it is diluted. The finished size contains from 40 to 60 percent water. Other methods of preparation are sometimes used. For example, B wood resin, which has a

high neutral content, may be completely neutralized with sodium hydroxide, and the neutralized size extracted with a hydrocarbon solvent to remove the portion of the rosin that did not react with the sodium hydroxide.

Rosin is used in a wide variety of soaps. Rosin soaps are much more soluble in water than are the ordinary fatty acid soaps. Soaps with a fairly high rosin content, therefore, are particularly useful in liquid soap. Laundry soaps and soap powders may be prepared from blends of fatty acids, rosin, and other components in minor amounts. Rosin improves the sudsing, the detergency, and the wetting rate of the soap. Rosin soaps also have germicidal activity.

Soaps composed entirely of sodium or potassium rosinate find specialized uses. A stabilized rosin soap, for example, serves as an emulsifying agent in the emulsion polymerization of butadiene and styrene for the manufacture of synthetic rubber. In fact, this type of rosin soap is used as the emulsifying agent in about one-third of all synthetic rubber now being produced. Because of its good solubility in water, this soap is especially effective in the low-temperature polymerization of butadiene and styrene. Rosin used for this soap should contain less than 1 percent abietic-type acids and should be free of inhibitors which retard the rate of polymerization.

Another advantage of using rosin soap in the emulsion-polymerization step in the preparation of synthetic rubber is that the rosin serves a dual purpose. The polymer is coagulated by the addition of salt and acid, the acid decomposes the soap, and practically all of the rosin used remains in the rubber to act as a softener.

Rosin soap is used in the polymerization of synthetic rubber. Rosin is used as a softening agent or plasticizer in both natural and synthetic rubber. A softener is usually included when the compounding ingredients, such as carbon black, sulfur, zinc oxide, and accelerators, are being mixed with the

raw rubber on the mixing rolls. In natural rubber the softener is usually chosen for its effect on processing or, in some cases, as an extender. In synthetic rubbers the effect on the properties of the compounded product is more important.

Frequently a small amount of terpene solvent is added to rosin used for this purpose. Both the rosin and the terpenes impart tack (a property in which the early synthetic rubbers were noticeably deficient) to the finished product.

Because of its peptizing or solubilizing action on gelled oils, rosin finds use in the preparation of linoleum and linoleum-type floor coverings. Since color is not of great importance here, the darker grades of rosin are commonly used.

A mixture consisting of about 20 percent rosin and 80 percent drying oils, with a small amount of oil-soluble salts of cobalt, manganese, and lead, is blown for about 15 hours. The mixture is thus converted into a rubbery plastic substance known as cement. The cement is used as a binder for the linoleum sheet. It is mixed with pigments and ground cork or wood flour and then passed between heavy rolls to form sheets on a woven or felted fabric base. These sheets must be seasoned. This is done by hanging them in large ovens at 150° to 200° F. for 1 to 10 weeks, depending on thickness.

Most of the rosin used in lubricating greases is in the form of rosin oil, a derivative prepared by the destructive distillation of rosin. It is a viscous liquid consisting of a mixture of resin acids, decarboxylation products of the various resin acids, and other acid and neutral pyrolysis products. Rosin oil is particularly useful in the preparation of lubricating grease by the "cold set" process. In this process the grease is prepared at a relatively low temperature (usually about 120° F.) by mixing mineral oil and a rosin oil with an emulsion of lime and water. This mixture sets up into a gel quickly.

Both rosin and rosin oil are also used

in the more common type of lubricating grease, which is essentially a gel prepared by dissolving a soap (usually of a heavy metal or alkaline earth) in a lubricating oil and allowing the solution to cool. In this type of grease, however, the fatty acid soaps are more common than those of rosin or rosin oil.

A wide variety of formulations of rosin and its derivatives enter numerous types of adhesives. They are particularly acceptable in the field of pressure-sensitive adhesives. Rosin, rubber, and a plasticizer, such as methyl abietate, in combination, make an excellent adhesive of this kind. The backing may be cellophane, paper, cloth, or metal foil, depending upon the intended use of the adhesive. Some other low-melting rosin derivatives used are abietyl alcohol, monoethylene and diethylene glycol esters of rosin, ester gum, and similar derivatives of hydrogenated, dehydrogenated, and the polymerized rosin.

Rosin is used frequently as a bonding agent to strengthen the sand cores of molds in preparing steel castings.

Most steel castings are made in sand molds which use a special type of sand or sand blended with other refractory materials. The interior surfaces of the castings are generally formed by sand cores, which may be formed by the pattern itself or may be made in a core box from special core-sand mixtures. Cores made in core boxes are baked and inserted in the mold after the pattern has been withdrawn. To give the molding sand the strength it requires to hold its form, various bonding

agents are used. The darker grades of rosin are commonly used for this purpose. The highly oxidized portion obtained in refining FF wood rosin is particularly well adapted to this use.

The foregoing uses account for about 90 percent of the total rosin consumption. The innumerable minor uses for rosin and rosin derivatives range from violin bows to preparations for dehairing hogs. Rosin and rosin derivatives are used in leather dressings and shoe polishes, belting adhesives and belt dressings, sealing wax, shoemaker's wax, soldering flux, and disinfectant and insecticide compositions, as a filler for bending pipe and copper tubing, and to harden candles.

Rosin is one of the few agricultural products that is not used primarily for food, clothing, and shelter. It is used almost entirely in manufacturing. With the increasing recognition of the chemical nature of the products manufactured from rosin there is an increased demand for specialized chemical products. In the past, rosin has been used without further modification, but with the increasingly rigid requirements and specific needs, improved rosin and rosin derivatives will be needed. This presents a challenge to naval stores producers—and an opportunity.

RAY V. LAWRENCE has been engaged in naval stores research since 1938. A graduate of the University of Alabama and the University of Tennessee, he is a member of the naval stores research division of the Bureau of Agricultural and Industrial Chemistry.

ABOUT HALF of today's commercial production of rosin comes from pine stumps that have been in the ground for half a century. One naval stores processor has recovered rosin from the ground itself—from a "rosin mine" in South Carolina. It is not a natural formation, of course. It is the result of supply and demand a century ago, when gum turpentine was in great demand, but rosin was not. The half ton of rosin produced with every barrel of turpentine that was distilled and collected was allowed to flow into some nearby gully, where it solidified and remained unchanged through the years. Today the market for rosin has increased, while industrial uses for turpentine have decreased.—*E. P. Waite, Southern Regional Research Laboratory.*