32–labeled demeton and its isomerization to the thiol isomer (*2*); the translocation and biochemistry of Systox (demeton) in plants; the determination and characterization of residues of Systox in citrus, walnuts, apples, pears, potatoes, and sugar beets; the preparation and determination of purity of phosphorus-32–labeled schradan; the determination of schradan residues in cotton; and the comparative biochemistry of schradan in the white mouse, squash bug, and American roach (*11*).

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Pest Control Limited, England	Technical schradan
Carbide and Carbon Chemicals Corp., New York	Hexaethylphosphoramide
Dow Chemical Co., Midland, Mich.	Decamethyltriphosphoramide
Monsanto Chemical Co., St. Louis, Mo.	*O*-Ethyl octamethyltriphosphoramide
	Unsymmetrical *O,O*-diethyl tetramethylpyrophosphoramide
Victor Chemical Works, Chicago, Ill.	Symmetrical *O,O*-diethyl tetramethylpyrophosphoramide

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PESTICIDE FORMULATIONS

A Selected Aromatic Fraction Naturally Occurring In Petroleum as a Pesticide Solvent

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Heavy aromatic naphtha, a selected fraction naturally occurring in petroleum, is an excellent solvent for pesticide formulations even at low temperatures. Its lower boiling range results in more rapid evaporation, an advantage when used for household or agricultural applications. Used in normal concentrations, it appears to be nonphytotoxic to pears, tomatoes, apples, celery, or citrus fruits and no more phytotoxic to corn than other commercial aromatic solvents. Animal toxicity studies indicate that there is no health hazard in connection with its use as a pesticide solvent.

EMULSIVE CONCENTRATES of pesticide formulations have increased greatly in use in the past few years. Emulsion prepared from these concentrates have less tendency to drift over adjacent fields than dusts, and they adhere better to plants. They are easier to use than wettable powders because there is no danger of orifice clogging. On the other hand, emulsive concentrates possess the disadvantage that when subjected to severe cold temperatures, certain pesticides may settle out. Also, in certain cases the solvent employed may possess herbicidal properties.

Aromatic products associated with petroleum may be obtained by thermal decomposition or cracking (whereby side chains are removed from aromatic nuclei and some cyclization takes place), catalytic reforming (whereby naphthenes are converted to aromatics), and physical separation of naturally occurring aromatics from an appropriate petroleum distillate. A study of aromatics from these sources indicates that the latter two possess similarity in solvent and stability properties, but commercial catalytic reforming processes tend to produce aromatics of undesirably low molecular weight. Efforts have therefore been concentrated on physical separation of aromatics. The molecular weight of the aromatic can be adjusted by selection of the proper distillate. The culmination of this research resulted in the production of heavy aromatic naphtha which, by reason of its physical properties as well as inherent solvent and stability characteristics, is an excellent and economical solvent for pesticides.

The following table is a usual inspection of heavy aromatic naphtha.

Initial boiling point, ° F.	328
10%	395
50%	448
90%	495
Final boiling point, ° F.	540
Specific gravity	0.9267
API gravity	20.9
Kauri butanol value	96
Per cent aromatics	85.5
Mixed aniline point, ° C.	25
Color, Tag Robinson	17
Flash (P.M.C.C.), ° F.	150

The boiling range, with 80% between 395° and 495° F., is considerably below that of many commercial petroleum pesticide solvents obtained from catalytically cracked distillates. This is of

Table I. Solubility of Pesticides in Heavy Aromatic Naphtha at Various Temperatures

