Pesticide Formulations AND Application Systems

ELEVENTH VOLUME

Bode/Chasin, editors

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Pesticide Formulations and Application Systems: 11th Volume

Loren E. Bode and David G. Chasin, editors

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Foreword

This publication, *Pesticide Formulations and Application Systems: 11th Volume*, contains papers presented at the symposium of the same name, held in San Antonio, TX on 14–15 Nov. 1991. The symposium was sponsored by ASTM Committee E-35 on Pesticides and its Subcommittee, E35.22 on Pesticide Formulations and Application Systems. Loren E. Bode of the University of Illinois at Urbana and David G. Chasin of ICI Specialty Chemicals in Wilmington, DE, presided as symposium co-chairmen and are editors of the resulting publication.

Overview

The 11th Symposium on Pesticide Formulations and Application Systems began the second decade of increased interaction between pesticide formulators, application scientists, and regulatory personnel. For increased efficiency and safety of pesticide use, more knowledge of the technical and regulatory aspects of formulations and application parameters must be obtained and shared among the disciplines involved with pesticides. The purpose of the symposium was to:

- Provide a forum for exchange of ideas and data among chemists and engineers working to improve the efficiency of pesticide use.
- Provide a data base to support ASTM Committee E–35 in development of guides and standards.
- Serve as a guide to Subcommittee E35.22 members in their future efforts to address the issues related to the use of pesticides.

This volume, in addition to previous symposia proceedings, adds significantly to the available resources on the important subject of pesticides. Topics in this STP include the technical aspects of pesticide application and formulation research, including equipment and concepts contributing to the effective and responsible use of pesticides. Safety aspects of pesticides are included as an integral part of pesticide development and use. Direction and suggestions for the development of standards were made available from material presented at the symposium.

The 22 papers in this STP are organized into three sections. The first section, *Safety and Environmental Impacts*, includes seven papers regarding humans, food, environmental issues, and presents new technology to insure that our safe supply of food is maintained. The second section, *Characteristics of Formulations and Adjuvants*, includes research regarding pesticide formulation and adjuvant technology. Seven papers regarding pesticide application comprise the final section, *Application Techniques and Pest Control*. This section includes research on new application systems and evaluations of pest control.

Safety and Environmental Impacts

Pesticide effects on the environment is a major factor in effective pesticide use. The papers in this section discuss some of the safety aspects of using pesticides to produce our food supply. The paper by Cummings compares the proposed California food safety initiatives and discusses the potential effects on formulation chemists and inert ingredient suppliers. Kogan and Gieseke's paper presents a computer model that provides quantitative information on human exposure to airborne particles in closed environments. Point source contamination of groundwater from loading and mixing sites can be prevented by use of a CARBO-FLO water treatment developed by Ohio State University. The treatment process uses a simple flocculation and filtration system that is described in the paper by Hall, Downer, and Chapple.

Controlled release granular formulations have the potential of reducing the amount of pesticide applied. Papers by Shasha and Wing present state of the art research regarding encapsulated herbicides. Stein describes a method to monitor release of pesticides from

granules into the soil, and Meyers showed that the change in release rate of chemicals in response to temperature is unique to microcapsules made from Intelimer polymers.

In addition to the formal papers, D. Lindsay and B. Omilinsky, EPA subcontractor Formulogics personnel, were invited to address the complex issues on the proposed rules regarding container management that is contained in FIFRA 88. The discussion provided a very interactive conclusion to the 11th symposium that was of value to the domestic as well as many international attendees who actively provided input regarding the rules being developed by the EPA.

Characteristics of Formulations and Adjuvants

Narayanan and Chaudhuri present a working model for emulsifiable concentrate formulations that explains the generality for the concentrates and high stability of emulsions observed on dilution with water. Duckworth and Cearnal present the results of a study to determine the effect of carrier temperature on the emulsification or dispersion of pesticide formulations. They suggest that the current ASTM standard be revised to include water temperatures that depend on the end use conditions of the pesticide. Becher shows that for testing compatibility in the laboratory, carriers must be representative of the type actually used in the field. Tann, Berger, and Berger demonstrated the application of dynamic surface tension to the study of adjuvants and emulsion stability.

Application Techniques and Pest Control

Wright described the new Expedite Pesticide Applicator System that is a combination of ready to use pesticide formulations, closed system packaging, and state-of-the-art, low-volume, controlled-droplet spray delivery. Ozkan outlined a comprehensive and complete set of guidelines which may help revise ASTM Standard E 641 that deals with measuring the wear rate of nozzle tips.

