

Weed Killer and Derivatives

 $\mathbf{D}_{ ext{iscovery}}$ of the weed killer 2,4dichlorophenoxyacetic acid (2,4-D) in the early 1940's touched off a whole new era in chemical weed control. Like DDT in the insecticide field, 2,4-D was a gigantic breakthrough in controlling one of the greatest threats to world agriculture. More effective than any chemical ever known before, 2,4-D provided farmers for the first time with a low cost method of selectively destroying weeds. Chemical weed control, in turn, meant greater crop yields, less backbreaking work, and lower labor costs. Manual weed control, as symbolized by the hoe, could gradually be cast into limbo.

Since 1943, when it was first introduced commercially, 2,4-D has won expanding acceptance. Production grew from less than 1,000,000 pounds in 1945 to 30,700,000 pounds in 1952. Since then, 2,4-D production has varied between about 25,000,000 and 35,000,-000 pounds annually. Last year's total: 30,900,000—in the face of competition from such newer selective herbicides as 2,4,5-T, IPC, chloro-IPC, and CMU.

Actually, chemical weed control was fairly common practice in the 1920's.

Shortly before World War II, some 50,000,000 pounds of chemical weed killers were used annually (6). Most of these compounds, however, had a serious drawback: They were nonselective. They destroyed all vegetation, regardless of species. If used on a lawn, they killed not only the weeds but the grass itself.

Most of the early weed killers were inorganics—sodium chloride, sodium chlorate, sodium arsenite, and various borates (10). Later, farmers also began using a number of organics—chlorinated benzenes and substituted phenols (such as the amine salt of dinitro-o-sec-butylphenol). However, all of these materials killed plants only by contact, and a really thorough job of control required a comparatively large amount of weed killer.

One of the great virtues of 2,4-D is its ability to act systemically. The material enters the plant and is translocated throughout the plant structure (3). In this way, the entire plant—roots and all—are destroyed, not just the part that has been sprayed. Furthermore, 2,4-D is highly selective. It kills broadleaved plants, while allowing narrowleaved plants, such as grasses and cereals, to grow unharmed.

2,4-D has other advantages. It is effective in very low concentration (only about 1/4 to 1/2 pound is needed per acre to destroy some of the important weeds in agricultural crops). This makes for low material cost. Furthermore, in the amounts normally used, 2,4-D is virtually nontoxic to man and animals.

Exactly how this hormone-type weed killer works no one knows for sure. Contrary to earlier theories, it does not kill plants by wildly accelerating their growth (making them "grow to death"). However, 2,4-D does upset the plant's growth mechanism. According to one theory, it may inhibit or poison the enzyme or system that is responsible for the hydrolysis or synthesis of highenergy phosphates in plants (12).

Attack on Weeds

While not particularly concerned about the exact mode of action of 2,4-D, most farmers, highway and railroad maintenance men, homeowners, and others are content to know that indeed it does work—and well. Today, 2,4-D is used to control more than 100 types of common weeds. Growers use it for weed control in wheat, rye, corn, barley, rice, and sugar cane. It is also used to destroy weeds along power lines, highways, canal ditches, and railroad rights-of-way. On lawns and golf courses, it kills plantain, thistle, and dandelion. In Gulf Coast waterways, it controls water hyacinth and alligator weed. It is also used to destroy brush on pasture and range lands (frequently in combination with 2,4,5-T, which is more effective against relatively resistant plants).

To a much lesser extent, 2,4-D is also used merely to modify plant growth. In very low concentrations, it is effective, for example, in stimulating the flowering of pineapple. An ounce of 2,4-D is enough to induce flowering in over 100,000 of these plants (15). In Hawaii and Puerto Rico, it enables pineapple to flower at any time during the year. 2,4-D is also effective in preventing the premature dropping of apples, oranges, and other fruit.

Actually, 2,4-D is seldom used as the unmodified acid. Even its sodium salt, although originally in wide demand, now finds only limited use (5). Both the free acid and the sodium salt are solids that are only slightly soluble in water. Although 2,4-D or its sodium salt can be applied as a dust, this type of application can be a problem. The dust may drift to nearby areas, accidentally destroying susceptible crops. In the early days, cotton growers raised strenuous objections, of course, when their neighbors dusted their farms carelessly with highly potent 2,4-D.