Pesticide, % Wt.	Temperature, ° F.													
	−20	−10	0	14	32	40	70	−20	−10	0	14	32	40	70
	24 Hours							5 Days						
DDT														
35	D	D	D	D	D	D	A	D	D	D	D	D	D	A
30	D	A	A	A	A	A	A	D	D	D	C	C	B	A
25	C	A	A	A	A	A	A	D	B	B	B	A	A	A
20	A	A	A	A	A	A	A	C	A	A	A	A	A	A
Lindane														
22.5	D	D	D	D	D	D	B	D	D	D	D	D	D	B
20	D	D	D	C	B	B	A	D	D	D	D	C	C	A
15	D	D	D	B	A	A	A	D	D	D	D	B	B	A
12.5	D	D	B	B	A	A	A	D	C	C	C	B	B	A
10	C	B	B	A	A	A	A	D	B	B	B	A	A	A
7.5	B	A	A	A	A	A	A	C	A	A	A	A	A	A
Benzene hexachloride, 38% gamma														
25	D	C	C	C	B	A	A	D	D	C	C	B	A	A
22.5	C	C	B	B	A	A	A	C	C	B	B	A	A	A
20	B	A	A	A	A	A	A	C	B	B	A	A	A	A
15	A	A	A	A	A	A	A	B	A	A	A	A	A	A
12.5	A	A	A	A	A	A	A	A	A	A	A	A	A	
10	A	A	A	A	A	A	A	A	A	A	A	A	A	A
7.5	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Chlordan														
75	E	A	A	A	A	A	A	E	A	A	A	A	A	A
Toxaphene														
75	F	F	F	E	E	A	A	F	F	F	E	E	A	A
Methoxychlor														
40	D	D	D	D	C	C	A	D	D	D	D	C	C	A
35	D	D	C	C	C	B	A	D	D	C	C	C	B	A
30	C	A	A	A	A	A	A	C	A	A	A	A	A	A
25	A	A	A	A	A	A	A	C	A	A	A	A	A	A
20	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Pentachlorophenol														
20	D	D	D	D	D	D	D	D	D	D	D	D	D	D
17.5	D	C	C	C	C	C	A	D	D	D	D	D	D	D
15	D	C	B	B	B	B	A	D	D	C	C	C	B	A
12.5	C	B	B	A	A	A	A	D	C	C	B	B	A	A
10	A	A	A	A	A	A	A	B	A	A	A	A	A	A
2,4-D isopropyl ester														
60	E + G	A	A	A	A	A	A	F + G	A	A	A	A	A	A
50	A	A	A	A	A	A	A	A	A	A	A	A	A	A
40	A	A	A	A	A	A	A	A	A	A	A	A	A	A
2,4,5-T isopropyl ester														
60	F + G	F + G	F + G	F + G	B + G	A	A	F + G	F + G	F + G	C + G	A	A	A
50	F + G	F + G	F + G	F + G	A	A	A	F + G	F + G	F + G	A	A	A	A
40	F + G	F + G	E + G	E + G	A	A	A	F + G	F + G	F + G	A	A	A	A
2,4-D *n*-capryl ester														
60	A	A	A	A	A	A	A	A	A	A	A	A	A	A
50	A	A	A	A	A	A	A	A	A	A	A	A	A	A
40	A	A	A	A	A	A	A	A	A	A	A	A	A	A
2,4,5-T *n*-capryl ester														
60	F + G	F + G	A	A	A	A	A	F + G	F + G	A	A	A	A	A
50	F + G	A	A	A	A	A	A	F + G	A	A	A	A	A	A
40	A	A	A	A	A	A	A	F + G	A	A	A	A	A	A

A. Satisfactory, no settling out.
B. Slight settling out.
C. Crystals present, light precipitation.
D. Heavy precipitation.
E. Thick but not solid.
F. Solid.
G. Back into solution at room temperature without shaking.

considerable importance in pesticide formulations because the solvent evaporates more rapidly. In the case of household sprays and aerosols, there are less oiliness and more rapid drying of residual type sprays. For agricultural pesticides, more rapid evaporation should decrease the possibility of phytotoxicity. Heavy aromatic naphtha contains no pyrroles, substances found in some catalytically cracked aromatic solvents which produce a blue-black coloration with some chlorinated pesticides. Although the typical inspection indicated a flash of 150° F., the guaranteed flash is 125° F.

Color and odor are very important in the case of household products and odor is of some importance for agricultural applications. Heavy aromatic naphtha usually has a color of Tag Robinson 17, with a minimum of 14. The product is especially processed to eliminate disagreeable odor and possesses mild aromatic odor with a slight naphthalenelike undertone, acceptable for household and agricultural use. This quality is carefully controlled by a trained odor panel.

The low mixed aniline point and high kauri butanol value indicate that the product is an excellent solvent for DDT, pentachlorophenol, lindane, and other pesticides. These pesticides were dissolved in heavy aromatic naphtha and subjected to temperatures of −20°, −10°, 0°, 14°, 32°, and 70° F. Table I indicates the results after 24 hours and 5 days at the given temperatures. After 5 days at a given temperature, the solution was seeded with a small crystal of the pesticide, left at the same temperature for an additional 24 hours, and examined.

At 70° F., the heavy aromatic naphtha retained 40% methoxychlor, 35% DDT, 20% lindane, 25% benzene hexachloride, 17.5% pentachlorophenol, and 75% toxaphene or chlordane for 5 days. At 32° F., the product retained 25% DDT, 20% benzene hexachloride, 10% lindane, and 60% isopropyl ester of 2,4-D. Even at −10° F., favorable solubilities were indicated, such as 20% DDT, 30% methoxychlor (90% commercial grade), 75% chlordan, 7.5% lindane, 15% benzene hexachloride, 10% pentachlorophenol. 70% isopropyl or *n*-capryl esters of 2,4-D and 60% of *n*-capryl ester of 2,4,5-T.

Phytotoxicity

Aromatic petroleum products used undiluted often possess herbicidal action and may even be used as weed killers. However, when used in emulsifiable pesticide formulations, they are sufficiently diluted with water to possess little, if any, herbicidal action.