Biological results from pesticide application were presented by Chambers, Prasad, Manthey, and Riley. Chambers paper shows that mineral oil as a carrier for low volume applications was superior to vegetable oils in weed control efficacy. Prasad found that some adjuvants enhance the effectiveness of glyphosate sprays without damaging the crop species and discussed the relation of droplet size to phytotoxicity. Manthey reported on the relationship between phytotoxicity of a postemergence herbicide and the physical properties of surfactants. Riley's paper provides a detailed assessment of spray deposition and efficacy from insecticides, when aerially applied to stands of fir for control of the western spruce budworm.

These papers confirm that the objectives of the symposium were met. This STP (in conjunction with previous symposia STPs, provides a database of information regarding pesticide formulations and application systems that will guide ASTM Subcommittee E35.22 members in the development of necessary standards.

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Safety and Environmental Impacts

GARY L. CUMMINGS

THE CALIFORNIA FOOD SAFETY INITIATIVES: THE IMPACT ON FORMULATORS

REFERENCE: Cummings, G. L., "The California Food Safety Initiatives: The Impact on Formulations," Pesticide Formulations and Application Systems: 11th Volume, ASTM STP 1112, Loren E. Bode and David G. Chasin, Eds., American Society for Testing and Materials, Philadelphia, 1992.

ABSTRACT: The November, 1990 California ballot contained two initiatives which would impact the agricultural chemical industry. The most noted initiative, Proposition 128 popularly called the Big Green or Hayden/Van de Kamp initiative, addressed several environmentally popular themes, including food safety. The most significant effect on agrichem companies would come from the outright banning of certain chemicals, independent of concentration or risk, in food production. Products would be banned based on toxic active ingredients, metabolites of actives, impurities in actives, degradates of actives, inerts, metabolites of inerts, and impurities in inerts. Production Agriculture had sponsored a second, alternate initiative as a more responsible approach to food safety, Proposition 135. This paper will compare both initiatives, will discuss the initiative strategies and will discuss the potential effects on formulation chemists and inert suppliers.

KEYWORDS: Environmental Protection Act of 1990, Pesticide Enforcement Act, inert ingredients.

BACKGROUND

Many states have an initiative process. Californians have the process and have been very active in using it to achieve change. The increasing use of initiatives results from voter frustration with the inability, unwillingness or refusal of the legislature to seriously face contemporary issues. Californians have been very proactive as illustrated by a tax initiative (Proposition 13), a toxic chemical initiative (Proposition 65) and with many other lesser known initiatives. This fall, two initiatives will be on the ballot which will have major effects on the agrichemical industry.

The first, and potentially most significant, is Proposition 128, the Environmental Protection Act of 1990 [1]; commonly referred to as "Big Green", "Hayden Initiative" or "Hayden/Van de Kamp".

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This initiative has wide support and deserves close attention, whether or not passed by the voters.

The second initiative, Proposition 135 (Consumer Pesticide Enforcement Act for Food, Water and Worker Safety [2]), was developed by production agriculture as a reaction to the Environmental Protection Act. This act also would have significant impact in the agrichemical industry. However, this act is much more consistent with the current regulatory climate. The California initiative process provided an opportunity for consumers, the food industry and many worker groups to counteract the food safety extremes in the Environmental Protection Act, yet strengthen food safety programs in a meaningful manner. Where provisions of two successful initiatives overlap, the provisions of the initiative with the most votes prevail.

This paper does not intend to discuss all aspects of the two Acts or to discuss the politics and economics. After a general description of the features of the Acts, the paper will focus on the sections that are likely to impact us, as formulators.

OVERVIEW OF ENVIRONMENTAL PROTECTION ACT OF 1990

This Act has been very skillfully designed to appeal to most voters by including several issues of concern to Californians. Included are such environmentally sensitive issues as depletion of the ozone layer, protection of redwood trees, restriction of off-shore drilling, water quality improvement and food safety. Passage had been expected due to the perceived widespread voter appeal.

Careful analysis of the food safety sections leads to the following observations:

Proposition 128

- Imposes arbitrary, inflexible standards;
- Moves regulatory authority from the Department of Food and Agriculture (CDFA) to the Department of Health Services (DHS);
- Eliminates consideration of benefits as well as risks;
- Eliminates scientific judgment from certain decisions;
- Heavily impacts inert ingredients;
- Bans all products that are reproductive toxins and Group A or B carcinogens, including metabolites, degradates, impurities, inerts, inert metabolites and inert degradates;
- Bans Group C carcinogens unless registrants demonstrate safety. The timetables for rebuttal are likely to be unworkable. Many products would be banned because of administrative inactivity, not science. Metabolites, degradates, impurities, inerts are included;
- Sets many inflexible standards for worker safety;
- Sets tougher analytical standards;
- Bans any foodstuffs shipped into or through California which contain residues of banned active ingredients or inerts;

