PESTICIDE FORMULATIONS and APPLICATION SYSTEMS: *SECOND CONFERENCE*

K. G. Seymour, *editor*

ASTM STP 795

PESTICIDE FORMULATIONS AND APPLICATION SYSTEMS: SECOND CONFERENCE

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Foreword

The papers in this publication were presented at the symposium on Pesticide Formulations and Application Systems: Second Conference, the second in a series of symposia on this subject. The first in the series was titled Pesticide Tank Mix Applications: First Conference and has been published as *ASTM STP 764* (1981). This second symposium was held in Kansas City, Mo., on 19 Oct. 1981. The sponsors were ASTM Committee E-35 on Pesticides and ASTM Subcommittee E35.22 on Pesticide Formulations and Application Systems. Dr. K. G. Seymour of the Dow Chemical Co. was chairman of the symposium and also served as editor of this publication.

Related ASTM Publications

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

Avian and Mammalian Wildlife Toxicology: Second Conference, STP 757 (1981), 04-757000-48

Avian and Mammalian Wildlife Toxicology: First Conference, STP 693 (1979), 04-693000-48

Vertebrate Pest Control and Management Materials (Third Conference), STP 752 (1981), 04-752000-48

Vertebrate Pest Control and Management Materials (Second Conference), STP 680 (1979), 04-680000-48

Test Methods for Vertebrate Pest Control and Management Materials (First Conference), STP 625 (1977), 04-625000-48

Aquatic Toxicology and Hazard Assessment (Fifth Conference), STP 766 (1982), 04-766000-16

Aquatic Toxicology and Hazard Assessment (Fourth Conference), STP 737 (1981), 04-737000-16

Aquatic Toxicology (Third Conference), STP 707 (1980), 04-707000-16

Aquatic Toxicology (Second Conference), STP 667 (1979), 04-667000-16

Aquatic Toxicology and Hazard Evaluation (First Conference), STP 634 (1977), 04-634000-16

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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Contents

Introduction

The 1981 symposium on Pesticide Formulations and Application Systems was the second in what is hoped will be a continuing series. These symposia were conceived and sponsored by ASTM Subcommittee E35.22 on Pesticide Formulations and Application Systems, a subcommittee of ASTM Committee E-35 on Pesticides. (As used here, the term pesticide includes herbicides and plant growth regulators as well as insecticides, fungicides, and so forth.) It was intended that the symposia provide an interdisciplinary forum for discussion of the many facets of pesticide formulation and application. Agricultural engineers, chemists, biologists, package technologists, and others have access to professional organizations centered around particular disciplines; however, a forum for mutual exchange of technical information and ideas among the concerned disciplines has been lacking. This symposium was intended as another small step towards filling that communication gap.

Pesticide formulation is an interdisciplinary, specialized field generally concerned with mixtures of pesticidal active ingredients, or of a single ingredient, with additives to achieve convenient physical properties, ease of application, and favorable biological performance. The manufacture, packaging, stability, field mixing, active ingredient availability to the target organism, residuality, and potential side effects of pesticides are key considerations. The importance of safety factors is pervasive; the hazards range from the acute toxicity of the formulated pesticides, through manufacture and distribution hazards, to those of actual use. Many aspects of pesticide formulation and use are subject to regulation by various government agencies. In general, the pesticide products used in agriculture, homes, and commerce are formulated products. (Only a very few pesticidal active ingredients have physical and biological properties suitable for direct application without formulation.)

Application systems, as used here, include agricultural engineering activities related to applying pesticides. They also include machinery and equipment, operating practices, the pesticide and diluent materials used, and, generally, any other subjects related to using or applying pesticides. Again, a number of other disciplines are involved, including meteorology, agronomy, entomology, weed science, safety engineering, and others.

The 1981 symposium was divided into sessions addressing the topics of containers, granular formulations, and spray-related subjects. These represent, deliberately, a variety of subjects of interest and of the speakers' interests, all contributing to a theme of knowledge about effective, efficient, and safe use of pesticides.

K. G. Seymour
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symposium chairman and editor.

J. P. McGreevy[1]

Package Development from the Pesticide Industry Viewpoint

REFERENCE: McGreevy, J. P., **"Package Development from the Pesticide Industry Viewpoint,"** *Pesticide Formulations and Application Systems: Second Conference, ASTM STP 795,* K. G. Seymour, Ed., American Society for Testing and Materials, 1983, pp. 3–6.

