

Decomposition of DDT from Thermal Aerosol Dispersers

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The object of this work was to determine the extent of DDT decomposition on dispersion in oil solution by thermal aerosol insecticide generators. Results showed that the decomposition, in general, was low and increased gradually with temperature to a maximum of about 17% at 700° F. At the normal temperature of operation of the generator (600° F.) it varied from 3 to 8%. Results also showed that decomposition was mainly due to the tem-

perature of dispersal, the effects of air being negligible. At the lower temperatures apparently only one chlorine atom was split off each decomposed DDT molecule, and at the higher temperatures from two to three chlorine atoms split off each decomposed DDT molecule. The reliability of the chemical analyses for DDT on the oil portions of the samples collected at various temperatures was checked by entomological analysis.

THE various methods for dispersal of DDT on the ground were reviewed by Geer and Scoville (?). One of these methods, dispersal by a mechanical thermal aerosol-type disperser (2, 3, 4, 8, 11), was reported to have proved satisfactory for area control, as it disperses a large volume of insecticide as an aerosol which can drift with the air currents over the area to be treated. It was also stated that a dosage of 0.25 pound of DDT per acre from this type disperser effectively controls mosquitoes under favorable operating conditions.

In work on this method of dispersal at the Army Chemical Center, a disperser designated "disperser, insecticide, aerosol, mechanical" was developed by Norton and co-workers. Engineering tests, including determinations of particle size output on this disperser, were reported by Norton (13). Later, mechanical smoke generator M2 (16) was modified by Norton and co-workers to produce a single unit that functions both as insecticide aerosol disperser and as smoke generator (1).

In evaluating the method of dispersal of DDT by a mechanical thermal aerosol-type disperser, information on the degree of decomposition of DDT when dispersed in oil solution by this method was desired. In work reported previously (10), the decomposition of DDT from the small mechanical smoke generator M2 was determined by collecting portions of the aerosol output on a filter backed up with bubblers to collect the material passing through the filter, followed by an analysis of the total chlorine and alkaline dehydrohalogenated chlorine in the samples. Results obtained by this procedure did not give all the information desired and are not considered to be strictly reliable, because of the difficulty of collecting a truly representative sample from a large aerosol cloud by this sampling procedure.

As the small amount of previous work done was regarded as unreliable, it was desired that decomposition data be determined more accurately with the latest type of insecticide generator (1).

Hydrogen chloride is removed from DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] by alcoholic caustic to yield 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene, which is relatively nontoxic to insects. Fleck and Haller (5, 6) found that hydrogen chloride may also be removed at 110° to 120° C. by catalysts such as anhydrous ferric, chromium, and aluminum chlorides, iron, iron oxides, and certain mineral materials. They also found that the removal of hydrogen chloride by these catalysts was promoted when DDT was in solution in some solvents, such as chlorobenzene, naphthalene, nitrobenzene, and 1-chloronaphthalene, and inhibited by some solvents, such as fuel oil (No. 2), xylene, kerosene, dioxane, and petroleum fractions boiling above 100° C.

The behavior of DDT on heating was investigated by Scholefield and others (15), who determined the rate of decomposition in an atmosphere of nitrogen by measurement of the volume of hydrogen chloride evolved at temperatures up to 260° C. (500° F.). They reported that the evolution of hydrogen chloride is only slight at the melting point of DDT but is rapid in the neighborhood of 200° C.

This previous work could be used only qualitatively to predict the behavior of DDT in a mixed oil solution of xylene, fuel oil No. 1, and fog oil No. 2, in the presence of small amounts of iron from containers and generator parts when flash-heated for intervals of less than a second with steam and cooled in air. The small amounts of iron and the elevated temperatures would be expected to cause marked decomposition, while the oils during a short interval of flash heating would be expected to inhibit decomposition.

