
PESTICIDE FORMULATIONS AND APPLICATION SYSTEMS

Sixth
Volume

Vander Hooven/Spicer Editors

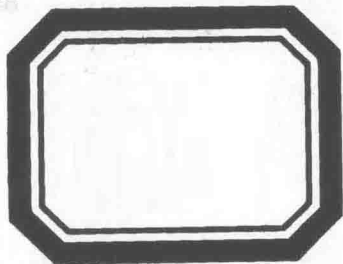


PESTICIDE FORMULATIONS AND APPLICATION SYSTEMS: SIXTH VOLUME

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on Pesticides
Bal Harbour, FL, 6-7 Nov. 1985

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NOTE

The Society is not responsible, as a body,
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Foreword

The papers in this publication, *Pesticide Formulations and Application Systems: Sixth Volume*, were presented at the Sixth Symposium on Pesticide Formulations and Application Systems, which was held on 6-7 Nov. 1985 in Bal Harbour, Florida. The symposium was sponsored by ASTM Committee E-35 on Pesticides. David I. B. Vander Hooven, The Andersons, presided as chairman of the symposium, and Larry D. Spicer, Rhone-Poulenc, Inc., was cochairman. Both men also served as editors of this publication.

Related ASTM Publications

Pesticide Formulations and Application Systems: Fifth Symposium, STP 915
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Pesticide Formulations and Application Systems: Fourth Symposium, STP
875 (1985), 04-875000-48

Pesticide Formulations and Application Systems: Third Symposium, STP
828 (1984), 04-828000-48

Pesticide Formulations and Application Systems: Second Symposium, STP
795 (1983), 04-795000-48

Pesticide Tank Mix Applications: First Symposium, STP 764 (1982),
04-764000-48

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Introduction

This volume contains the published results of papers presented at the Sixth Symposium on Pesticide Formulations and Application Systems, held in Bal Harbour, Florida, in November 1985. The technical aspects of pesticide application and formulation, including procedures, equipment, and characteristics of formulations contributing to the effective and responsible use of pesticides, was the focus of this ASTM symposium.

The symposium, one of an ongoing series held each year, was sponsored by ASTM Committee E-35 on Pesticides and its Subcommittee E35.22 on Pesticide Formulations and Application Systems.

This publication is based on a continuing concern that members of ASTM Subcommittee E35.22 share with the public, which is the need to improve pesticides and their application methods in order to preserve the quality of our environment and, at the same time, increase the production of food to meet the demands of the growing world population.

Many of the papers presented at this symposium and published herein deal with spray systems. These papers cover such topics as the phytotoxicity of selected hydrocarbon solvents and oils, the use of nonionic surfactants as thickeners in aqueous formulations, performance characteristics of certain rotary and electrostatic atomizers, and the effectiveness of various liquid formulations in the field.

In addition to sprayable formulations, several of the papers deal with granular formulations and mineral carriers and their current uses. One paper discusses methods of determining the delivery rates of granules in push-type spreaders.

Since pesticides constitute a group of chemicals that we cannot do without, the need for continuous improvement of them is paramount. Future symposia will address such subjects as emulsion tests, tank mix compatibility, granular carriers, closed system transfer, and bulk pesticide tanks. It is the intent of ASTM Subcommittee E35.22 to continue this series of symposia to present and publish technical papers that address these needs.

This publication advances a clear picture of current, ongoing research in improved pesticide formulations and applications systems. It will serve as a stimulant to researchers the world over to continue progress in this demanding field of technology.

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The Relative Phytotoxicity of Selected Hydrocarbon and Oxygenated Solvents and Oils

REFERENCE: Krenek, M. R. and King, D. N., "The Relative Phytotoxicity of Selected Hydrocarbon and Oxygenated Solvents and Oils," *Pesticide Formulations and Application Systems: Sixth Volume, ASTM STP 943*, D. I. B. Vander Hooven and L. D. Spicer, Eds., American Society for Testing and Materials, Philadelphia, 1987, pp. 3-19.

