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CHEMICAL AND THERMAL METHODS FOR DISPOSAL OF PESTICIDES

BY

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Chemical and thermal methods for disposal of pesticides

By

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I. Introduction

The disposal of pesticide wastes and pesticide containers is one of the pressing problems of modern agricultural leaders. It is of grave concern to many leaders in other segments of the population as well. The problem is merely magnified by the all too frequent reports of accidental poisoning involving these potent chemicals.

Several methods of disposal of these waste pesticides and the resulting containers have been investigated, but none have proven to be ideal procedures although some have varying degrees of merit. Perhaps the most widely circulated recommendation at present is to bury the materials in a sandy soil at a depth of 18 inches in a private disposal site or take them to a sanitary land-fill type of dump (*U.S. Department*

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of Agriculture, ARS, August 1964) (*U.S. Department of Agriculture*, ARS, *New York State College of Agriculture*). Of course, this site then cannot be used for agricultural purposes again at any time in the forseeable future.

Another method of disposal which has been used quite extensively is incineration. Here again some serious objections must be overcome if this procedure is to be accepted on a nation-wide basis. Simple incineration without entrainment of the resulting gases would present a definite threat from the standpoint of air polution. Also, it would endanger humans, animals, and vegetation for some distance around the incineration site upon combustion of certain of the pesticides. These, as well as economic problems concerned with the energy source for incineration, need further investigation.

II. Materials studied

Twenty pesticide chemicals were used for the present investigation. Basically the study was divided into two distinct phases. These were thermal treatment of pesticides and chemical treatment of pesticides.

a) Reference standards

2,4-D (isooctyl ester of 2,4-dichlorophenoxyacetic acid)
Picloram (potassium salt of 4-amino-3,5,6-trichloro-picolinic acid)
Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine
Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]
Trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine)
Bromacil (5-bromo-3-*sec*-butyl-6-methyluracil)
DSMA (disodium methanearsonate)
DNBP (alkanolamine salt of 4,6-dinitro-*o*-*sec*-butyl-phenol)
Dicamba (2-methoxy-3,6-dichlorobenzoic acid)
Dalapon (sodium salt of 2,2-dichloropropionic acid)
Paraquat (1,1-dimethyl-4,4-bipyridylium salt)
Vernolate (*S*-propyl dipropylthiocarbamate)
2,4,5-T (trichlorophenoxyacetic acid)
Carbaryl (1-napthyl *N*-methyl carbamate)
DDT (dichlorodiphenyl-trichloroethane)
Dieldrin (hexachloroepoxyoctahydro-*endo*, *exo*-dimethanonaphthalene)
Malathion (*0,0*-dimethyl dithiophosphate of diethyl mercaptosuccinate)
PMA (phenyl mercuric acetate)
Zineb (zinc ethylenebisdithiocarbamate)
Nemagon (1,2-dibromo-3-chloropropane)

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b) Commercial formulations

2,4-D (4 lb./gal. "Formula 40")
Picloram (11.6% solution)
Atrazine (80% wettable powder)
Diuron (80% wettable powder)
Trifluralin (4 lb./gal. – liquid)
Bromacil (80% wettable powder)
DSMA (3.2 lb./gal.)
DNBP (3 lb./gal. "premerge")
Dicamba (4 lb./gal.)
Dalapon (85% wettable powder)
Paraquat (2 lb./gal.)
Vernolate (6 lb./gal., liquid)
2,4,5-T (4 lb./gal.; 44.1% acid equivalent)
Carbaryl (10% dust)
DDT (technical flakes)
Dieldrin (17.8% solution)
Malathion (5 lb./gal.; 57% solution)
PMA (Mersolite – 88 W; 95% water dispersable)
Zineb ("Parazate" –C; 75% wettable powder)
Nemagon (8.6 lb./gal.)

III. Thermal treatments

Investigations involving thermal treatment or incineration involved three methods: (1) differential thermal analysis, (2) dry combustion, and (3) ashing in a muffle furnace. Additionally, pyrolysis will be used in future investigations to identify the volatile products of incineration.

a) Differential thermal analysis

This method is used primarily for the classification and identification of clays, although recently it has been further developed and has been employed extensively in solving problems of general chemical interest (CHESTERS *et al.* 1959).

