Pesticide Formulations

Innovations and Developments

EDITED BY
Barrington Cross and
Herbert B. Scher

ACS Symposium Series
371

ACS SYMPOSIUM SERIES 371

Pesticide Formulations

Innovations and Developments

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Developed from a symposium sponsored
by the Division
of Agrochemicals
at the 194th Meeting
of the American Chemical Society,
New Orleans, Louisiana,
August 30–September 4, 1987

American Chemical Society, Washington, DC 1988

Library of Congress Cataloging-in-Publication Data

Pesticide formulations.
Barrington Cross, editor. Herbert B. Scher, editor.

Developed from a symposium sponsored by the Division of Agrochemicals at the 194th Meeting of the American Chemical Society, New Orleans, Louisiana, August 30–September 4, 1987.

p. cm.—(ACS Symposium Series, 0097–6156; 371).
Includes bibliographies and indexes.

ISBN 0–8412–1483–2
1. Pesticides—Formulations—Congresses.

I. Cross, Barrington, 1935– . II. Scher, Herbert B., 1937– . III. American Chemical Society. Division of Agrochemicals. IV. Series

TP248.P47P485 1988
668'.65 88–10419
CIP

PRINTED IN THE UNITED STATES OF AMERICA

ACS Symposium Series

M. Joan Comstock, *Series Editor*

Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

OPTIMIZING PESTICIDAL ACTIVITY THROUGH FORMULATION is the major theme of this book. This volume complements the 1984 book *Advances in Pesticide Formulation Technology,* ACS Symposium Series 254, edited by Herbert B. Scher, which addressed controlled release, flowables, and computer applications to fomulation technology.

The current book covers three major topics and has a general section dealing with diverse topics. The first section deals with the effects of surfactants on pesticide wetting, penetration, and transport in plants. Authors trace the transport of pesticides in plants. They present models for these processes and new methods for determining permeation effects of surfactants.

Although the major theme of the book is the optimization of pesticidal activity through formulation, the second section discusses toxicity reduction through formulation.

The third section is devoted to emulsion technology; these chapters survey techniques to select surfactants. Cohesive energy density parameters are discussed as a means of selecting solvents. Solvent-phase interactions in microemulsions and the mode of action of structure agents in suspension concentrates are reviewed.

The last section covers topics on the controlled release of herbicides, insecticides, and natural products, in addition to granulation techniques and the effects of droplet size on distribution and efficacy.

This book provides much needed information on the current trends in pesticidal formulation for researchers working in industry, universities, or government agencies. As such, it should provide a valuable status review of pesticidal formulation for scientists involved in the development of formulations as well as those who use them. The agrochemical community at large should find this book a useful source of information.

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December 1987

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Chapter 1

Innovations and Developments in Pesticide Formulations

An Overview

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Pesticide formulators are concerned with development of physically and chemically stable pesticide compositions which can be applied uniformly by the user and which result in effective and efficient pest control. The various types of pesticide formulations and the factors which affect formulation choice have been well documented (1). Pesticide formulation ingredients include biologically active agents, clays, solvent diluents, surfactants and polymers.

New concepts and developments in the use of surfactants and polymers in pesticide formulations form the basis for the collection of papers in this book. Even though most surfactants and polymers are biologically inert when applied to plants or insects, these same chemicals can profoundly affect the biological activity of the pesticide when used as part of a pesticide formulation.

Surfactants play many roles in pesticide formulations (2), serving as:

1) Emulsifiers for Emulsifiable Concentrates and Microemulsions and Wetting and Dispersing Agents for Wettable Powders, Water Dispersible Granules and Flowables.

2) Spray Tank Additives to aid droplet adhesion and wetting of foliage.

3) Spray Tank Additives to enhance performance of pesticides by increasing uptake into the plant.

Polymers also play many roles in pesticide formulations, including:

1) Protective Colloids in concentrated emulsions and dispersions (3).

2) Suspending Agents in concentrated emulsions and dispersions (1, 4).

0097–6156/88/0371–0001$06.00/0

3) Binders for extruded and agglomerated granule formulations.

4) Barriers in controlled release formulations (5).

