OLD PEOPLE in Germany used to say that moths would not attack woolens dyed green. The saying was untrue, but it influenced the investigations that led to the discovery of DDT as an insecticide. Born thus of a fiction, the almost miraculous killer of disease-carrying insects is still the center of a good deal of fiction.

In a few years it has excited the imagination of scientists and laymen alike—and rightly, for it is effective against a wider variety of agricultural pests than any other synthetic insecticide heretofore tested; it gives control of those history-old scourges, the body louse, the mosquito, and the fly; and, wonderful to relate, its effect lasts, sometimes as long as a year. Evidence of the tremendous interest in DDT is that more than 2,000 articles have appeared in scientific, trade, and general magazines and newspapers about it, almost all of them acclaiming its merits. A colleague of ours, R. C. Roark, in 1944 compiled a 12-page list of publications that had appeared on the subject since 1874; in the next few months, so great was the flood of writing on it, he had to revise and expand the list twice.

This tremendous interest in one compound created one near-fiction involving DDT, the impression in some minds that few studies have been made to find chemicals effective for the control of injurious insects. Actually, the use of chemicals to control insect pests has been going on for centuries. The earliest insecticides were arsenicals and sulfur. Systematic attempts to control insects were first made about 1865 when, in this country, paris green, which was available as a paint pigment, was used to destroy the Colorado potato beetle. Paris green was so effective that for many years it was the most widely used agricultural insecticide; even today our farmers and gardeners use about 4 million pounds of it a year.
In 1892 lead arsenate was developed for use against the larva of the gypsy moth, a serious foe of shade and forest trees. Lead arsenate was found to be effective against many insect pests; its use has continued to increase, and about 80 million pounds of it were used in 1945.

Actually, also, the modern era of the development of new insecticides began about 1910. Investigators here and abroad became interested in how insecticides kill and emphasized the importance of physical characteristics, such as wetting and spreading of sprays on foliage and insects. At that time some of the more important insecticides and fungicides, the arsenicals, nicotine, pyrethrum, derris, lonchocarpus, lime-sulfur, and bordeaux mixture, had been known a long time and some of them had been in use. Much of the effort since then has been devoted to the study of these and related products in order to discover their range of usefulness; to increase their efficiency; and to find more powerful substitutes, safer to man, domestic animals, and plants.

The studies leading to the discovery of DDT as an insecticide can in a measure be traced back to some research initiated about 30 years ago. In 1915 the Bayer dyestuffs company in Leverkusen, Germany, undertook an intensive investigation of chemicals that might be suitable for mothproofing wool. The early investigations were influenced by the saying that woolens dyed green are not attacked by the clothes moth. Investigations proved the saying to be erroneous. Further investigation showed that the early green dyestuffs had a bluish shade, and in order to produce better greens it was the practice to add a yellow dye. For this purpose, Martius Yellow, 2,4-dinitro-l-naphthol, was commonly used. Tests showed the compound to be effective against the clothes moth. For practical use, however, it had faults, primarily color and lack of fastness. The findings were followed by the testing of many synthetic organic compounds against the clothes moth and led to the development of several products; one group was named "Eulans."

The "Eulans" achieved some commercial success and stimulated interest in mothproofing agents by other chemical manufacturers. Soon after the "Eulans" were made commercially available, J. R. Geigy, S. A., in Switzerland started a research on mothproofing agents. After an extensive series of investigations, the Geigy firm developed and marketed a class of mothproofing agents known as "Mitins." The studies in the Geigy organization on mothproofing agents were expanded to the testing of compounds against other insects and led to the discovery of DDT.

Probably the most accurate account of the introduction of DDT into this country is given by Victor Froelicher, an official of the Geigy company in this country. In an article in Soap and Sanitary Chemicals, he wrote:

"In August 1942, we received from Switzerland 100 pounds each of ‘Gesarol’ spray, containing 5 percent active ingredient, and ‘Gesarol’
dust, containing 3 percent active ingredient. At about the same time, we received news that Maj. A. R. W. De Jonge, American Military Attaché at Berne, Switzerland, had shown great interest in our new lousicidal composition called ‘Neocid,’ which contained the same active ingredient as the ‘Gesarol’ products. It was indicated that ‘Neocid’ had great significance in controlling the typhus-carrying body louse.

“On October 16, 1942, we contacted Dr. R. C. Roark at Washington, and handed him a Swiss report giving the results of tests which had been made with ‘Gesarol’ on a great variety of insects, some of which, like the Colorado potato beetle, are familiar to us in the United States.

“Dr. R. Wiesmann, Assistant Chief of the Swiss Agricultural Station, was responsible for these reports, which, incidentally, seemed altogether too good to be true. These reports indicated that ‘Gesarol’ was not only a contact, but a stomach poison as well. Entomologists were at first reluctant to accept the statements which were made, and frankly, we felt the same skepticism, for, of over 3,000 products which had been tested by the United States Department of Agriculture, a rare one or two could claim both contact and stomach insecticidal properties.