Thermal analysis is defined as "the process of determining the temperature at which changes in atomic rearrangement accompanied by a usually abrupt change in heat content occur in materials, by observing the aberrations which the heat content changes impose on the rate of temperature change of a specimen situated in an environment whose temperature is changing in a known manner" (SMOTHERS and CHANG 1966). Essentially, the analysis consists of recording the temperature of a sample as it is heated and plotting the resulting data. The differential method is considered to be superior to other methods, such as the inverse-rate method or the time-temperature method, because it is less subject to errors due to drafts, power changes, etc.

The differential analysis method employs a test sample and a "dummy" or neutral body as a reference standard.

Both the sample and the standard are heated simultaneously at the same rate through the same temperature interval. When the test sample undergoes rearrangement, the heat effect creates a difference in temperature between the specimen and the reference standard. This difference in temperature is plotted against the temperature at which this difference occurs; however, the temperature is determined by a second thermocouple located in the test assembly.

The thermal effects which take place may be either exothermic or endothermic. Causes of these changes may be boiling, vaporization, sublimation, fusion, or crystalline-structure inversion. Other changes may take place which are primarily chemical, such as oxidation or reduction, dehydration, combination, and decomposition. Many of these changes produce endothermic heat effects; however, oxidation, crystalline-structure inversion, and decomposition may cause exothermic heat effects.

Each compound will give an individually distinctive reproducible curve which can be used to qualitatively identify the substance. Each of the various endothermic and exothermic peaks will have the same shape, number, and position from one analysis to the next.

The curves are not as strictly reproducible as the X-ray diffraction pattern or the infrared spectrum, but experience has shown that careful reproduction of all conditions will give an identical pattern from one analysis to the next.

Differential thermal analyses of pesticides were carried out on a "Deltatherm," Model D2000 [1] differential thermal analysis apparatus. The sample holder block was fabricated from inconel metal, having service for four sample cups, four reference cups, and one temperature monitor cup. The cups were constructed from an alloy of platinum with 13 percent rhodium and had an inside diameter of 3/16 inch. The thermocouples were spot-welded directly to the bottom of the pans.

The material employed in the temperature cups and in the furnace monitor cups was aluminum oxide. In these analyses the temperature of the sample block was increased at a linear rate of 10° C./minute. The recording of the differential thermal curves was accomplished by an electrical current between a scanning stylus and sensitized paper.

In this investigation, no attempt was made to quantify the results obtained, since the primary interest was to establish the temperature for complete combustion. However, the same quantity of sample was used for analysis from one compound to the next.

The temperatures at which endothermic and exothermic peaks and the complete combustion of pesticides occurred are summarized in Tables I and II. All but four analyses were run at 25 percent sensitivity

[1] Technical Equipment Corporation, 917 Acoma Street, Denver, Colorado.

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Table I. *Differential thermal analysis of pesticides (temperatures of endothermic and exothermic peaks of reference standards and formulations)*

Pesticide	Sensitivity (%)	Temperature (° C.)	
		Endothermic peaks	Exothermic peaks
		Phenoxyalkyl acids	
2, 4-D			
Standard	25	165, 310, 479	348, 541
4 lb./gal.	25	154, 300, 363	550
2, 4, 5-T			
Standard	25	168, 309, 504	596, 675
4 lb./gal.	50	687	307, 380, 496, 683
		Chlorinated alkyl and aryl acids	
Dicamba			
Standard	25	50, 140, 310, 420, 460	810
4 lb./gal.	25	132, 260, 276, 290, 325	479, 496, 600, 840
Dalapon			
Standard	25	125, 220	
85% W.P.	25	50, 425, 840	210, 382, 471
Tordon			
Standard	25	225, 270, 482	
11.6% solution	25	145, 160, 171, 173, 334, 355	190, 386, 475, 580
		Chlorinated hydrocarbons	
DDT			
Standard	25	60, 110, 180, 350	545
Technical flakes	50	70, 110, 240, 275, 355	375, 578, 825
Dieldrin			
Standard	25	135, 175, 540, 585	325, 360, 420
1.5 lb./gal.	25	50, 240	325, 360, 415, 423, 513
		Heterocyclics	
Atrazine			
Standard	25	210, 308, 334, 360, 400, 480	290, 385, 582
80% W.P.	25	182, 280	250, 315, 550
Bromacil			
Standard	25	168, 300, 314, 330	239, 396, 509, 658
80% W. P.	25	170, 250, 307, 370	25, 248, 261, 452, 630
Paraquat			
Standard	25	173, 400, 472, 530	431, 560
2 lb./gal.	25	161, 200, 261, 300, 454	556
		Carbamates	
Sevin			
Standard	10	160, 287	656, 683
10% dust	25	159, 169, 249	274, 550
Vernam			
Standard	25	263, 409	
6 lb./gal.	25	61, 196, 369	465