ABSTRACT: An outline of the general activities and concerns associated with package development for agricultural chemicals is given: Storage stability studies are initiated at accelerated and normal warehouse conditions, with the prospective product packaged in various candidate containers. Subsequent chemical and physical evaluations are conducted. Compatibility with materials of construction of application equipment is examined. Various pieces of laboratory test equipment, used in package development and later for quality control, are discussed. The impact of future performance-oriented package specifications, instead of current U.S. Department of Transportation detailed construction requirements, is considered. The use of the laboratory transportation simulator is outlined. Palletization and various packaging regulations are important aspects of package development. The end result of various tests and considerations is a satisfactory specification and package.

KEY WORDS: chemical stability, physical stability, package compatibility, application equipment compatibility, test equipment, quality control, package specifications, transportation simulator, palletization, regulations, pesticides

At the Agricultural Chemicals Division of Mobay Chemical Corp., package development is a function of the research and development department, specifically in conjunction with the formulation research section. As part of this group, the author believes that an early insight into special packaging requirements is gained through a hand-in-hand working relationship within the same group that develops the formulation. One can begin immediately to study the chemical and physical nature of an experimental product. These properties generally dictate the selection of materials which will be used in the package.

Discussion

A typical storage study involves packaging the experimental pesticide in various candidate containers and placing them in storage at various loca-

[1] Research chemist, Mobay Chemical Corp., Agricultural Chemicals Division, Research and Development Department, Kansas City, Mo. 64120.

tions and atmospheric conditions for specified periods of time. Preliminary screening tests, that is, a "tropical" storage test for powders, and a metal strip test for liquids, help to select the candidate containers. Storage conditions include a 40°C oven (accelerated storage for up to six months), a Kansas City warehouse and at least one outside warehouse location (Florida, Mississippi, or California) for up to three years, and a −6°C cold room specimen as a control standard. Periodic physical and chemical evaluations are scheduled for both the product and the package during this study. Obviously, chemical analysis is important from a stability standpoint, but so are physical evaluations such as corrosion potential, weight loss or gain, odor control, moisture or humidity protection, caking, staining, and chemical attack. The key words are, therefore, "physical and chemical stability" and "package compatibility."

Another phase of compatibility is the testing of various materials used in construction of typical application equipment. The pesticides are tested in both the concentrated and typical dilution form on gaskets, O-rings, hoses, various metals and fiberglass, polymers and plastics, coatings, and other materials. Results of these tests often lead to recommendations for the selection of materials used in spray systems.

Other important areas that must be considered include the following.

Packaging Testing—Research and Quality Control

In the course of package development, and later for quality control of incoming packages, we utilize various pieces of test equipment in the laboratory:

(*a*) *air pressure test* (example: DOT-17E steel pail)—0.345 kg/cm^2 for 5 min, and

(*b*) *drop test* (example: DOT-17E steel pail)—1.22 m diagonally on top chime.

These are obviously related to the U.S. Department of Transportation (DOT) construction requirements, which are rigidly detailed in the regulations.

This brings up an interesting point worthy of mention here. The DOT recently announced its intention to adopt United Nations-based, *performance-oriented* requirements for containers. If this is done, it would represent a dramatic change in philosophy. Instead of specifying the exact manner and materials from which a container must be fabricated, the performance-oriented standards would require only that the container meet certain criteria.

This would allow greater flexibility in package design and development, but at the same time, it would place greater responsibility and liability upon chemical manufacturers to ensure that their designs will perform safely and effectively. Package manufacturers will be similarly affected.

Another tool which will assist in the development of such performance-oriented containers is this company's "transportation simulator." This unit is about 12 years old now and may be somewhat outdated by today's standards, but it has served us well through the years. The frequency and table amplitude (or displacement) are variable. Its capacity is in excess of 1000 kg, so heavy pallet loads can be tested as well as individual packages. The literature states that 1 h on this machine, at any setting for 1 g of force, is equivalent to 1600 km of transportation. I do not know how this was established, nor do I know the validity of that statement. However, we do believe that the transportation simulator is a valuable test tool for package development—especially in situations where a side-by-side comparison among a group of container variables can be evaluated. For example, we have used it to compare everything from rubbing effects on printed polyethylene sleeve labels on plastic jugs in corrugated boxes to an evaluation of strapping versus shrink-wrapping versus stretch-wrapping as methods of unitizing or palletizing. We think this type of performance testing will take on greater significance in package development in the near future, in light of the DOT announcement.

Palletization

The container selected must be compatible with our standard palletizing program and procedures regarding size, style, and strength. Where possible, package dimensions are established based upon pallet dimensions, so that a perfect pattern results on our standard 1200 mm by 1000-mm pallet.