To evaluate the decomposition quantitatively, it was considered necessary to make a determination as close to actual conditions as practicable and to collect samples for analysis of DDT content truly representative of the output. It was thought that a sample of any portion of the aerosol cloud would not be sufficiently representative, as each portion of the cloud would be subjected to slightly different conditions of flash heating and condensation in air. On the other hand, it was thought that if the entire output were condensed after leaving the nozzle, a truly representative sample of the entire output could be obtained.

A chemical analysis of the DDT content of the original oil solution and the oil portion of the condensate should then give a measure of the DDT recovered and decomposed. As large samples of oil solution and condensate would be available, microchemical analytical methods would not be required. Such analytical methods for DDT as the nitration method of Schechter and Haller (14) are not applicable to oil solutions of DDT, but the dehydrochlorination procedure of Gunther (9) as modified by LeClair (12) for determination of total DDT in oil solutions has been successfully used for this application. As it was planned to use aerosol-grade DDT, which has *p,p'*-DDT content of 95% or better, a determination of the total DDT content would be almost all *p,p'*-DDT.

It was also thought that a chemical analysis of the water portion of the condensate for chloride and acidity would give further information regarding the nature of any decomposition. As reported in the literature (5, 6, 15), DDT on catalytic or thermal decomposition releases hydrogen chloride to form the ethylene compound. There is also the possibility of the complete

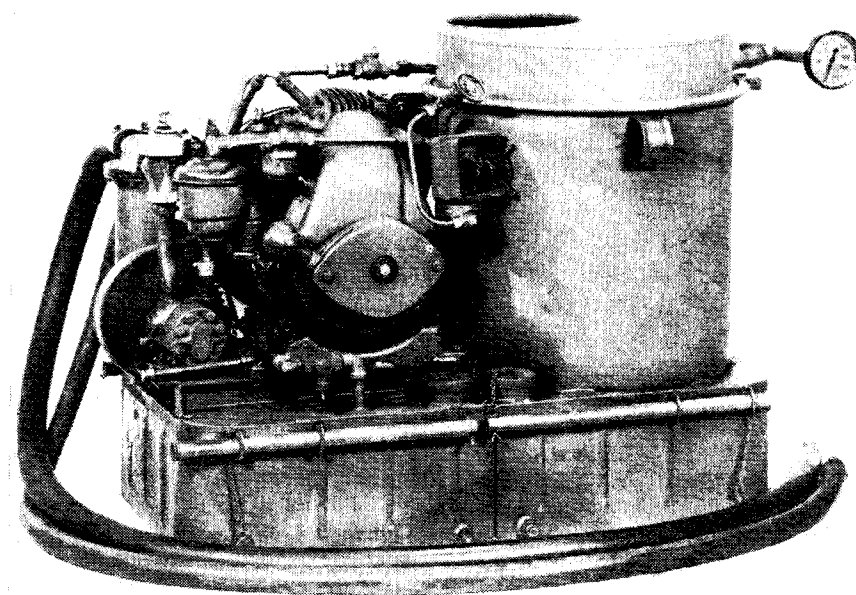


Figure 1. Mechanical Thermal Insecticide Aerosol Dispenser

pyrolysis of a portion of the DDT at elevated temperatures. In these experiments the hydrogen chloride would be absorbed in the water portion of the condensate, and the ratio of moles of hydrogen chloride in the water portion to moles of DDT decomposed should indicate the nature of any DDT decomposition under these dispersal conditions.

MATERIALS AND EQUIPMENT

An oil solution of the following composition was used for dispersion: 8 gallons of xylene, 25 pounds of DDT (aerosol grade), 25 gallons of smoke generator fog oil No. 1, 15 gallons of fuel oil No. 2, to give a total solution volume of 50 gallons. The DDT was first dissolved in the xylene, followed by addition of the fuel oils and mixing. The specific gravity of this solution at 25° C. was approximately 0.924.