ABSTRACT: Phytotoxicity is a significant factor in the selection of solvents or oils for a pesticide formulation. This project was undertaken to develop relative data on the phytotoxicity of 20 solvents and oils for four major agricultural crops: corn, soybeans, wheat, and cotton. The solvents and oils were applied neat at a 32.7-L/ha (3.5-gal/acre) rate in a spray booth to approximately two-week-old postemergent plants grown in a greenhouse.

All the solvents and oils were rated by crop for relative phytotoxicity and assigned a relative rating. None of the plants died. No solvent or oil was found to be significantly more phytotoxic than the "industry standard" xylene range aromatic solvent, and the paraffinic and narrow-cut aliphatic solvents were observed to be nonphytotoxic at the 32.7-L/ha rate. Phytotoxicity was shown to be related to polarity, solvency, and the aromatics content of hydrocarbons. Surface tension was seen to be a contributing factor. Volatility did not show up as a major phytotoxicity determinant. The two grasses were seen to be more resistant to solvent-induced phytotoxicity than the two broadleaves.

KEY WORDS: phytotoxicity, pesticides, agricultural chemicals, oils, solvents, pendimethalin, polarity, volatility, surface tension, corn, wheat, cotton, soybeans

Petroleum-based hydrocarbon and oxygenated solvents and oils have been used for many years in all types of pesticides (herbicides, insecticides, fungicides, and others) for both agricultural and home and garden applications. Most often, in the United States, solvents and oils have been used in emulsifiable concentrate (EC) formulations, in which the solvent is part of a pesticide sold as a concentrate designed to be diluted with water for final application. They have also been used for ultralow-volume (ULV) formulations applied at rates significantly less than the EC rates—for example, 2 L/ha of liquid for ULV application versus 150 L/ha for an EC. The use of ULV application methods has grown rapidly in many parts of the world.

Typical carriers used in ULV applications have been paraffinic oils or solvents (such as Exxon Orchex 796 and Isopar M solvent) and vegetable oils (such as soybean and cottonseed oil). In ECs, xylene, "xylene range aromatic" solvents [as defined by the U.S. Environmental Protection Agency (EPA)], paraffinic solvents and oils, aromatic solvents, isophorone, and acetates have all been used.

In postemergent EC and ULV applications, phytotoxicity is a major concern and can show up in crops or plants as discoloration, wilting, and stunting of growth. Phytotoxicity is defined here as the *observed undesirable* herbicidal effect of a pesticide on a crop or plant and is measured in

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this work as a percentage of leaf damage. It can lower yields and income for the farmer and mar the appearance of plants for the home gardener. Obviously, phytotoxicity is a critical factor in formulating pesticides for use on growing plants.

Given a need to avoid undesirable phytotoxic damage, pesticide manufacturers and formulators must have data on phytotoxicity for the various components of a pesticide formulation. These formulators generally either have or develop the needed data on the active ingredients (AIs), but they have indicated that phytotoxicity data are often not available for many of the inert ingredients and adjuvants used in pesticide formulations. (One source of information available is the Weed Science Society of America publication *Adjuvants for Herbicides* [1].) Therefore, the general purpose of this research was to determine and document the *relative* phytotoxic effects of one part of the pesticide formulation package—the solvents and oils—on the four major agricultural crops in the United States: corn, cotton, soybeans, and wheat.

These four crops were selected because they account for the largest use of pesticides in the United States, and the data generated in this work can be used immediately by those formulating products for the American market. Also, the combination of two grasses and two broadleaf crops allows comparisons within and between the two groups. In addition, the results and conclusions can be more easily “transferred” to other crops and plants, since the work includes a mix of plant types.