“Up to that time nothing was known of the chemical constitution of the product, as little factual information could be obtained because of the difficulties of communication. Dr. H. L. Haller at Beltsville had extracted the active ingredient in ‘Gesarol,’ and analyzed and synthesized some of the active ingredient in his laboratory, simultaneous with which there arrived... the information of its chemical composition.”

The symbol DDT is a contraction for dichloro-diphenyl-trichloro-ethane, the generic name of the active insecticidal principle. Theoretically, there are 45 possible dichloro-diphenyl-trichloroethanes, excluding stereoisomeric forms. However, the term DDT has been confined to the product obtained on condensation of chloral (or its alcohólate or hydrate) with chlorobenzene in the presence of sulfuric acid. The product thus obtained is termed technical DDT. It is a white to cream-colored powder, possessing a fruitlike odor. Its major constituent is 1-trichloro-2,2-bis(p-chlorophenyl)ethane, which has the formula $(ClCoH_4)_2 CHCCI_3$ and is called $p,p'$-DDT.

This compound may be obtained pure by recrystallization of technical DDT from 95-percent ethanol. The pure compound melts at 108.5° to 109° C. It was first described in 1874 by Zeidler, who prepared it while working on his doctor’s thesis at the University of Strasbourg.

The preparation of DDT is relatively simple. It requires no elaborate equipment, and all the starting materials—ethanol, chlorine, benzene, and sulfuric acid—are readily available. The basis of the commercial process is the original procedure of the first chemist to make the compound—that is, the condensation of monochlorobenzene with chloral...
in the presence of sulfuric acid. A considerable amount of research has been carried out in this country, as well as in Great Britain and Canada, on the optimum conditions for the condensation, such as temperature and concentration of reactants, and for preparing the starting materials.

As its name implies, technical DDT is a commercial grade. Since it melts over a range of several degrees, the solidification point rather than the melting point is used to give an indication of its purity.

Intensive studies, involving fractional crystallization, chromatographic adsorption, distillation in high vacuum, and cryoscopic analysis showed the presence of 14 different compounds in the early samples of technical DDT. The \( p,p' \)-DDT varied in the samples of different manufacturers from 65 to 75 percent. The major impurity was found to be 1-trichloro-2-(\( o \)-chlorophenyl)-2-(\( p \)-chlorophenyl) ethane (which is called \( o,p' \)-DDT) which was present to the extent of 19 to 21 percent. This compound is considerably less toxic than \( p,p' \)-DDT to insects. The other impurities were isolated in amounts ranging from 0.007 to 4.0 percent. The impurity present to the extent of 4.0 percent was identified as 1,1-dichloro-2,2-bis-(\( p \)-chlorophenyl) ethane (TDE). It is formed from dichloroacetaldehyde, an impurity in chloral, and chlorobenzene. TDE is also an effective insecticide but the other minor components are relatively nontoxic to insects.

DDT is practically insoluble in water, but is soluble in a wide variety of organic solvents, such as acetone, benzene, xylene, chloroform, carbon tetrachloride, vegetable oils, petroleum oils, and many others. Crude or unrefined kerosene can be used to prepare solutions containing 5 percent of DDT, but refined kerosenes require the addition of 10 to 20 percent of an auxiliary solvent. For this purpose xylene, cyclohexanone, and alkylated naphthalenes have been used.

When pure, \( p,p' \)-DDT is a reasonably stable compound. It can be heated at 115° to 120° C. for several hours without decomposition. Irradiation of the solid material, spread in a thin layer, for 35 hours with a mercury-vapor lamp caused only a slight depression in melting point and an alcoholic solution showed no change after exposure to sunlight for over a year. Under certain conditions (temperatures above 95°-100° C. or in some organic solvents) it has been shown that a number of materials, even in very small quantities, cause decomposition of DDT with the formation of products that are of little or no value as insecticides.

**DDT Formulations**

In its undiluted form DDT is not suitable for use as an insecticide. It would be uneconomical for most purposes to use so potent an agent without diluting it greatly and the physical properties of DDT make it unsuited for direct application. DDT is practically insoluble in water and by itself will not form a satisfactory suspension in water. Its crystals
are so soft that they lump or cake easily, and they cannot be ground alone to make a satisfactory dust. When DDT is mixed with talcs, clays, pyrophyllite, or various other diluents, however, it can be ground to a fine powder, which can be applied as an insecticide dust or—after treatment with a wetting agent—can be suspended in water for use as a spray. DDT can be dissolved in various petroleum oils, xylene, or other organic solvents for making spray solutions or water emulsions. It has been incorporated also in insecticidal aerosols.