Table I. (Continued)

Pesticide	Sensitivity (%)	Temperature (° C.) Endothermic peaks	Temperature (° C.) Exothermic peaks
Phenols			
DNBP			
Standard	25	143, 191, 339, 483	527
3 lb./gal.	25	94, 446	221, 527, 575, 588
Ureas			
Diuron			
Standard	25	173, 330, 400, 492	535, 757
80% W.P.	25	50, 154, 276	293, 460
Organophosphates			
Malathion			
Standard	25	500	250, 308, 333, 422
5 lb./gal.	25	145, 441, 475	261, 308
Miscellaneous			
DSMA			
Standard	10	121, 171, 202, 367, 600, 659	446, 558
3.2 lb./gal.	25	145, 556	388, 470
Nemagon			
Standard	25	50, 196, 358, 396, 432, 456, 500	579, 781
8.6 lb./gal.	25	170, 181	356, 377, 381, 532
PMA			
Standard	25	170, 242, 250, 253	275, 323, 358, 515
95% water dispersable	25	157, 232	259, 311, 334, 376, 400, 563
Treflan			
Standard	25	50, 261, 494, 619	272, 850
4 lb./gal.	25	138, 239	504, 515, 615, 808
Zineb			
Standard	25	185, 496	196, 245, 525, 675, 690, 749, 767, 795
75% W.P.	25	187, 290, 390, 452, 550	215, 232, 620

The 2,4,5-T and DDT formulations and carbaryl and DSMA standards were run at different sensitivities to bring out the peaks more sharply and thereby facilitate the determination of the exact temperature for each peak.

It may be noted from Table I that most of the peaks occurred between 50° and 600° C.

Table II summarizes the temperatures of complete combustion of pesticide materials estimated from the differential thermal curves. The temperature ranges for complete combustion of reference standards

Table II. *Differential thermal analysis of pesticides (temperatures of complete combustion of reference standards and formulations)*

Pesticide	Sensitivity (%)	Temperature (° C.) of reference standard	Sensitivity (%)	Temperature (° C.) of formulation
Phenoxyalkyl acids				
2,4-D	25	602	25	623
2,4,5-T	25	717	50	731
Chlorinated alkyl and aryl acids				
Dicamba	25	840	25	850
Dalapon	25	250	25	850
Tordon	25	550	25	640
Chlorinated hydrocarbons				
DDT	25	560	50	850
Dieldrin	25	620	25	640
Heterocyclics				
Atrazine	25	650	25	600
Bromacil	25	716	25	671
Paraquat	25	613	25	592
Carbamates				
Sevin	10	724	25	678
Vernam	25	447	25	508
Phenols				
DNBP	25	639	25	656
Ureas				
Diuron	25	775	25	550
Organophosphates				
Malathion	25	663	25	715
Miscellaneous				
DSMA	25	665	25	612
Nemagon	25	800	25	596
PMA	25	545	25	646
Treflan	25	879	25	842
Zineb	25	840	25	690

and formulations are from 250° to 879° C. and from 508° to 852° C., respectively. A conspicuous variation in temperatures is particularly evident between the reference standard and its formulation. Dalapon may be singled out as an extreme in this respect. Combustion of the dalapon standard is completed at or about 250° C.; however, the

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complete incineration of the formulation requires more than a three-fold elevation of this temperature.