Heavy aromatic naphtha with emulsifying agents, but without a pesticide, was sprayed on several crop plants at a rate of 2 quarts per acre. No phytotoxicity resulted in tomatoes, beans, and Golden Delicious and Stayman apples. In the case of corn, both this solvent and a commercial pesticide solvent used as a control resulted in some injury where excessive spray collected in the whorl of the plant.

An emulsive concentrate with DDT, Rhothane, and Perthane used under field conditions with a number of applications resulted in no phytotoxicity with tomatoes, beans, celery, and Golden Delicious, MacIntosh, and Rome apples. In the case of corn, however, injury occurred where the spray collected excessively in the whorl; two commercial agricultural solvents used as controls also produced injury. Emulsive concentrates of DDT and Rhothane exhibited no phytotoxicity on several varieties of California lemons and oranges.

Greenhouse tests were made on tomatoes, beans, and corn by the New Jersey Agricultural Experiment Station (*2*), using two commercial 25% DDT concentrates, in which the product consists of 25% DDT, 72% heavy aromatic naphtha and 3% Triton X-100. The results given in Table II indicate that it would probably be safe to use this product for pest control on tomatoes, beans, and similar crops—i.e., potatoes, peppers, egg plants, soybeans, and other legumes. Injury to corn was moderate and no greater than with other commercial products. In this case, the test plants were of small size, only 4 weeks old.

Toxicity to Animals

The toxicity of heavy aromatic naphtha (Formula 132) has been investigated by Kehoe and associates (*1*), to determine its suitability for use as an insecticidal solvent for household use. The studies involved the intermittent exposure of experimental animals to low pressure aerosols of the solvent and patch testing of 100 human subjects for evidence of primary skin irritation or photosensitization. A control solvent, widely used in household insecticides and accepted by the U. S. Department of Agriculture for this purpose, was tested concurrently with heavy aromatic naphtha.

The inhalation studies involved the intermittent, daily exposure of mice, rats, guinea pigs, rabbits, and dogs to aerosols made with the solvents according to the following procedure recommended by the U. S. Department of Agriculture (*3*). During the first week the animals were placed in the 10-cubic-foot exposure chamber 0.5 hour per day without treatment, just to become acclimatized. The second week 0.5 gram of aerosol was sprayed in the chamber and the animals were exposed 0.5 hour each morning. The third week, 0.5 gram of aerosol was sprayed twice a day, morning and noon, and the animals were exposed 0.5 hour during these periods. The fourth week three applications of 0.5 gram of aerosol each were made—morning, noon, and evening—with the 0.5 exposure period after each application. Mortality figures, growth rates, blood picture (peripheral and bone marrow), organ weights, and microscopic observations of tissues were comparable for the two solvents. A low order of toxicity was indicated in these short-term, intermittent vapor exposure tests.

In the patch testing of 100 human subjects no significant degree of primary skin irritation was induced by either of the solvents. Subsequent exposure of the test sites to ultraviolet light produced only a mild intensification of skin reaction in five of the subjects tested with heavy aromatic naphtha. Four of these reactions subsided after 3 hours. In the fifth subject the reaction persisted for 6 hours. The control sample induced a mild intensification of reaction after ultraviolet light exposure in three out of 100 subjects tested. All of these reactions subsided after 3 hours. Neither sample induced a significant order of skin irritation or photosensitization reaction.

These studies indicate that heavy aromatic naphtha, if used as a household insecticidal solvent, would involve no greater hazard than that of an already widely used solvent that has been accepted by the U. S. Department of Agriculture for such purposes. No problems have been associated with the approved solvent in its field use. The U. S. Department of Agriculture has accepted heavy aromatic naphtha for registration for aerosol and other pesticide formulations as far as health hazards are concerned.

Table II. Phytotoxicity of Emulsive DDT Concentrates

Concentrate, 1 Qt./100 Gal.	Degree of Phytotoxicity	Av. Plant Height, Inches: Before spraying	Av. Plant Height, Inches: 7 Days after spraying
	Beans, Bountiful Variety[a]		
Commercial product A	None	9.5	9.5
Commercial product B	None	8.75	8.25
Heavy aromatic naphtha 132	None	8.75	8.25
Untreated	None	8.25	8.25
	Tomatoes, Rutgers Variety[a]		
Commercial product A	None	12.5	14.0
Commercial product B	None	13.75	15.25
Heavy aromatic naphtha 132	None	12.0	13.25
Untreated	None	14.75	16.0
Concentrate, 3 Qt./100 Gal.			
	Corn, Iowa Chief[b]		
Commercial product A	Moderate-severe[c]	11.25	14.0
Commercial product B	Severe	10.0	Dead[d]
Heavy aromatic naphtha 132	Moderate-severe[c]	11.0	12.75
Untreated	None	10.75	12.0

[a] Average of 3 replicates (4 plants/replica); plants sprayed to near run-off.
[b] Average of 3 replicates (3 plants per replica); plants sprayed to near run-off.
[c] Necrotic spots.
[d] Collapsed at topmost whorl.

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