With sprays, droplet size can be precisely regulated by choosing the correct spray nozzle, thereby minimizing drift during application. Sprays can also be directed and controlled more readily than dusts. And because sprays are able to wet the foliage, they adhere better to plants.

Amine Salts and Esters

Today, the great bulk of 2,4-D is used in liquid form either as an amine salt or as an ester. Highly soluble in water, amine salts can be easily formulated as aqueous solutions (1). The most common amine salts consist of 2,4-D combined chemically with dimethylamine, trimethylamine, triethylamine, diethanolamine, triethanolamine, or isopropylamine.

These 2,4-D amine salts are generally less volatile than the esters, which may be an important advantage if susceptible crops, such as tomatoes, beans, or cotton, are in the immediate area. On the other hand, the amines are somewhat less powerful herbicides than the esters and cannot be used too successfully against resistant plants, such as brush. About 50% of all the 2,4-D used today is in the form of esters; about 50%is amines. As the esters are essentially insoluble in water, they are used either as oil sprays or in oil-water emulsions, together with an emulsifying agent (7).

The methyl, ethyl, isopropyl, and *n*butyl esters are among the most effective 2,4-D derivatives. However, in recent years, the trend has been toward use of the less volatile, higher molecular weight esters, such as the butoxyethyl, butoxypropyl, or butoxyethoxypropyl derivatives. Compared to the amines, the esters are not only more potent herbicides but, being less soluble in water, are less apt to be washed off by rain shortly after application.

Early Research on 2,4-D

The discovery of 2,4-D's weed-killing properties was an unexpected outgrowth of early work on chemicals to alter plant growth. Chemists were looking for powerful new compounds similar to indolebutyric acid which could speed up or modify the growing process. For years, researchers at Boyce Thompson Institute for Plant Research in Yonkers, N. Y., and Imperial Chemical Industries in England had been testing a variety of these materials.

One of the early discoveries was that 2,4-dichlorophenoxyacetic acid and related compounds in very low concentration (1 to 3 p.p.m.) could greatly speed up plant growth. In 1943, a patent (17) disclosed a broad range of materials useful as plant growth control agents. These compounds were classified as nuclear halogenated arylketo monocarboxylic acids (which would include 2,4-D).

Shortly after these early discoveries, researchers at the New York Agricultural Experiment Station in Geneva, N. Y., as well as at the USDA laboratories in Beltsville, Md., and in research centers elsewhere in the United States and England, found that, at higher concentrations (100 p.p.m.), 2,4-D and a number of its derivatives were highly toxic to most broad-leaved plants.

The way was quickly opened for the use of 2,4-D as a selective weed killer. In 1945, Amchem Products Inc. (then known as American Chemical Paint Co.) received a patent (9) on a large variety of halogenated phenoxyacetic acid compounds for use as herbicides, among them 2,4-D and derivatives.

Start of Commercial Manufacture

Amchem Products Inc., The Dow Chemical Co., J. T. Baker Chemical Co., Monsanto Chemical Co., The Sherwin-Williams Co., and Thompson Chemicals Corp. were among the first to manufacture 2,4-D commercially, along with Du Pont and Kolker Chemical Works (now part of Diamond Alkali Co.). Under such trade names as Esteron, Weedone, and Weed-No-More, 2,4-D formulations in increasing numbers became available to the American public.

Today, U. S. producers of 2,4-D include The Dow Chemical Co., Monsanto Chemical Co., Diamond Alkali Co., Pittsburgh Coke & Chemical Co., Chipman Chemical Co., Thompson Chemicals Corp., Frontier Chemical Co., and Thompson-Hayward Chemical Co., Various derivatives of 2,4-D are made by most of these companies, as well as California Spray-Chemical Corp., and others.