A slightly modified M2 thermal aerosol generator (16) was used. The M2 smoke generator was converted by removing the fog control valve, feed water regulator, water line, and fog nozzle. The fog valve was replaced by a specially designed mixing valve through which the water and DDT solution were metered and mixed before they entered the pump. The water line was capped, and the standard M2 fog nozzle was replaced with a special dispersing nozzle having a temperature gage mounted in one end. This disperser is shown in Figure 1 and more completely described in other reports (1, 16).

The disperser requires four liquids for operation—namely, gasoline for the burner and engine, lubricating oil for the engine, clean water, and DDT solution. The water and DDT solution are carried in 55-gallon steel drums. The gasoline tank is an integral part of the disperser and is mounted under the gasoline engine. The DDT solution and water are pumped into a steel coil contained in a combustion chamber. The liquids are flash-vaporized, and the vapors discharged through a manifold into the air, where rapid chilling condenses them into a fine liquid aerosol.

In the tests to be described, a tube leading to a condenser was connected directly to the manifold of the disperser, so that the entire aerosol output could be condensed and collected without addition of air. The condenser coil was made from steel pipe. A connection was also inserted in this tube so that the air from an air compressor could be introduced into the output from the nozzle. Figure 2 is a schematic diagram of the equipment used.

EFFECT OF TEMPERATURE OF DISPERSAL

In the first test 4 parts of the DDT-oil solution to 1 part of water were discharged at a rate of approximately 40 gallons of oil per hour. The output temperatures were varied from 350° to 750° F. in 50° steps, and no air was introduced. The entire smoke output of the disperser at these temperatures was collected

by condensation. The oil and water layers of the condensate were separated, and the oil portion was centrifuged to remove residual amounts of water. The oil portion was then analyzed for total DDT by the dehydrochlorination method (9, 12), and the water portion was analyzed for hydrogen chloride by an acid-base titration and a Volhard chloride titration. Table I (test 1) gives analytical results on the oil portion. The acid-base titration values and the Volhard chloride titration values on the water portion were in close agreement, an indication that the acidity of the water portion was due to the presence of hydrogen chloride, no sulfuric acid having been introduced by sulfur in the oil. As the ratios of DDT-oil solution to water were determined only approximately in this test, no attempts were made to interpret the nature of the DDT decomposition by the amounts of hydrogen chloride found in the water portions. Although entomological tests are not strictly quantitative and do not show degrees of decomposition so closely as chemical analytical methods, check entomological analyses were performed on the oil portions of the samples from the first test, using a method with roaches. These tests led to the conclusion that significant amounts of DDT approaching 5% or higher were present in all the samples.

TABLE I. ANALYTICAL RESULTS OF FIRST AND SECOND TESTS OF DDT DECOMPOSITION

Test No.	Oil Dispersion Temp., ° F.	Total DDT, %	Total DDT Decomposed, %
1	Original DDT-oil soln.	6.63	...
	350	6.57	0.9
	400	6.60	0.5
	450	6.61	0.3
	500	6.53	1.5
	550	6.53	1.5
	600	6.44	2.9
	650	6.22	6.2
2	700	5.80	12.9
	Original DDT-oil soln.	6.65	...
	375	6.54	1.7
	400	6.59	0.9
	425	6.55	1.5
	450	6.58	1.1
	475	6.56	1.4
	500	6.55	1.5
	550	6.41	3.6
	600	6.22	6.5
	650	5.97	10.2
	700	5.92	11.0

In the second test graduated tanks were installed adjacent to the generator for closer measurement of oil and water output. The DDT-oil solution was discharged at a rate of 38 gallons per hour to 12.5 gallons of water per hour. Temperatures were varied in 25° steps from 375° to 500° F., and in 50° steps from 500° to 700° F. No air was introduced in this test. The entire aerosol output was collected by condensation. It was found that 98% or better of the aerosol output could be collected by passing it through the long coil condenser, and by carefully measuring the input volumes and the condensed output volumes at several temperatures. The oil and water layers were separated and the oil portion was centrifuged to remove residual amounts of water. The oil portion was analyzed for total DDT by the dehydrochlorination method (9, 12), and the water portion was analyzed for hydrogen chloride by a Volhard chloride titration.