It appears from these analyses that temperatures for complete combustion of pesticide materials under study are well within the ranges readily obtainable under most practical conditions. With a very few exceptions, it seems safe to assume that temperatures at or near 1000° C. will be sufficient to degrade 99 percent or more of most commercial pesticidal formulations.

b) Dry combustion

In another research area involving thermal analysis of pesticides, a dry combustion furnace was utilized. The method employed was a slightly modified version of that used for the determination of total carbon by dry combustion (ALLISON *et al.* 1965). It involved the burning of 50 to 100 mg. of a pesticide at 900° C. for 15 minutes in a resistance-type furnace in a stream of purified oxygen and the absorption of the carbon dioxide in the effluent gas stream by ascarite. The evolved carbon dioxide was determined gravimetrically. A plug of platinized asbestos serving as a catalyst was inserted in the combustion tube at the rear of the heated zone to insure complete oxidation of carbon monoxide to carbon dioxide. The boat was heated by radiation, conduction and convection in a tube surrounded by heating elements made of high-resistance material. Gaseous products of thermal breakdown of organic molecules other than carbon dioxide which would also be absorbed and could introduce a large error in estimating the carbon dioxide were removed from the air stream. The purification system used to free the incoming and outgoing stream of oxygen was as follows: (1) concentrated sulfuric acid was used to trap ammonia, hydrocarbons, and water vapor, (2) activated manganese dioxide to absorb nitrogen and sulfur oxides and halogens, (3) magnesium perchlorate to pick up water vapor, and (4) ascarite to absorb carbon dioxide.

Table III presents a partial list of total carbon recoveries of analytical grade pesticides. The results show a wide range of recoveries. Roughly ten percent of the carbon was not accounted for as carbon dioxide. Dicamba, atrazine, paraquat, bromacil, and PMA stood out with extremely low recoveries ranging from 67 to 88 percent. These data indicate that under similar conditions of incineration the pesticides may yield volatile carbon products other than carbon dioxide.

c) Ashing (muffle furnace)

Thermal treatment of pesticides was also carried out utilizing a regular combustion (muffle) furnace. Since the commercial formulations of pesticides contain certain inorganic materials as carriers or fillers it was desirable to ascertain the quantity of the pesticide mixtures which would be completely combustible at selected temperatures.

Table III. *Total carbon of analytical grade pesticides*

Pesticide	Carbon (%)		
	Calculated	Determined	Accounted for
Phenoxyalkyl acids			
2,4-D	43.4	41.6	95.9
2,4,5-T	37.6	37.4	99.5
Chlorinated alkyl and aryl acids			
Dicamba	43.2	37.9	87.7
Tordon	29.5	26.9	91.2
Chlorinated hydrocarbons			
DDT	46.8	47.5	101.5
Dieldrin	37.4	36.5	97.6
Heterocyclics			
Atrazine	44.5	31.8	71.5
Paraquat	56.0	37.4	66.8
Bromacil	41.4	35.4	85.5
Carbamates			
Sevin	71.5	65.4	91.5
Phenols			
DNBP	49.5	47.4	95.8
Ureas			
Diuron	46.3	35.5	76.7
Miscellaneous			
PMA	28.2	23.1	81.9
Zineb	17.4	19.4	111.5

The quantity of pesticides lost to combustion at five selected temperatures was determined and is presented in Table IV. It may be noted that the majority of the formulations approach complete combustion at 800° C. However, atrazine, malathion, zineb, bromacil, dalapon, diuron, DSMA, and Sevin have considerable quantities remaining even after combustion at 1000° C. Approximately one-fourth of the zineb formulation is made up of uncombustible materials at the highest temperature tested.