This book is divided into four sections. The first section (Effects of Surfactants on Pesticide Wetting, Penetration and Transport in Plants) and the second section (Toxicity Reduction Through Formulation) are related in that the pesticides must penetrate through a complex natural barrier. In the case of plants the barrier is called the cuticle and the formulator attempts to maximize pesticide penetration through the cuticle in order to maximize pesticide effectiveness. In the case of skin the barrier is called the stratum corneum (6) and the formulator attempts to minimize pesticide penetration through the skin in order to minimize dermal toxicity. Both types of barriers are complex in that they have hydrophilic and liphophilic components. The plant cuticle has a layered structure. The outer surface of the cuticle is composed of wax. Under the wax is the cutin layer which is a crosslinked matrix of hydroxy-fatty acids forming a three dimensional polyester network infiltrated with waxes. Below the cutin is a hydrophilic layer composed of pectin and cellulose. The skin stratum corneum is composed of hydrophilic Keratin (protein) and lipids (fatty acids).

The formulation factors which affect pesticide penetration through both the cuticle and stratum corneum are:

- Oil/Water Partition Coefficient of Pesticide
- Formulation Type
  - Physical properties of pesticide (solid or liquid)
  - Presence of organic solvents
  - Presence of barriers in controlled release formulations
- Type and Concentration of Surfactants

The third section (Emulsion Technology) concentrates on the use of surfactants and polymers in the formation of pesticide emulsions and microemulsions and the fourth section (General Topics - Advances in Pesticide Formulations) concentrates on the use of polymers in the production of controlled release pesticide formulations.

Introductory remarks for each Section follow, along with a discussion of how the papers relate to the general subject matter and to each other.

Effects of Surfactants on Pesticide Wetting, Penetration and Transport in Plants

This first section of the book focuses on the effects of surfactants on pesticide spray droplet size distribution, adhesion, spreading and wetting, penetration and transport (7, 8). The type and concentration of surfactant has a large effect on both the surface tension at the air/water interface and the contact angle at the water/plant interface. The surface tension affects the spray droplet size distribution which in turn affects both the efficiency of transport to the plant surface (drift losses) and the sticking efficiency on the plant surface (reflection losses). The product of the surface tension and the cosine of the contact angle (9) affects adhesion which in turn affects sticking efficiency on the plant surface. The product of the surface tension and the cosine of the contact angle also affects spreading and wetting which in turn affects plant coverage and runoff. The type and concentration of surfactant also has a large effect on pesticide permeation through the plant cuticle and pesticide transport within the plant. The surfactant can move into the cuticle, cause swelling and hence increase permeability. However, the surfactant effect on increasing permeability of the plant to the pesticide can often be offset by decreasing pesticide transport within the plant.

Pesticide Toxicity Reduction Through Formulation

Insights into the physiochemical factors that control percutaneous absorption are given in the paper by Ridout and Guy. These authors suggest a practical and inexpensive means of assessing the relative risk from dermal exposure for a structurally related series of chemicals. Their method involves correlating lipid-water partition coefficients with permeabilities through a model membrane composed of the same lipid.

The formulation type chosen for a particular pesticide is often dictated by a combination of the physical properties of the pesticide and the economics of the marketplace. However Hudson and Tarwater suggest that within the physical property and economic constraints there is still opportunity for reduction of pesticide toxicity through formulation and packaging choices.

The paper by Morgan, Rodson and Scher demonstrates a technique for reduction of toxicity of insecticides which involves combining the effects of a microcapsule wall barrier with a surfactant monolayer barrier created at the water/skin interface.

Emulsion Technology

The ease of emulsion formation and wetting of a surface is influenced by the rate of surfactant migration to the interface and the extent to which the interfacial tension is reduced by the surfactant at the interface. In the paper by Berger, Hsu, Jimenez, Wasan and Chung the maximum bubble pressure technique is used to measure the dynamic surface tension for a series of nonionic and anionic spray tank adjuvants and it is shown that there is a good correlation between rapid surface tension lowering and rapid wetting using the Draves wetting test.

Theory involving the use of the cohesive energy density concept can be useful in the initial phase of choosing emulsifiers for a pesticide emulsifiable concentrate formulation. The paper by Meusburger shows how one goes about calculating the cohesive energy for the organic pesticide phase (Group Contribution Method) and for an aqueous phase containing electrolyte.

The paper by Graff, Bock and Robbins shows the effect of solvent structure on the phase behavior of solvent in water micro-emulsions. They demonstrate that alkyl chain branching, allyl chain cyclization and the presence and position of hydrophilic functional groups in the solvents profoundly influence the observed phase behavior. The authors also suggest that the emulsion stability of macroemulsions should also be influenced by the same trends recognized for the phase behavior in microemulsions.