Table I (test 2) gives analytical results on the oil portion. Good agreement with these chemical analytical results was also obtained in a check entomological analysis with roaches. Table II compares these results with those obtained by chemical analysis. Using the ratio of 38 gallons of oil solution to 12.5 gallons of water and the results obtained by analyses of the water layer for hydrogen chloride, it was indicated that at the lower temperatures apparently only one chlorine atom was split off each decomposed DDT molecule, and that at the higher temperatures from two to three chlorine atoms were split off each decomposed DDT molecule. Table III shows these results.

In the tests described thus far, no air was introduced into the output from the disperser, and the results show mainly the effects of temperature of dispersal on the DDT.

EFFECT OF AIR

In the third test two runs were made with output rates of 35 gallons of DDT-oil solution and 12 gallons of water per hour, one without introduction of air, and one with air introduced at 4 cubic feet per minute into the dispersed aerosol immediately after leaving the generator nozzle. This test was intended to determine the effects on the DDT of the air encountered by the hot aerosol as it is released from the nozzle of the disperser into the atmosphere. As before, the output of the disperser was collected by condensation, and the oil and water portions were analyzed. Table IV gives analytical results on the oil portions of the samples; they indicate that the release of the hot aerosol into the atmosphere under actual operating conditions does not contribute toward decomposition of DDT, but appears to have a somewhat beneficial effect at the higher temperatures. This beneficial effect may possibly be due to more rapid cooling action by the air.

In connection with the run in which air was introduced, a check was made of the recovery by condensation compared to the input. Careful measurement showed that 47 gallons of oil solution and water were dispersed, and slightly over 46 gallons of condensate were collected, which corresponds to 98% recovery.

The ratio of 35 gallons of oil solution to 12 gallons of water and the results obtained on the same samples by the analysis of the water portion for hydrogen chloride indicated, as in the second

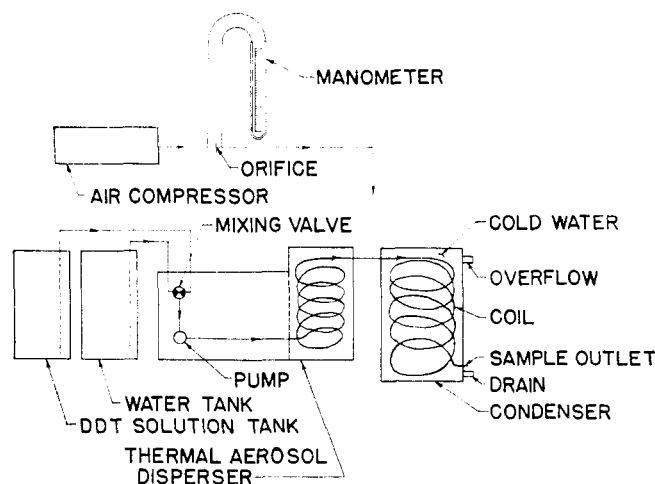


Figure 2. Schematic Illustration of Equipment for Determining DDT Decomposition When Dispersed by Thermal Aerosol Generators

test, that at the lower temperatures apparently only one to two chlorine atoms were split off each decomposed DDT molecule, and at the higher temperatures from two to three chlorine atoms were split off each decomposed DDT molecule. Table V shows these results.

A check analysis by an entomological method with roaches, carried out on the oil portion of the sample dispersed at 700° F. when air was introduced, indicated that the reliability of the chemical analytical method was not affected by the introduction of air. This check analysis led to the conclusion that the entomological effectiveness of the sample is approximately that of a 5% solution of DDT, and the symptoms of the roaches used in the analyses were typical of roaches poisoned with DDT emulsion.