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Table IV. *Percent loss on combustion of commercial formulations of pesticides at five temperatures*

Commercial formulation	Loss (%) at				
	600° C.	700° C.	800° C.	900° C.	1000° C.
Picloram	90.8	91.8	95.6	98.7	99.2
Atrazine	87.8	88.1	88.8	88.9	89.0
Nemagon	99.6	99.6	99.6	99.6	99.6
Trifluralin	99.7	99.8	99.8	99.8	99.8
Malathion	95.3	96.0	96.3	96.4	96.7
2,4,5-T	99.9	99.9	99.9	99.9	99.9
Zineb	70.1	71.3	71.5	72.7	72.8
Vernam	99.6	99.6	99.6	99.6	99.6
Paraquat	98.3	98.6	99.0	100.0	100.0
Dicamba	98.6	98.7	98.9	99.0	99.4
Bromacil	88.8	89.1	89.4	90.5	91.3
Dieldrin	99.1	99.4	99.5	99.5	99.5
DDT	99.2	99.3	99.7	99.9	100.0
Dalapon	64.3	64.3	67.8	73.8	91.0
2,4-D	99.8	99.9	99.9	99.9	99.9
Diuron	94.6	95.0	95.4	95.5	95.7
DNBP	99.8	99.8	99.8	99.8	99.8
DSMA	80.6	80.7	80.7	81.2	81.2
Sevin	88.7	88.8	88.8	89.1	89.5

Another phase of the investigations involved exposure of analytical grade pesticides to "thermal shocks" [2] at selected temperatures.

The procedure was as follows: A small sample (0.5 to 1.0 g.) of a pesticide was weighed accurately in a Coors No. 0 crucible and subsequently heated for 30 minutes in a muffle furnace at a desired temperature. Temperatures were selected on the basis of the DTA curves. Following the heating the residue was cooled to room temperature and a small sub-sample removed for infrared analysis. Weights were obtained and recorded after the heating and removal of a portion of the residue for the infrared determinations. The remaining residue was heated to the next higher temperature plateau starting out with a cold muffle and the above-described procedure repeated.

The following pesticides were used in this study: DNBP, dicamba, paraquat, 2,4,5-T, dieldrin, nemagon, zineb, dalapon, malathion, and vernolate. The percentage losses at selected temperatures are summarized in Table V. Under these conditions of heating roughly two-thirds of the weight of most pesticides was lost between 200° and 300° C. In some cases practically all of the weight lost by a pesticide due to heating was in a single 100° C. rise in temperature increment; typical examples are shown in Table V.

[2] Heating with intermittent cooling.

Table V. *Effect of heating on weight loss, color, and physical appearance of pesticides* [a]

Pesticide	Heated (° C.)	Loss (%)	Color	Physical appearance
DNBP	200	48.7	Yellowish-brown	Liquid
	250	98.7	Dark-brown	Liquid solidifies on cooling
	300	98.9	Dark-brown	Solid
	400	98.9	Black	Flakes
	500	99.9	Grey	Powder
Banvel D (dicamba)	200	77.1	Colorless	Liquid solidifies on cooling
	250	99.1	None	No residue
	300	99.7	None	No residue
	400	99.8	None	No residue
Paraquat	200	2.0	White	Crystals
	250	2.1	Light brown	Crystals
	300	94.9	Black	Crystals
	400	98.5	Black	Crystals
2,4,5-T	200	27.4	Light brown	Liquid solidifies on cooling
	250	63.6	Light brown	Liquid solidifies on cooling
	300	99.7	Grey	Powder
	400	99.6	Reddish-brown	Powder
	500	100.0	None	No residue
Dieldrin	200	40.8	Yellow	Liquid solidifies on cooling
	250	80.7	Dark-brown	Liquid solidifies on cooling
	300	91.6	Dark-brown	Solid
	350	95.9	Black	Flakes
	400	96.8	Black	Flakes
	500	99.9	Black	Grains
Nemagon	100	71.7	Colorless	Liquid
	150	100.0	None	No residue
Zineb	200	10.0	Brownish-black	Granules
	250	11.9	Brownish-black	Granules
	300	44.8	Black	Granules with metallic sheen
	400	50.3	Yellowish-brown	Granules with metallic sheen
	500	51.9	Yellowish-brown	Granules with metallic sheen
	600	57.6	Yellowish-brown	Granules with metallic sheen
Dalapon	200	100.0	None	No residue
Malathion	200	58.7	Dark-brown	Liquid
	250	72.9	Dark-brown	Liquid, jelly-like on cooling
	300	76.2	Dark-brown	Silk flakes
	350	80.3	Dark-brown	Silk flakes
	400	80.3	Dark-brown	Silk flakes
	500	80.3	Dark-brown	Silk flakes
	600	80.3	Dark-brown	Silk flakes
Vernolate	200	99.6	Grey	Powder
	250	99.6	Grey-brown	Powder
	300	99.9	Brown	Powder
	400	100.0	None	No residue

[a] Analytical standards.