Phytotoxicity is obviously a complex phenomenon, and looking at solvents and oils alone will not necessarily provide the complete picture on the phytotoxic effects of these. For example, additive or synergistic effects between or among two or more formulation components (AIs, solvents, surfactants, and so on) may cause a combined phytotoxic effect quite different from that caused by any one of the components alone. In addition, the weather, the method of pesticide application, and other factors are known to influence phytotoxicity. Nonetheless, knowing the phytotoxic effects of individual pesticide components is an important first step in building a formulation.

Experimental Procedure

Neat, undiluted solvents and oils were applied “over the top” in a one-time application to the four crops grown in a greenhouse. The solvents were applied using a spray booth at a controlled nominal rate of 32.7 L/ha (3.5 gal/acre). The crops were grown side by side in flats and were approximately two weeks postemergent at the time of application. Two replications were run for each “treatment,” or solvent-crop combination. After application, observations were made at varied intervals over a 56-h period.

Flats containing one row each of cotton, wheat, soybeans, and corn were planted and maintained in a greenhouse. The crops were watered with distilled water or distilled water containing Peters professional soluble plant food (Grade 20-20-20) at 0.33 mL/L ($\frac{1}{4}$ teaspoon/gal) of water. The results reported here are for crops treated 12 to 14 days after emergence from the soil.

The crop strains used in this study were the following:

- (a) cotton—Stoneville 825,
- (b) soybean—Hutton,
- (c) corn—H-TAM50, and
- (d) wheat—Sturdy.

Treatment of the crops was accomplished in the U.S. Department of Agriculture (USDA) spray chamber at Texas A & M University, College Station, Texas, using coded solvent and oil samples whose composition was not known by the researchers conducting the tests. The spray chamber incorporated a spray nozzle and reservoir mounted on an overhead rail that passed over a stationary table. Two flats were sprayed simultaneously for each solvent. The spray noz-

zle moved in a path parallel to the crop rows. The distance of the nozzle from the crop and the linear speed of the nozzle were adjusted to maintain the 32.7-L/ha application rate of solvent to crop. The delivery rate from the nozzle was a function of the flow characteristics of the solvent as the nozzle and spraying pressure were held constant. In order to model conventional application methods in the United States, a fan spray nozzle (800067) at 206.85 kPa (30 psig) spraying pressure was used.

The flats containing the crops were brought to the spray chamber at approximately 8:00 A.M. on the day of the spraying. A schedule for the spraying of the crops and additional details are included in Table 1. For each solvent sprayed, the spraying mechanism was rinsed with distilled water and calibrated using the solvent to be sprayed next.

After the spraying, the crops were moved, en masse, back to the greenhouse for evaluation. The evaluation of the phytotoxicity was accomplished using visual inspection and comparison with untreated crops. One researcher was responsible for all ratings throughout the testing. The ratings were made using a scale of 0 to 100, with the untreated controls rated 0. The rating reflected the percentage of the leaf surface affected by the treatment.

In addition to the untreated controls, an oil considered to be phytobland and used in agriculture for many years was used as a treated control (Exxon Orchex 796).

The 32.7-L/ha spray rate was judged to be sufficiently high to ensure that a range of phytotoxic effects would occur with the solvents and oils chosen. In field EC and ULV applications, the actual solvent or oil concentration in the final diluted formulation is often only in the range of 2 to 4 L/ha, and little or no phytotoxic effects are noticeable. Since the purpose of this re-