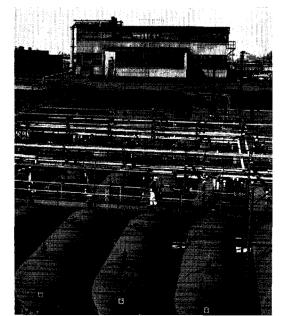
Methods of Manufacturing 2,4-D

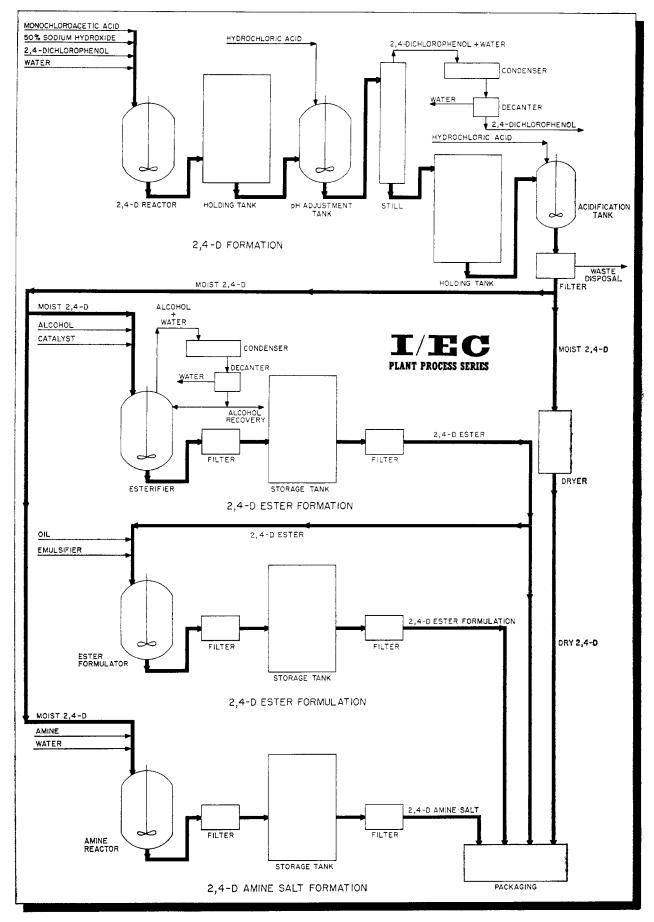
From the beginning, almost all commercial producers of 2,4-D have used fundamentally the same process. It consists of reacting 2,4-dichlorophenol with monochloroacetic acid in the presence of aqueous sodium hydroxide (4). The reaction mixture is then treated with a mineral acid to convert the sodium salt of 2,4-D to the free acid.

Haskelberg (8) has described a laboratory method involving the reaction of 2,4-dichlorophenol, elemental sodium, and ethyl chloroacetate, followed by hydrolysis of the ester. Manske (13) received a patent for a process based on the chlorination of phenoxyacetic acid. Chlorine gas is fed directly into the acid, which is kept molten throughout the reaction by progressively raising the temperature from 100° to 150° C.

According to one of the standard commercial processes (2), 2,4-dichlorophenol is first reacted at elevated temperature with monochloroacetic acid in the presence of sodium hydroxide to produce the sodium salt of 2,4-D. In this step, an excess of 2,4-dichlorophenol minimizes

The 2,4-D plant's tank farm contains about 40 storage tanks. The plant is in the background





Flowsheet for the manufacture of 2,4-D weed killer and derivatives, The Dow Chemical Co., Midland, Mich.

the hydrolysis of the monochloroacetic acid to glycolic acid. The time, temperature, rate of addition, and agitation must all be carefully regulated.

The pH is then lowered to about 5 with hydrochloric acid to convert the excess sodium salt of dichlorophenol to the free compound. The reaction mixture is distilled to recover the dichlorophenol, which not only is too valuable to discard but would also cause a serious water pollution problem because of its extreme odor potential.

The residue is then acidified to about $pH \ 1$ to precipitate the 2,4-D. The solid is filtered, washed, and dried. The crude wet solid may be recrystallized from a solvent such as benzene, then washed and dried. This general procedure is very similar to the one used by The Dow Chemical Co.

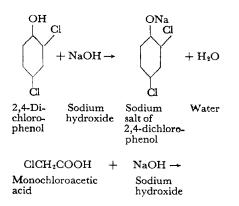
Dow Enters Herbicide Field

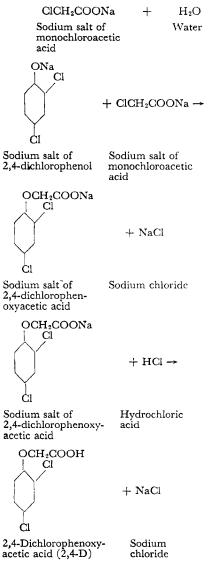
Dow's interest in weed killers dates back to the late 1930's when it attempted to develop substitutes for the nonselective chlorate-type herbicides. In about 1938, the company began marketing its first organic herbicide, a dinitrophenol compound, used in controlling vegetation in citrus groves along the West Coast.