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IV. Chemical treatment

Commercial formulations of pesticides were subjected to selected concentrations of five different chemicals with the objective either to partially degrade or to decompose the compounds. The compounds selected were atrazine, malathion, nemagon, carbaryl, dieldrin, trifluralin, bromacil, picloram, diuron, dicamba, DNBP and 2,4-D.

Solutions of the pesticide formulations were treated with three different concentrations of hydrogen peroxide, nitric acid, sulfuric acid, sodium hydroxide, or ammonium hydroxide. Thin-layer chromatography (WALKER and BEROZA 1963) and infrared analysis (SADTLER INDEX 1960) were used to determine the effect of treatment on the pesticides.

The procedure for analysis was as follows: The formulations were either reacted directly or made up in benzene at the rate of 10 mg. of active ingredient/ml. of solution. Chemical agents were prepared as aqueous solutions at strengths shown in Table VI.

Table VI. *Degradation or decomposition reagents utilized*

Reagent	Concentration of solution		
	A	B	C
Hydrogen peroxide	5%	15%	30%
Nitric acid	4*N*	8*N*	16*N*
Sulfuric acid	9*N*	18*N*	36*N*
Sodium hydroxide	2*N*	4*N*	8*N*
Ammonium hydroxide	5*N*	7.5*N*	15*N*

For the benzene solutions an excess amount of the chemical agent to the pesticide was arbitrarily chosen in a 5:1 (v/v) ratio. After addition of the chemical, the mixtures were thoroughly shaken, allowed to stand for five to ten minutes, shaken again vigorously, and allowed to react at room temperature for 24 to 36 hours. The solvent layer was drawn off, evaporated to approximately 1.0 ml. in a Kuderna-Danish evaporative concentrator and analyzed by either thin-layer chromatography or by infrared analysis. The aqueous layer was extracted three times with either chloroform-benzene or *n*-hexane and subjected to infrared analysis.

The effects of chemicals on pesticides as revealed by infrared analysis may be summarized as follows:

1. Hydrogen peroxide treatment had no significant effect.
2. Nitric acid induced changes in carbaryl and atrazine. The 16*N* acid treatment produced nitrobenzene from carbaryl and a 2-hydroxy compound from atrazine which is believed to have resulted from the acid hydrolysis of 2-chloro-*s*-triazine (ZWEIG 1964).
3. Sulfuric acid effected a definite change in the structure of bromacil.
4. Sodium hydroxide caused only slight changes in the structure of dieldrin while malathion was broken down sufficiently to yield inorganic phosphate. Dicamba exhibited no change when treated with sodium hydroxide, yet 2,4-D was hydrolyzed to the sodium salt. DNBP was altered structurally by sodium hydroxide but the spectrum produced is still unresolved. Upon treatment with sodium hydroxide picloram was decarboxylated and the chlorine present was replaced by an OH group. Structural changes were also produced in bromacil when treated with sodium hydroxide.
5. Ammonium hydroxide treatment of carbaryl produced 1-naphthol but effected only a color change in trifluralin.

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Summary

Investigations concerning chemical and thermal decontamination of 20 pesticide chemicals are described. These are 2,4-D, picloram, atrazine, diuron, trifluralin, bromacil, DSMA, DNBP, dicamba, dalapon, paraquat, vernolate, 2,4,5-T, carbaryl, DDT, dieldrin, malathion, PMA, zineb, and nemagon.