In the paper entitled "Mechanism of Action of Hydroxyethyl-cellulose as Structure Agent for Suspension Concentrate Formulations" Wedlock concludes that the mechanism involves controlled flocculation by bridging. These same type of mechanistic studies should also be conducted for the stabilization of concentrated emulsion formulations since it is likely that different mechanisms of stabilization (protective colloid action and immobilization of emulsion particles by creation of a structure with a yield value) are involved.

<u>General Topics - Advances in Pesticide Formulations</u>

Controlled release pesticide formulations (<u>10</u>) can be categorized (<u>4</u>) as follows.

1) Polymer Membrane - Pesticide Resevoir Systems

2) Matrix Systems Containing Physically Trapped Pesticides

3) Polymer Systems Containing Covalently Bound Pesticides

4) Coated Pesticide Granule Systems

The first category includes microcapsule systems. The paper by Morgan, Rodson and Scher in the second section (Pesticide Toxicity Reduction Through Formulation) deals with a microcapsule system.

The paper by Lohmann and D'Hondt fits into the third category where alkali-catalyzed hydrolysis, photolysis or cation exchange were employed to trigger the cleavage of susceptible chemical bonds connecting the active agents with the macromolecular carrier.

The paper by Van Voris, Cataldo, Cowan, Gordon, Cline, Burton and Skeins demonstrates the use of inert matrices (2nd category) such as polyvinylchloride and polypropylene to control the release of herbicides and the paper by Connick demonstrates the use of a biodegradable alginate matrix (2nd category) to control the release of biological control agents.

The paper by Lin describes the use of fluidized bed technology to produce water dispersible granules and water soluble granules. However fluidized bed technology can also be used to produce coated pesticide granules (4th category).

The paper by Hall discusses the effects of spray particle size distribution on the efficiency of pesticide transfer from the spray equipment to the plant. Water soluble polymers are often used to modify the properties of the spray solution in order to control drift or effect a controlled release response. This paper could have just as easily fit into the first section (Effects of Surfactants on Pesticide Wetting, Penetration and Transport in Plants) of the book.

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RECEIVED December 28, 1987

EFFECTS OF SURFACTANTS ON PESTICIDE WETTING, PENETRATION, AND TRANSPORT IN PLANTS

Chapter 2

Factors Affecting Foliar Penetration and Translocation of Pesticides

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Foliar uptake of 12 radio-labelled agrochemicals, following microsprayer application, has been measured in maize, rape, strawberry, and sugar beet with and without a non-ionic surfactant. Uptake rates during the first 24 h after application were up to 50 times greater than those during the second and third 24 h periods and they were always greater in waxy (strawberry and rape) than non-waxy (sugar beet) leaves. Highest uptake rates were measured for highly lipophilic compounds [log P (partition coefficient) >3] applied with surfactant but rates of translocation within the treated leaves for these compounds were low. Lowest uptake rates were found for water soluble compounds. Greatest rates of uptake and translocation were observed for compounds of median lipophilicity [log P 1-2; log S (molar water solubility) -1.5 - -3.5] both with and without surfactant. Addition of surfactant enhanced uptake of active ingredient up to 27-fold but had little effect on translocation. For compounds of similar water solubility, log (% uptake) increased linearly with log P reaching a maximum at log P ~ 1 in strawberry, sugar beet and rape leaves. For compounds of similar log P, log (% uptake) into rape, strawberry and sugar beet in the presence of surfactant was linearly correlated with log S.

Interest in the efficient delivery of foliar applied pesticides as a means of optimising biological performance has led to considerable advances in spray technology with major improvements in product formulation [1] and the development of new types of application equipment. Thus, sprays, formulated as emulsion concentrates, suspension concentrates, wettable powders, water dispersible granules and oil or water solutions, can be applied to leaves in widely differing volume rates (1-500 l ha^{-1}), droplet sizes (100-500 μm) and application rates (0.05 - 10 Kg ha^{-1}) [2]. However, relatively little attention has been given to systematic studies of the factors controlling the redistribution of pesticides and spray formulants into and through the outermost layers of the leaf and in consequence these complex interactions are poorly understood.

0097-6156/88/0371-0008$06.00/0