Dust mixtures of DDT usually are prepared by grinding technical DDT with talc, clay, pyrophyllite, sulfur, or another diluent. Because technical DDT softens at a temperature somewhat below 89° C., care must be exercised during grinding to avoid overheating the mill. In this way dusts that contain a wide range of DDT concentrations can be obtained readily. By grinding DDT with a conditioning agent, such as certain grades of silica gel, preparations containing up to 90 percent of DDT can be made that are fine and free flowing and can be diluted with any of the diluents mentioned. For most purposes the final concentration of DDT used in dusts ranges from 1 to 10 percent. By the addition of a wetting agent to the dusts, they also can be dispersed or suspended in water for use as sprays. When certain types of clays are used as the diluent, water-dispersible powders containing as much as 50 percent of DDT can be prepared without the addition of any wetting agent. The concentration of DDT in sprays prepared from water-dispersible powders is 0.1 to 5 percent.

Dusts also have been prepared by the impregnation of the diluent with a solution of DDT in a volatile solvent such as acetone or benzene. The solution may be mixed with the dust diluent, the solvent allowed to evaporate, and the mixture then ground, or the solution may be gradually sprayed into the diluent during the grinding process. Solutions of DDT in nonvolatile solvents such as certain alkylated naphthalenes from petroleum may be incorporated in the diluent provided that the amount of solvent required is not so great as to impair the dusting qualities of the mixture.

Solutions of DDT in various petroleum oils, such as kerosene, have been used for spraying or painting walls, furniture, screens in buildings, and the like. A solution containing 5 percent of DDT is most commonly used. The solubility of DDT varies greatly with the type of oil used. In the case of kerosenes the solubility is higher in those of naphthenic base than in those of paraffinic base. If the purified, deodorized type of kerosene generally used in household insect sprays is used as the solvent, it is desirable to add about 15 percent of an auxiliary solvent (for example, certain petroleum products rich in alkylated naphthalenes) to increase the solubility of the DDT, especially if the product is to be stored at low temperature. More volatile solvents, such as acetone, xylene, and dry-
cleaning solvents, have been used for the preparation of DDT solutions to impregnate clothing and other fabrics.

Aqueous emulsions prepared from solutions of DDT in solvents that are substantially insoluble in water have proved very useful. Watermiscible solvents should not be used for the purpose. Two types of emulsions have been used—those in which the DDT is dissolved in a volatile solvent, such as xylene, which evaporates after spraying to leave a deposit of DDT crystals, and those in which the DDT is dissolved in a relatively nonvolatile solvent, such as a petroleum oil, which leaves the sprayed surface coated with a solution of DDT in oil after evaporation of the water. A great variety of emulsifying agents is available for the preparation of DDT emulsions. The use of excessive amounts of emulsifier should be avoided in order to prevent excessive runoff of the spray and to avoid coating of the DDT deposit by the emulsifier after evaporation of the water and solvent. A convenient type of preparation for many purposes is an emulsion concentrate, consisting of a xylene solution of DDT containing an aralkyl polyether alcohol as emulsifier, from which emulsions ranging from 0.1 to 10 percent in DDT content can be prepared by mixing with water.

DDT has been incorporated in the pyrethrum-Freon aerosol, which has been widely used by the armed services and is now on the civilian market. Because of the low solubility of DDT in Freon–12 it is necessary to add an auxiliary solvent to the formula. Cyclohexanone and certain aromatic hydrocarbons derived from petroleum have been used for the purpose.

Insecticidal preparations containing DDT have a longer lasting residual effectiveness than other commonly employed insecticides, but the length of the effective residual periods varies considerably. In field tests on agricultural crops, the residual effect is relatively short. Under certain conditions (indoors or protected from sunlight and wind) where the physical environment is more uniform than under agricultural conditions, much longer periods of effectiveness have been reported. The type of surface is important, as would be expected in a contact poison. When DDT is applied to screens, its action lasts longer on copper screening than on iron. Iron has been shown to decompose DDT.

Whenever a new chemical is produced for large-scale use as an insecticide it becomes necessary to develop analytical procedures for it. DDT has five chlorine atoms in its molecular structure. They constitute 50 percent of the compound by weight. One of the chlorine atoms is readily removed as hydrogen chloride and is termed labile or hydrolyzable chlorine.

Methods for the determination of total chlorine or of hydrolyzable chlorine content are generally used for the analysis of DDT residues or preparations containing DDT. Neither of these methods is specific for
DDT, since other compounds containing chlorine interfere. Considerable
discretion must be used in interpreting results obtained with either of
these methods especially when minute amounts of chlorine, such as are
found in spray or dust residues, are determined.

Several methods that are specific for the determination of DDT have
also been developed. One of these, which has found considerable use, is
based on the fact that when DDT is treated with a mixture of concen-
trated nitric acid and sulfuric acid, a tetranitro derivative is formed.
This product when treated with sodium methylate yields a blue color with
pure \( p,p' \)-DDT and a wine-red color with \( o,p' \)-DDT. Intermediate colors
are obtained when technical DDT is determined.

The methods so far developed have proved useful, but further work
is needed in this field.

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