Differential thermal analysis showed that complete incineration temperatures of the reagent-grade pesticides ranged from about 250° C. to approximately 850° C.; 15 of the compounds were completely combustible at 700° C. or below, while five required 700° and 900° C. Under similar conditions the commercial formulations required essentially the same temperature ranges; dalapon, trifluralin, and nemagon required higher temperatures than the respective reagent-grade compounds.

The incineration of commercial formulations showed a similar temperature range. All but six formulations approached complete combustion at 800° C. Atrazine, carbaryl, bromacil, and dalapon contained about ten percent of uncombustible residue at 1,000° C., whereas DSMA and zineb yielded 19 and 23 percent ash, respectively, at 1,000° C.

Ten compounds, subjected to stepwise heat treatment, showed a temperature range similar to that for differential thermal analysis. Infrared spectra indicated that nemagon disintegrated completely between 0° and 150° C.; whereas dalapon and vernolate did so between 0° and 200° C. Dieldrin, banvel D, and malathion showed no IR absorption after heating to 200° to 250° C. Malathion left a residue of phosphate which remained stable above 600° C. Disappearance of 2,4,5-T and DNBP occurred between 250° and 300° C.; however, DNBP degraded at 250° C. to 2-*sec*-butyl phenol. Paraquat dichloride degraded between 300° and 400° C. and zineb between 500° and 600° C.; zineb yielded between 200° to 250° C. a thermal degradation product which was tentatively identified as $S=C=N-CH_2-CH_2-N=C=S$ or $CH_3-CH_2-N=C=S$.

Results from the incineration of reagent-grade pesticides by the

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dry combustion procedure indicate that on the average ten percent of the carbon is not accounted for as CO_2 at 900° C.

Eight of the pesticide compounds when treated with strong acid or strong alkali exhibited partial decomposition. However, acid or alkaline hydrolysis was not complete in any case for the lengths of time studied.

Results indicate that incineration is superior to chemical methods for the destruction of waste pesticide chemicals.

Résumé *

Méthodes chimiques et thermiques de destruction des pesticides

On décrit des recherches concernant la destruction chimique et thermique des 20 pesticides chimiques suivants : 2,4-D, picloram, atrazine, diuron, trifluraline, bromacile, DSMA, DNBP, dicamba, dalapon, paraquat, vernolate, 2,4,5-T, carbaryl DDT, dieldrine, malathion, PMA, zinèbe et nemagon.

L'analyse thermique différentielle a montré que les températures d'incinération complète des pesticides chimiquement purs se rangeaient entre 250° et 850° C. environ ; 15 d'entre eux étaient complètement combustibles à 700° C. et moins, les cinq autres l'étaient entre 700° et 900° C. Dans des conditions similaires, les formulations commerciales ont nécessité des températures du même ordre de grandeur ; cependant, le dalapon, la trifluraline et le nemagon ont requis les températures plus élevées qu'à l'état pur.

L'incinération des formulations commerciales a mis en évidence une gamme de températures similaire à celle de l'analyse thermique différentielle. Exception faite de six formulations, la température de combustion complète était de 800° C. L'atrazine, le carbaryl, le bromacile et le dalapon contenaient environ 10 pourcent de résidu incombustible à 1000° C., tandis que le DSMA et le zinèbe donnaient respectivement 19 et 23 pourcent de cendres à 1000° C.

Dix composés soumis à un chauffage par paliers ont présenté une gamme de températures similaire à celle de l'analyse thermique différentielle. Le spectre infra-rouge a indiqué que le nemagon se désintégrait complètement entre 0° et 150° C.; le dalapon et le vernolate entre 0° et 200° C. La dieldrine, le banvel D et le malathion n'ont présenté aucune absorption IR après chauffage de 200° à 250° C. Le malathion a donné un résidu de phosphate stable à une température supérieure à 600° C. Le 2,4,5-T et le DNBP avaient disparu entre 250° et 300° C. ; cependant, le DNBP s'était décomposé en 2-butylphénol *sec* à 250° C. Le dichlorure de paraquat s'est décomposé entre 300° et 400° C. et le zinèbe entre 500° et 600° C. Le zinèbe a donné entre 200° et 250° C. un produit de dégradation thermique identifié

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expérimentalement comme S = C = N – CH_2 – N = C = S ou CH_3 – CH_2 – N = C = S.