Dow's interest in 2,4-D as a laboratory chemical extended as far back as 1935, when it did basic research on this material, long before its weed-killing properties were known. Dow's commercial production of the herbicide began in 1945 in one of the company's pilot plants at Midland, Mich. Production of 2,4-D and its esters rapidly increased at Midland and in 1946 was moved to facilities that were 10 times larger. Dow also began making the amine salts and the lower alkyl esters of 2,4-D, as well as the low-volatile esters.

For its production of 2,4-D, Dow decided not to use the direct chlorination of phenoxyacetic acid (the Manske process) because of low yields (70% or less) and the difficulty of separating the products.

The chemical reactions involved in the Dow process are:





Sodium hydroxide is used in this process to force the reaction in the direction of the products, giving a 2,4-D yield of about 90%. If 2,4-dichloro-

This is a battery of 2,4-D esterifiers. At left are the meters used to measure the liquid chemicals into the reactors phenol were treated directly with monochloroacetic acid without the presence of sodium hydroxide, the yield would be quite low.

Dow's Plant and Its Operation

The present 2,4-D facilities of The Dow Chemical Co. were built at Midland in 1949 and are 30 times larger than Dow's original 2,4-D pilot plant. The present building is 150 by 280 feet in area and 40 feet high, with an adjoining tank farm containing about 40 storage tanks. The plant is equipped with its own analytical laboratory which runs all of the analyses needed for the 2,4-D operations.

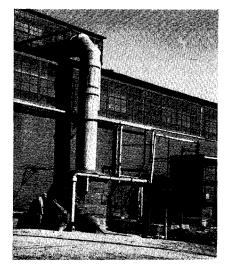
All raw materials for the 2,4-D process are made at Midland. The preparation of monochloroacetic acid by chlorination of acetic acid is carried out in another part of the Midland plant.

Production of 2,4-D is a batch process. It starts with the charging of a 3500gallon, steam-jacketed, steel reactor with equal amounts of 50% sodium hydroxide and water. A 50% molar excess of 2,4-dichlorophenol is then pumped in. While the materials are continuously agitated, the monochloroacetic acid is added. The reaction is carried out at 60° to 80° C. and lasts for 6 to 8 hours.

During the reaction, the pH is checked with a pH meter every hour to make sure it is maintained above 7.0. The course of the reaction is followed by chemical analyses every half hour. The reaction is stopped when there is no further increase in concentration of the sodium salt of 2,4-D over a half-hour period.

The reactor contents are then pumped to a 7000-gallon steel holding tank. From there, the mixture goes to a 3500gallon, porcelain-enamel-lined tank where the pH is adjusted. This is a





Leaving the 2,4-D building is a 3-footdiameter pipe that carries airborne 2,4-D from the scrubber to one of the Midland plant's power houses. There it is decomposed by the heat of the furnace so it cannot be carried to the outside atmosphere

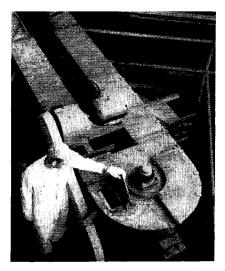
paddle-agitated vessel that requires no cooling.

A 33% solution of hydrochloric acid is added to lower the pH to 5. This converts the sodium salt of dichlorophenol to the free dichlorophenol and also results in the separation of an oily phase. The pH is not lowered sufficiently to cause precipitation of 2,4-D. Adjustment of pH usually takes about 1 hour and is checked every 30 minutes with a pH meter.

The contents of the pH adjustment tank are then pumped to a brick-lined steam still, 30 feet high and 5 feet in diameter. This still, packed with Raschig rings, is heated to 100° C. by live steam fed in at the bottom.

The two-phase mixture enters near the top. During the distillation, dichlorophenol and water leave at the top. After passing through a stainless steel, water-cooled condenser, where the temperature is lowered to about 40° C., the mixture goes to a 50-gallon, stainless steel decanter. There, water is separated off and goes to a water storage tank for re-use in the process. As elsewhere in the process, great care is taken with waste products to minimize outside pollution with materials containing 2,4-D derivatives or 2,4-D itself.