OVERVIEW OF PESTICIDE ENFORCEMENT ACT

This Act also has many features which are of interest to the voters. The single most important feature of Proposition 135 is that science and cost/risk remain as policy features in administering the food and worker safety program. Salient observations of this Act are high-lighted as follow:

Proposition 135

- Utilizes science and science advisory boards;
- Focuses on active ingredients and EPA Inerts of Toxicological Concern (List 1), not on degradates, impurities, metabolites;
- Funds more research into alternatives for pesticides;
- Continues to administer food safety through CDFA;
- Improves safety in transportation of agricultural commodities;
- Funds research and alternatives to medfly spraying;
- Increases state testing of raw and processed foods;

ENVIRONMENTAL PROTECTION ACT - DEFINITIONS

We have briefly examined the general strategies and main features of the two Acts. The next step is to evaluate Proposition 128, the Environmental Protection Act, in more depth. The definitions of several terms are important and provide insight into the comprehensive approach of the Act. These definitions are taken directly from the text (Article 5, 26914).

"Pesticide" or "pesticide chemical" means any substance which alone, in chemical combination, or in formulations with one or more substances, is an "economic poison" as defined by Section 12753 of the Food and Agriculture Code or a pesticide as defined in Section 2(u) of the Federal Insecticide, Fungicide and Rodenticide Act, but including the active ingredient, metabolites, contaminants, degradation product or inert ingredients and which is used in the production, storage or transportation of any food.

"Active ingredient" means a pesticide, excluding its inert ingredients, but including its metabolites, contaminants and degradation products.

"Inert ingredient" means an ingredient that is not active, as defined in Section 2 (m) of the Federal Insecticide, Fungicide and Rodenticide Act and including any contaminant therein or any substance which is the result of metabolism or other degradation of the inert ingredient.

"Contaminant" means a constituent of a registered pesticide which is unavoidably produced during the manufacture of the active ingredient.

"Degradation product" means the result of the biotransformation or breakdown of the parent compound by food processing or environmental factors including but not limited to air, sunlight or water.

"Metabolite" means the result of biotransformation or breakdown of the parent compound by a living organism.

ENVIRONMENTAL PROTECTION ACT - SECTIONS AFFECTING FORMULATORS

Certain features of Proposition 128 will impact formulators directly or indirectly.

BANNING OF PESTICIDES

All active ingredients known to cause cancer or reproductive harm, registered for use on food or having a tolerance, shall be banned by January 1, 1996. No new registrations or tolerances are allowed. No pesticides with missing data or inadequate data shall be registered for food use. (Article 1, 26901).

Any active ingredient is known to cause cancer or to cause reproductive harm if it is characterized by EPA as a Group A or B carcinogen or is on the California Proposition 65 Carcinogen List.

The following factors should be noted:

- There are no risk assessment or de minimus references.
- The active ingredient definition includes metabolites, contaminants and degradation products.
- Trace materials would be included.
- Missing data, tests in progress, etc. would preclude registration of new products.

REVIEW OF PESTICIDES

Producers can petition for review of "high hazard pesticides" which are defined as EPA Class C carcinogens. Petitions must be filed by November 7, 1994 and the DHS must evaluate the petition and data within one year. If the DHS does not respond favorably within one year, the pesticide shall be considered to be known to cause cancer. The criteria for assessment are the criteria of a Group B carcinogen (Article 2, 26903).

The following factors should be noted:

- The time frames are unrealistic.
- Products may be canceled due to DHS's inability to complete reviews within one year. Products may be canceled by default, not science.
- The time frames may not allow development of data to meet the assessment criteria. This would particularly impact metabolites, contaminants or degradates.

BANNING OF PESTICIDE INERT INGREDIENTS

No food use pesticide containing an inert ingredient known to cause cancer or reproductive harm may be registered or granted a tolerance. The time table for cancellation is two years (November 7, 1992). DHS shall not permit the use of any inert

known to cause cancer or reproductive harm in the formulation of a pesticide (Article 2, 26904).

EPA Group A or B carcinogens or Proposition 65 listed inerts are banned, Registrants may petition to have Group C carcinogens approved. If the inert is determined not to be a carcinogen, it must still be evaluated to determine that it poses no other risk.

The following factors should be noted:

- No exceptions are given for trace impurities.
- The definition of inerts includes metabolites and degradates.
- The review time tables are unrealistic. Little data may already exist for inerts, ingredients of inerts, metabolites or degradates.
- Inerts may be banned by default, not toxicity.
- California will be breaking new ground in administering inerts.
- "Other risks" is not defined.

PESTICIDE ENFORCEMENT ACT - SECTIONS AFFECTING FORMULATORS

Proposition 135 uses existing definitions within the California Food and Agricultural Code or FIFRA. The term "inert ingredient" is specifically defined as "an ingredient" in a pesticide which is not an active ingredient as defined in the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C., Sec. 136 (a)).