Les résultats de l'incinération par combustion sèche des pesticides chimiquement purs indiquent qu'en moyenne dix pourcent du carbone ne doivent pas être considérés comme du CO_2 à 900° C.

Huit des pesticides ont présenté une décomposition partielle par traitement à l'aide d'un acide fort ou d'une base forte. Cependant, l'hydrolyse acide ou alcaline n'était complète dans aucun cas pour les durées étudiées.

Les résultats indiquent que l'incinération est supérieure aux méthodes chimiques pour la destruction de déchets de pesticides chimiques.

Zusammenfassung *

Chemische und thermische Methoden für die Beseitigung von Pestiziden

Untersuchungen über die chemische und thermische Dekontamination von 20 Pestizidchemikalien werden beschrieben. Diese sind: 2,4-D, "Picloram," Atrazin, Diuron, "Trifluralin," Bromacil, "DSMA," DNBP, "Dicamba," Dalapon, Paraquat, Vernolat, 2,4,5-T, Carbaryl, DDT, Dieldrin, Malathion, "PMA," Zineb und Nemagon.

Differential-Thermalanalysen zeigten, dass Temperaturen für die vollständige Einäscherung von reinsten Pestiziden von etwa 250° bis ungefähr 850° C. rangierten, 15 der Verbindungen konnten vollständig verbrannt werden bei 700° oder niedriger, während fünf 700° bis 900° C. erforderten. Unter ähnlichen Bedingungen erforderten die kommerziellen Formulierungen grundsätzlich dieselben Temperaturbereiche; Dalapon, Trifluralin, und Nemagon erforderten höhere Temperaturen als die entsprechenden Reinsubstanzen.

Die Einäscherung von kommerziellen Formulierungen zeigten einen ähnlichen Temperaturbereich. Alle ausser 6 Formulierungen erreichten vollständige Verbrennung bei 800° C. Atrazin, Carbaryl, Bromacil und Dalapon enthielten etwa 10 prozent von unverbrennbarem Rückstand bei 1000° C., während "DSMA" und Zineb bei 1000° C. 19, bezw. 23 prozent Asche ergaben.

Zehn Verbindungen, welche stufenweiser Hitzebehandlung ausgesetzt waren, zeigten einen ähnlichen Temperaturbereich wie für die Differential-Thermalanalyse. Infrarotspektren deuten an, dass Nemagon sich vollständig zwischen 0 und 150° C. zersetzt, während Dalapon und Vernolat sich zwischen 0 und 200° C. zersetzten. Dieldrin, "Banvel D" und Malathion zeigten keine Infrarotabsorption nach Erhitzung auf 200 — 250° C. Malathion hinterliess einen Phosphatrückstand, welcher über 600° C. hinaus stabil blieb. Das Verschwinden von

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2,4,5-T und DNBP wurde zwischen 250 und 300° C. erreicht, jedoch DNBP zerfiel bei 250° C. zu 2-sek.-butylphenol. Paraquatdichlorid zerfiel zwischen 300 und 400° C. und Zineb zwischen 500 und 600° C., Zineb ergab zwischen 200 und 250° C. ein thermisches Abbauprodukt, welches versuchsweise als $S=C=N-CH_2-CH_2-N=C=S$ oder CH_3-CH_2-NCS identifiziert wurde. Ergebnisse nach der Veräscherung von reinsten Pestiziden mit der trockenen Verbrennungsmethode zeigten, dass im Mittel 10 prozent des Kohlenstoffs nicht als CO_2 nachgewiesen wurde bei 900° C.

Acht der Pestizidverbindungen zeigten teilweise Zerstörung, nachdem sie mit starker Säure oder starkem Alkali behandelt worden waren. Jedoch war die saure oder alkalische Hydrolyse in keinem Fall vollständig für die untersuchten Zeiten.

Die Ergebnisse zeigen, dass Veraschung den chemischen Methoden der Zerstörung von Abfall-Pestizidchemikalien überlegen ist.

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