Dichlorophenol is removed from the bottom of the decanter and is pumped to a storage tank for re-use in the process. The residue from the still (an aqueous solution of the sodium salt of 2,4-D) goes temporarily to a 7000-gallon, bricklined holding tank. It is then pumped to a 1000-gallon acidification tank. Under agitation, 33% hydrochloric acid is added to lower the pH to 1. This tank is water-jacketed to keep the con-



The enclosed conveyor carries the 2,4-D acid to the esterification and packaging operations

tents at about room temperature, even though the conversion of the sodium salt of 2,4-D to the free acid is highly exothermic.

The 2,4-D precipitates fairly rapidly as fine white crystals. After about 1 hour, the reaction is complete, and the thick slurry is pumped to a rotary filter to remove most of the water. The crystals are washed on the filter to remove the solution of sodium chloride and hydrochloric acid.

The filtrate goes through a special sewer to the biochemical sewage disposal system. There, it is acted on by bacteria to decompose the 2,4-D before the waste is discarded.

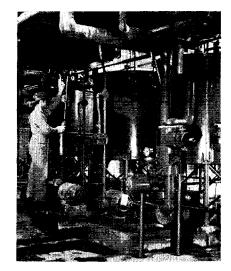
Handling of Moist 2,4-D

The moist crystals may then be processed in one of three ways—dried, converted to an ester, or converted to an amine salt.

A portion of the wet product, containing about 25% moisture, goes to a continuous automatic shelf dryer, where its water content is reduced to less than 0.5%. This 15-foot-high dryer contains 16 rotating shelves. The moist product, entering at the top, falls from shelf to shelf through radial slots. The material on the rotating shelves is pushed off by stationary blades. Retention time in the dryer is about 1 hour. The moisture content of the product as it comes from the dryer is checked every hour.

Heat for drying is provided by a rising stream of 100° C. air. Special care must be taken with the exit air to prevent it from carrying 2,4-D out into the atmosphere.

The air from the dryer goes first to a water scrubber which picks up about 95% of the 2,4-D dust. The water from the scrubber then goes to the 2,4-D filter.



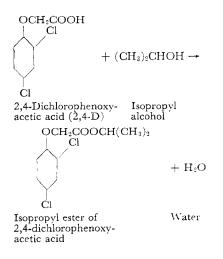
These recovered alcohol receivers are used in connection with the esterification reaction

As the scrubber does not remove all of the 2,4-D dust, the air then goes through an underground duct to the air intake of one of the Midland plant's power houses. There, the airborne 2,4-D is decomposed by heat of the furnace. The required interconnecting duct, 3 feet in diameter, runs for 5000 feet and was installed at considerable cost. This is one reason why the problem of controlling effluent wastes adds materially to the expense of building and operating a 2,4-D plant. When the furnace is shut down for repairs, the 2,4-D plant must also be shut down.

The 2,4-D from the dryer is carried by an enclosed chain conveyor to the packaging section. It is packed in either 100- or 200-pound unlined fiber drums.

Production of Esters

Dow makes four esters of 2,4-D by reacting the acid with either isopropyl alcohol, *n*-butyl alcohol, iso-octyl alcohol, or butoxypropyl alcohol. The alcohol most commonly used is isopropyl. The reaction with this compound is:



The operating procedure is essentially the same regardless of the alcohol involved. Assuming that isopropyl alcohol is used, a 10% excess of this material is pumped into a 1000-gallon, enamel-lined esterifier (the excess of alcohol ranges from about 5 to 20%, depending on the compound). An acid catalyst is then pumped in. While the mixture is stirred by a paddle agitator, the wet or dry 2,4-D is added by a chain conveyor.

The reactants are heated by a steam jacket to the reflux temperature of 80.3° C. The water formed by the esterification is continuously removed at the top as a water-alcohol azeotrope. The overhead stream goes to a resin-bonded graphite condenser where it is cooled to 30° C. The condensate then passes into a 20-gallon, stainless steel decanter. The overflow water from the decanter goes to a water storage tank for re-use in the process. The alcohol layer is returned to the still.

The reactants are refluxed for 6 to 8 hours. Esterification is completed when no more water is collected in the decanter.