TABLE II. COMPARISON OF DDT CONTENT IN OIL DETERMINED BY CHEMICAL ANALYSES AND FROM ENTOMOLOGICAL DATA

Oil Dispersion Temp., ° F.	Mortality, Dead Treated	Kill, %	DDT Content, %	
			From entomological data ^a	By chemical analysis
Orig. DDT-oil soln.	50.67	74.6	6.65	6.65
500	31.40	77.5	6.65 ^b	6.55
600	29.40	72.5	6.3 ^b	6.22
700	22.40	55.0	4.8 ^b	5.92

^a Obtained with roaches.

^b Estimated from dosage-mortality curve determined by injecting various doses of the original DDT-oil solution. No deaths were observed in roaches given comparable amounts of oil without DDT. The injection medium was prepared by emulsifying one part of sample with six parts of a 5% aqueous solution of gum acacia.

TABLE III. COMPARISON OF AMOUNTS OF DECOMPOSED DDT WITH HYDROGEN CHLORIDE RELEASED IN SECOND TEST

Dispersion Temp., ° F.	DDT Decomposed (from Analyses of Oil Portion), %	HCl in Water Portion Calcd. as DDT on Basis of 1 Cl to 1 DDT, %	Ratio (Approx.) of DDT from HCl Found to DDT Decomposed
375	0.11	0.11	1:1
400	0.06	0.08	1:1
425	0.10	0.09	1:1
450	0.08	0.10	1:1
475	0.09	0.20	2:1
500	0.10	0.20	2:1
550	0.24	0.5	2:1
600	0.43	1.1	2 to 3:1
650	0.68	1.6	2 to 3:1
700	0.73	1.4	2:1

TABLE IV. ANALYTICAL RESULTS OF THIRD TEST OF DDT DECOMPOSITION

Oil Dispersion Temp., ° F.	Without Air		4 Cu. Ft. Air Introduced per Min.	
	Total DDT, %	Total DDT decomposed, %	Total DDT, %	Total DDT decomposed, %
Orig. oil-DDT soln.	6.32	...	6.32	...
375	6.29	0.5	6.31	0.2
400	6.28	0.6	6.28	0.6
425	6.27	0.8	6.28	0.6
450	6.23	1.5	6.22	1.6
475	6.25	1.1	6.23	1.5
500	6.19	2.1	6.17	2.4
550	6.08	3.8	6.07	4.0
600	5.79	8.4	5.97	5.5
650	5.67	10.3	5.73	9.3
700	5.15	18.5	5.27	16.6

TABLE V. COMPARISON OF AMOUNTS OF DECOMPOSED DDT WITH HYDROGEN CHLORIDE RELEASED IN THIRD TEST

Oil Dispersion Temp., ° F.	DDT Decomposed (Calcd. on Original DDT-Oil Soln.)					
	Without Air			With Air		
	Oil portion ^a , %	Water portion ^b , %	Ratio (approx.) ^c	Oil portion ^a , %	Water portion ^b , %	Ratio (approx.) ^c
400	0.04	0.05	1:1	0.04	0.05	1:1
425	0.05	0.09	2:1	0.04	0.10	2:1
450	0.09	0.12	2:1	0.10	0.15	2:1
475	0.07	0.18	2:1	0.09	0.25	2:1
500	0.13	0.22	2:1	0.15	0.30	2:1
550	0.24	0.95	3:1	0.25	0.70	3:1
600	0.53	1.45	3:1	0.35	0.95	3:1
650	0.65	2.10	3:1	0.59	2.05	3:1
700	1.17	3.25	3:1	1.05	3.15	3:1

^a By difference.

^b HCl calculated as DDT on basis of 1 Cl to 1 DDT.

^c Of DDT found to DDT decomposed.