The Director of CDFA may require any registrant that has registered a pesticide which contains an inert ingredient which has been listed by EPA as an Inert of Toxological Concern (List 1), or any other inert ingredient which has been deemed by the director to be of significant toxological concern, to submit appropriate and relevant acute toxicity, chronic toxicity and residue data to the department for the inert ingredient in question.

The following comments are appropriate:

- The administration of inerts appears to follow EPA guidelines.
- Risk and science are included in the assessments.
- Impurities, metabolites and degradates are not specifically covered, although the Act allows CDFA to assess and regulate inerts of unspecified toxicological concern.

GENERAL IMPACT ON FORMULATORS

The Pesticide Enforcement Act primarily would appear to strengthen CDFA's administration of inerts, without adding significant requirements beyond those imposed by EPA. However, the Environmental Protection Act would have a profound impact on formulators and suppliers, and many new or expanded demands on formulators can be predicted from passage of Proposition 128.

- Many currently registered products will be banned.
- Formulators are frequently responsible for product degradation studies. The need to elucidate degradation mechanisms and to identify degradates will expand.
- More information will be required on the identity and fate of impurities used by formulators.
- Inert suppliers will need to be educated. Formulator's new responsibilities with respect to inerts, such as impurity or metabolite identification, will be beyond the knowledge, experience, capability or financial interest of many suppliers.
- Great care will be necessary in selection of brands or suppliers of inerts. We will need to work closely with many suppliers to learn for ourselves or help them learn more about their products.
- Many more back-up or alternate formulations will be needed. We will not be able to predict which inerts will become objects of concern, and we will not always be able to predict the outcome of regulatory reviews of inerts.
- Formulation considerations will become more important in business decisions. More emphasis on data development programs, strategies or task forces will be necessary to support specific inert usage.
- Uncertainty will remain over what "other health risks" means.
- Many inerts will no longer be useful options for formulators.
- There will be considerable chaos as agrichemical producers and inert suppliers begin to translate the ramifications of the Act into specific programs.

SPECIFIC IMPACTS ON FORMULATORS

Certain key ingredients are potentially impacted by the Environmental Protection Act. The following list identifies key inerts or impurities of concern. This list results from a relatively superficial survey of commonly used inert ingredients. Many other ingredients will be affected due to contaminants, degradates or metabolites whose potential presence may be indicated by literature searches, more in-depth discussions with suppliers or in-house data. Proposition 65 lists the following substances as chemicals known to the State to cause cancer. These substances are potentially associated with agricultural chemical inert ingredients:

> Acetaldehyde, benzene, ethylene thiourea, formaldehyde, silica, lead, dichloromethane, methylene chloride, methylene oxide, ethylene oxide, heavy metals, ethyl alcohol, soots, tars, mineral oils, propylene oxide, 1,4-dioxane.

Certain inerts have particular significance to formulators, since they have wide spread usage in pesticide formulations. The following comments are very general but can be illustrative of problems that will become apparent in inerts evaluations.

Emulsifiers

Most agricultural chemical emulsifiers contain one or more ethoxylates. When you examine the MSDSs for many emulsifiers, you frequently find a reference to the possible presence of ethylene oxide. It is difficult to foresee continued use of one of

these emulsifiers under Proposition 128. Fortunately, ethoxylators should be able to eliminate free ethylene oxide and remove the reference from their MSDSs.

Solvents

Tank trucks may carry gasoline or solvents, at times without thorough clean-out in the changeover. Benzene, from previous gasoline loads, may cause contamination of solvents. Fortunately this is a solvable problem.

Clays

The potential presence and characterization of silica (crystalline of respirable size) is a difficult issue for clay producers. Failure to resolve this issue may have a major impact on our ability to formulate granular, dust or wettable formulations. Heavy metal impurities may have an impact also.

SUMMARY

Californians will be voting on two initiatives. The effect on the agricultural chemical industry and pesticide formulation process will be major if the Environmental Protection Act passes, and gains more votes than the Pesticide Enforcement Act. The impact will be much less dramatic if the Pesticide Enforcement Act passes, and gains more votes then the Environmental Protection Act.

We must face a broader issue also. Food safety is a major focus of the environmental activism of the 90s. Inerts, impurities, degradates and metabolites are being drawn into the food safety debate. Decisions as to selection, source of supply, processing, contamination, degradation, and overall research on inerts will play an increasing important role in agricultural chemical business.

REFERENCES

[1] Environmental Protection Act of 1990 (Proposition 128). California Voter Initiative.

[2] Consumer Pesticide Enforcement Act for Food, Water, and Worker Safety (Proposition 135). California Voter Initiative.