The mixture is then heated to 82° C. to boil off the excess isopropyl alcohol, which requires about 2 to 4 hours. The alcohol goes to a recovery still, and the distillate is re-used in the process.

The remaining contents of the esterifier pass through an enclosed plate-andframe filter press to remove the catalyst. This filter, as well as the other plateand-frame presses in the 2,4-D plant, use either Dacron or nylon filter cloths because of their chemical resistance. The filtrate is pumped to a 20,000-gallon steel storage tank. The over-all yield in the esterification step is 90%.

Before the product is packaged, it is filtered again in an enclosed plate-andframe filter to remove small amounts of rust and other contaminants accumulated during storage. The ester is shipped in 55-gallon drums or tank cars. Before shipment, each batch is checked for ester content, color, and

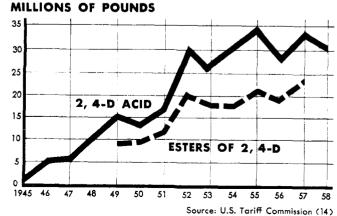
Physical Properties of 2,4-D and Its Isopropyl Ester		
	2,4-D	Isopropyl Ester of 2,4-D
Appearance	White, crys- talline solid	Water- white liquid
Molecular weight	221	263
Specific gravity at 20°/20° C. Melting point,		1.269
°C. Boiling point	138	24
At 49 mm.	241 (with de-	
Hg, ° C.	composi- tion)	-
At 18 mm.		
Hg, °C.		183
Refractive index		1.5208
at 25° C., n _D		
Viscosity at 25°		32.6
С., ср.		
Solubility at 25°		
C., grams/		
100 grams		
of solvent in Water	0.09	0 0020
Ethyl alcohol	130	0.0039 Inf.
Ethyl ether	243	Inf.
Toluene	0.67	Inf.
<i>n</i> -Heptane	0.11	Inf.
Acetone	Sol.	Inf.
Benzene	Sol.	Inf.
Carbon tetra-	Sl. sol.	Inf.
chloride		~

acidity (caused by unreacted 2,4-D). The product contains 99% ester.

A variety of formulations are made by combining the ester with an oil (diesel oil or kerosine) and an emulsifier. The emulsifier makes it possible to suspend the product in water for aqueous spray applications. One of these formulations, Dow's Esteron 44, consists of 44% of the isopropyl ester of 2,4-D and 56% oil and emulsifier.

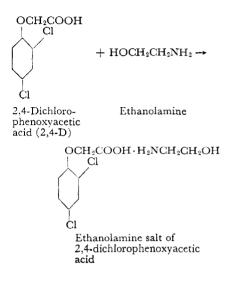
Formulations are prepared in a 4000gallon, steel, agitated tank. These are filtered in a plate-and-frame press and stored in a 20,000-gallon steel tank. After storage, they are filtered again and packaged in 1-, 5-, and 55-gallon drums. They are also shipped by tank car.

Since 1952, the production of 2,4-D acid has varied from 25,000,000 to 35,000,000 pounds per year



Production of Amine Salts

The amine salts are made by reacting 2,4-D with such compounds as ethanolamine or dimethylamine. In preparing the ethanolamine derivative (the most widely used 2,4-D amine salt), the reaction is:



Dow makes only the aqueous solutions of amine salts and does not attempt to isolate the pure compounds. First, a 4000-gallon, steel, agitated tank is charged with water. Then the amine is pumped in, followed by an equimolar amount of either wet or dry 2,4-D which is added by means of a chain conveyor.

The reaction takes place rapidly at room temperature and is completed after about 30 minutes. The resulting solution contains about 65% of the ethanolamine salt of 2,4-D and 35%water, which is the concentration at which the product is sold. The yield of amine salt in this reaction is nearly 100%.

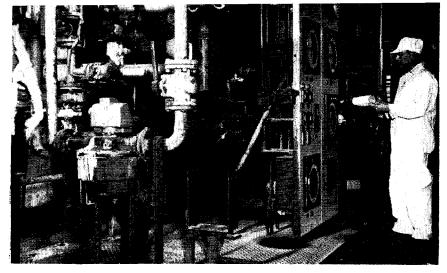
The product is analyzed and adjustments are made by adding either amine or 2,4-D acid or both, and it is then reanalyzed. This procedure is followed until the material meets specifications.