TABLE 1—Detailed spraying data.^{a,b}

Solvent/Oil	Time, A.M.	Swath, in.	Output, mL/min	Speed, ft/min	Volume, gal/acre
Isoparaffinic solvent 1	9:33	34	194	242	3.26
Isoparaffinic solvent 2	10:15	33	204	242	3.53
Isoparaffinic solvent 3	10:42	30	194	258	3.47
Normal paraffinic solvent 1	9:53	35	210	242	3.42
Normal paraffinic solvent 2	9:17	32	196	242	3.50
Normal paraffinic solvent 3	10:31	32	200	242	3.57
Narrow-cut aliphatic solvent 1	9:40	34	194	242	3.26
Narrow-cut aliphatic solvent 2	10:08	33	200	242	3.46
Deodorized kerosene	9:46	33	200	242	3.46
Mineral spirits 1	8:44	37	194	214	3.38
Mineral spirits 2	8:39	37	196	214	3.42
Highly aromatic solvent	10:01	36	192	214	3.44
Xylene	8:21	36	196	214	3.51
Xylene range aromatic solvent	8:33	37	190	214	3.31
Heavy aromatic—alkyl benzene	8:59	37	179	214	3.12
Heavy aromatic—alkyl naphthalene	10:22	36	192	214	3.44
Isophorone	9:27	34	178	207	3.50
Oxoheptyl acetate	8:50	37	188	214	3.28
Oxoheptyl acetate	9:06	37	186	214	3.24
Orchex 796 ^c	10:54	29	182	248	3.49

^aNozzle: 800067; pressure: 206.85 kPa (30 psig); date sprayed: 12 July 1984.

^bMetric conversion factors:

1 in. = 25.4 mm.

1 ft/min = 0.005 m/s.

1 gal/acre = 9.354 L/ha.

^cRegistered trademark of the Exxon Corp.

search was to determine a relative rank order of phytotoxicity, the much higher spray rate was chosen to "force" a range of phytotoxic effects that could be easily seen, rated, and compared.

The solvents and oils tested generally complied with U.S. Department of Transportation (DOT) regulations for combustible materials [liquids with a flash point equal to or greater than 37.8°C (100°F)] and the EPA regulations related to the use of inert ingredients in pesticides (40 CFR 180.1001³). Xylene, the only solvent or oil that did not meet the DOT criterion for classification as a combustible liquid, was included because of its historic widespread use in pesticides. The recently introduced oxohexyl and oxoheptyl acetates are currently being reviewed by the EPA for the first time for exemption from a tolerance under 40 CFR 180.1001 (c). (Table 2 includes a list, with a description and properties of the oils and solvents tested.)

Results

The phytotoxicity was rated as a percentage of the leaf damage in comparison with that for an untreated control observed at set intervals after application: 4, 8, 24, 32, 48, and 56 h. Observations ceased at 56 h because, at this point, all the plants involved in the test had begun to show evidence of renewed growth and recovery from any phytotoxic effects inflicted by the solvent or oil spray. None of the plants died or failed to resume what appeared to be normal growth.

The 0 to 100 ratings recorded in the greenhouse were converted to a simplified, sliding A-to-D scale for each crop, where A represented the minimum and D the maximum phytotoxic effects observed for that crop.

The final A-to-D ratings were assigned based largely on the observed readings at 32 h. The phytotoxic effects were generally seen to be the most severe overall at this point. The cumulative reading for the full 56 h was also used, however, as a tie-breaker among solvents showing similar readings at 32 h.

The overall results are listed in Table 3, and the more detailed data by crop are listed in Tables 4 through 7. Note that the scales for each crop are independent of each other. For example, a D rating with corn for a given solvent does not correspond to the same percentage of leaf damage as a D rating in soybeans with the same solvent.

Conclusions

1. None of the solvents or oils tested was significantly more phytotoxic than the xylene range aromatic solvent included in the test, and many were less phytotoxic. (The isoparaffinic and normal paraffinic solvents, the narrow-cut aliphatic solvents, and the deodorized kerosene all caused no observable phytotoxic damage at the 32.7 L/ha rate; the normal paraffinic solvents caused no damage at even double that rate—65.7 L/ha. The results for the isoparaffinic solvents agree with earlier reported data [2,3].) Since the xylene range aromatic solvent is often considered the industry standard solvent for EC pesticides, it seems reasonable to conclude that any of the solvents or oils tested would be suitable from a phytotoxicity standpoint for use in pesticide formulations for which xylene range aromatic solvents are currently used or accepted. It is possible, however, that the phytotoxic effects would be different for a given pesticide formulation when the solvent is changed.