ENTOMOLOGICAL METHOD

One milliliter of the oil sample was emulsified with 9 ml. of 5% gum acacia solution, and the emulsion was injected into ten roaches at a dosage of 5.8 cu. mm. per gram weight. The resulting mortality in 40 hours was 80%. From standard curves previously determined, this mortality corresponds to a dosage of 30 mg. of DDT per kg. of roach weight, or 30 micrograms of DDT per gram of roach weight. This indicates that 5.8 cu. mm. of oil emulsion contains 30 micrograms of DDT or 5.17 micrograms per cu. mm. As the dilution in preparing the emulsion is 1 to 10, there are then 5.17×10 (dilution factor) or 51.7 micrograms of DDT per cu. mm. of the oil sample, or 5.17% (a specific gravity of 1 was also used in preparing the standard curves). The chemical analytical value for this sample was 5.27% DDT (Table IV).

DISCUSSION OF RESULTS

Although these tests were conducted at temperatures up to 700° F., the normal operating temperature of this generator is thermostatically controlled in the range around 600° F. The results of the three tests indicated that the percentage of DDT decomposed at these temperatures varied from about 3 to 8%, which is considered not to be excessive for this method of dispersal. It is quite low in comparison to decompositions encountered with dispersal devices such as candles, in which the decomposition has been found to be 25% and higher.

Tables III and IV indicate that, even at the highest temperatures observed, none of the DDT was completely pyrolyzed; at the lower temperatures apparently only one chlorine atom was split off each decomposed DDT molecule, and at the higher temperatures from two to three chlorine atoms were split off each decomposed DDT molecule. However, from the insecticidal standpoint, the elimination of only one chlorine atom as hydrochloric acid results in a compound which is ineffective as an insecticide.

Some question might be raised as to the effects on vegetation of the hydrogen chloride released by the small amount of DDT decomposed when dispersed by the thermal aerosol method. A calculation, such as the following, shows that the amounts of hydrogen chloride released are so small as to be considered negli-

gible for practical purposes: 46.7 grams of hydrogen chloride are released by every pound of decomposed DDT. Assuming decomposition of 8%, which is the maximum found at 600° F., there would be 3.7 grams or 0.008 pound of hydrogen chloride released for every pound of DDT dispersed at 600° F. If the dosage is 0.25 pound of DDT per acre, the hydrogen chloride released would be 0.9 gram or 0.002 pound per acre, which is thought to be an insignificant amount.

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Fungicidal Activity of Bisphenols

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In continuation of experiments previously reported (12), thirty-nine additional bisphenols and closely related compounds have been tested for fungicidal activity as mildew preventives on cotton fabric, bringing the total number of compounds tested to seventy-three. Some of these compounds are much more effective per unit weight on fabric than others as fungicides, and the trend toward high activity is correlated with certain features of chemical structure. The data do not appear to warrant the selection of any single bisphenol from among the group tested as having unique high potency but suggest rather that high potency is related to a certain generic type of structure within the group. For convenience in presenting the data, 2,2'-methylenebis(4-chlorophenol) has been selected arbitrarily from among the more active compounds and used as a point of reference for comparison with other compounds in both activity and chemical structure. Bisphenolic bridges consisting of $-\text{CH}_2-$, $-\text{CHCH}_3-$, $-\text{CHC}_6\text{H}_5-$, $-\text{CH}=\text{CH}-$, and $-\text{S}-$ have been found compatible with high activity, whereas $-\text{SO}-$ or $-\text{SO}_2-$

bridges are much less satisfactory. The presence of halogen atoms in all four positions ortho to the bisphenolic hydroxyls is consistently accompanied by low activity. Bromine has been found less desirable from the standpoint of fungicidal potency than chlorine in bisphenols of high total halogen content. Bisphenols with a chlorothymol type of structure, with unusually high molecular weights, a complete lack of halogen, or ether linkages blocking both phenolic hydroxyls have been found low in activity.

A PREVIOUS report (12) described experiments which dealt with the fungicidal activity of the bisphenols in tests as mildew preventives on cotton fabric. The present paper gives results of a continuation of this earlier work. The previous report pointed out certain relations between chemical structure and fungicidal activity within the bisphenols. Among the thirty-four different compounds tested, several highly active materials were noted in a certain generic structural group, typified for conven-