The product is filtered to remove suspended matter, stored, and filtered again before packaging. The equipment involved is the same as that used in making the ester formulations. The aqueous amine salts are shipped in 1-, 5-, 30-, and 55-gallon drums and tank cars.

Instrumentation, Manpower, and Safety

The 2,4-D plant uses recording devices primarily for measuring temperature. Flow meters are used for determining the gallons of liquid being transferred. pH is measured either with indicating paper or a pH meter.

The plant is operated 24 hours a day, seven days a week. Eight operators, in



The instrument panel is used in controlling the 2,4-D reaction. The liquid meter (left) measures one of the raw materials added to the 2,4-D reactor

addition to two analytical technicians, are required per shift. Quality control is maintained in all steps of the process, and each lot is analyzed before shipment to be sure it meets specifications.

To maintain high standards of plant safety, all operators are thoroughly informed of the hazards involved. Supervisors make a special point of emphasizing safety. Such materials as monochloroacetic acid, hydrochloric acid, and dichlorophenol are all potentially dangerous and must be handled with care. Although 2,4-D, the amine salts, and the esters are not particularly hazardous, the operators must observe normal cleanliness.

Because the volatile alcohols are a potential fire hazard, all esterification steps are carried out in an enclosed area of the 2,4-D plant. Motors, switches, and other electrical devices in this area are explosion-proofed. Also to reduce hazards in manufacturing and later handling, the organic solvents used in preparing the ester formulations are all high-flash-point materials.

In the outside storage area, the vents on all tanks are equipped with charcoal absorbers, which are changed every three months. Both monochloroacetic acid and dichlorophenol, for example, are odor problems. Inside the plant, the 2,4-D packaging area is equipped with special forced ventilation to minimize the dust problem.

To guard against the escape of 2,4-D to the atmosphere, the windows of this building are always kept closed. Forced air circulation is used in the summer. Dow's waste control department keeps a continuous check on small product losses by use of tomato plants growing at 12 separate locations for two miles around in the Midland area. If these plants, which are highly sensitive to 2,4-D, show typical damage, it is a warning that too much 2,4-D may be escaping.

Efforts are continually being made to improve the 2,4-D process, with emphasis on increasing yields, minimizing labor requirements, improving safety, and reducing maintenance.

Simplified work methods have been introduced, resulting in a labor saving of 10% during the past 5 years. Through various process and operating improvements, the capacity of the plant has been increased about 50%. Some of the equipment has been enlarged to eliminate bottlenecks. Automatic drum-filling units have been installed to speed up the packaging of liquid products. Improved pumps with mechanical seals are now used to minimize maintenance.

Dozens of Formulations

Last year, the Dow plant made 47 different products and formulations of 2.4-D and its derivatives. This is about twice the number of compositions made five years ago. Many of the newer products are the result of Dow's own field research on the handling of specialized weed control problems.

About half of Dow's 2,4-D output is in the form of amine formulations, with the other half consisting of ester formulations. This output is sold mainly to dealers, contract farmers, railroads, and highway departments. Only about 10% is sold to outside companies for chemical conversion or formulation.

Today, the commercial future for 2,4-D looks extremely good. That's because, on a broader scale than ever, U. S. growers, government agencies, public utilities, and industrial firms are recognizing the value-economic and otherwise-of efficient chemical weed control.

Acknowledgment

The authors wish to express their sincere thanks to Charles A. Highhill, superintendent of the 2,4-D plant, and to Ellis N. Brandt of Dow's public relations department for their valuable help in preparing this report.

Some of Dow's Trade Named Products Based on 2,4-D

- Esteron Ten-Ten. Emulsifiable, contains 70.5%butoxypropyl ester of 2,4-D
- Esteron 44. Emulsifiable, contains 44% isopropyl ester of 2,4-D
- Esteron 99. Emulsifiable, contains 38% low-volatile butoxypropyl ester of 2.4-D
- Esteron Brush Killer. Emulsifiable, contains 34.8%butoxypropyl ester of 2,4-D and 33.0% of the same ester of 2,4,5-T
- 2-4 Dow Weed Killer, Formula 40. Aqueous solution, contains about 65% alkanol-amine salts of 2,4-D
- 2-4 Dow Weed Killer Powder. Contains 95%monohydrated sodium salt of 2,4-D

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