It is important to remember that the ratings are relative. Even though the xylene range aromatic solvent is rated at C (moderate effect) and D (maximum observed effect) for the various crops, these are based on neat solvent at 32.7 L/ha rates. Phytotoxic effects for a given formulation with this or another solvent will vary with the concentration, method of application, and

³That part of the United States Code of Federal Regulations administered by the EPA covering exemptions from the requirement of a tolerance for certain pesticide chemicals.

TABLE 2—*Descriptions and properties of the solvents and oils tested.*

General Description/ Predominant Composition	Weight % of Saturates	Weight % of Aromatics	Flash Point, °C	Boiling Range, °C	Viscosity at 25°C, cP
Isoparaffinic solvent 1	99.9	0.06	61	188 to 207	1.61
Isoparaffinic solvent 2	99.8	0.2	80	206 to 253	2.46
Isoparaffinic solvent 3	99.35	0.65	124	255 to 295	7.38
Normal paraffinic solvent 1	99.5	0.6	69	188 to 219	1.26
Normal paraffinic solvent 2	99.8	0.2	93	226 to 243	1.84
Normal paraffinic solvent 3	100	0.01	118	252 to 277	2.50
Narrow-cut aliphatic solvent 1	99	0.8	73	202 to 232	1.58
Narrow-cut aliphatic solvent 2	99	0.9	102	233 to 252	2.31
Deodorized kerosene	97.0	3.0	70	197 to 252	1.69
Mineral spirits 1	92.1	7.7	41	159 to 203	0.90
Mineral spirits 2	83.0	16.0	42	159 to 204	0.95
Highly aromatic solvent	13	86	67	182 to 277	2.00
Xylene	0.1	99.9	28	138 to 140	0.62
Xylene range aromatic solvent	2	98	43	155 to 173	0.78
Heavy aromatic—alkyl benzene	2	98	66	183 to 210	1.20
Heavy aromatic—alkyl naphthalene	2	98	103	226 to 279	2.57
Isophorone	88	210 to 218	2.6 ^a
Oxohexyl acetate	57	162 to 176	1.04
Oxoheptyl acetate	66	176 to 200	1.24
Orchex 796 ^b	c	c	182	337 to 415	20.6

^aAt 20°C.^bRegistered trademark of Exxon Corp.^cMinimum unsulfonated residue is 92.0 volume %.

TABLE 2—Continued.

General Description/ Predominant Composition	Surface Tension, dynes/cm	Polarity, δ_p	Pendimethalin Solubility at 25°C, g pendimethalin/ 100 mL of solvent
Isoparaffinic solvent 1	25.9	0.0	14
Isoparaffinic solvent 2	26.6	0.0	13
Isoparaffinic solvent 3	30.8	0.0	11
Normal paraffinic solvent 1	24.8	0.0	13
Normal paraffinic solvent 2	25.8	0.0	12
Normal paraffinic solvent 3	27.0	0.0	10
Narrow-cut aliphatic solvent 1	25.7	0.0	17
Narrow-cut aliphatic solvent 2	26.7	0.0	12
Deodorized kerosene	25.4	...	16
Mineral spirits 1	25.2	...	28
Mineral spirits 2	22.3	0.1	33
Highly aromatic solvent	29.5	0.4	55
Xylene	28.0	0.5	54
Xylene range aromatic solvent	29.4	0.5	49
Heavy aromatic—alkyl benzene ^a	30.0	0.3	47
Heavy aromatic—alkyl naphthalene	33.0	...	53
Isophorone	32.3	4.0	55
Oxohexyl acetate	25.0	3.4	55
Oxoheptyl acetate	25.0	3.3	55
Orchex 796 ^a	33.4

^aRegistered trademark of Exxon Corp.