Packaging Regulations

Packaging and shipping regulations play an important role in the course of package development. Many of our products are hazardous materials by DOT definitions. Typical products may be labeled "poison," "flammable," or "corrosive"—some may even have dual hazards within one product. As such, they must be packaged and labeled in accordance with strict regulations, which outline minimum requirements of package construction.

We must maintain a working knowledge of all regulations that might affect our products and be aware of all changes. In addition to the domestic DOT regulations, regulations of the International Air Transport Association (IATA), International Maritime Consultative Organization (IMCO) for export shipments, and Canadian Transport Commission (CTC) must be complied with since this company has a branch in Canada. Incidentally, Transport Canada is in the process of finalizing a complete revision of their regulations (Dangerous Goods Code), apparently patterned after IMCO. The *Federal Register* is an important source of information on all regulatory activities.

We must also comply with joint U.S. Environmental Protection Agency (EPA) and DOT regulations under the Resource Conservation and Recovery Act (RCRA), which governs the use of "hazardous substances," as specifically designated by name by the EPA, and "hazardous waste" generation and shipment for disposal. Again, packaging and hazard labeling for these materials are carefully defined in the regulations.

Pesticides intended for home and garden or residential use are further regulated by the EPA regarding "child-resistant" packaging—if they meet certain toxicity or hazard criteria.

It is clear that various regulations can have a dramatic impact on package development and the final container specifications. Another example is California's regulations for worker safety regarding handling of and exposure to toxic pesticides. Water-soluble film packaging for toxic powders is required, unless you have a dust-free formulation. A standardized size and type of closure (opening) may be dictated for containers of toxic liquids in order to make them more compatible with the closed transfer and metering systems now available.

Conclusion

In summary, the ideal end result of all the testing and various considerations is a specification for a container that (*a*) is economical, (*b*) is operationally feasible, (*c*) satisfies the needs of marketing and all regulatory concerns, and finally, (*d*) performs as intended throughout the distribution cycle. This is our goal.

R. B. Schaefer[1]

Package Selection, Testing, and Transportation Regulations

REFERENCE: Schaefer, R. B., **"Package Selection, Testing, and Transportation Regulations,"** *Pesticide Formulations and Application Systems: Second Conference, ASTM STP 795,* K. G. Seymour, Ed., American Society for Testing and Materials, 1983, pp. 7–14.

ABSTRACT: Agchem package selection, as done by a large company, is reviewed, including methodology, cost study, and specification development. Certain testing methods, standards, and regulatory problems are discussed in detail.

KEY WORDS: pesticides packaging, transportation regulations, compatability, testing, pesticides

From providing chemical packaging for the Pennwalt Corp. for the last 30 centuries (it seems), it has become apparent to the author that the company does have a highly developed system that deals effectively in a defined order with the following concerns:

1. What is the competitive picture? To package properly, it is necessary to understand the market into which the product is to be entered. Who uses it and how is it used?
2. What are the cost considerations?
3. What are the advantages and disadvantages to the manufacturing and sales departments which affect their approval of particular packaging?
4. What are the regulatory considerations (from a packaging and transportation standpoint)?
5. How is a final package specification—with enough detail for competitive pricing and the meeting of all regulations—prepared? At this time, approvals are obtained and a reevaluation of the package/product/use situation is made to check safety considerations.

When a new product develops or a packaging situation changes, an informal meeting is held with the product manager. Appendix I shows the type of questions discussed.

[1] Manager, Packaging, Pennwalt Corp., Philadelphia, Pa. 19102.

This process is pretty straightforward except for the forecasting. Over the years, experience has shown that the quantity of packages affects what types of package you can consider more than a lot of other things. Care must be taken in working on a new package not to pick something that is impractical to buy. The tooling costs, testing, and low volumes can make the real costs prohibitive.

The next step is to develop several candidate packages. The form in Appendix II is used to present the economics of a new container with quotations. Note that the form also allows us to compare a new package with one previously used and to determine the annual cost effect. This analysis is worthwhile not only in presenting the new package but in enabling us to check a year later to see if the goal was accomplished. Samples or prototypes are also shown to the marketing people at this stage.

Still another purpose of the form is to point out to the manufacturing and sales people any foreseeable problems or advantages of the change from a practical handling standpoint.

The next step is a formal approval stage wherein the proposed specification is routed through the technical service, manufacturing, sales, and, finally, product safety and purchasing departments.

Our final product is the package specification, which details the package, including the regulatory aspects, where it is needed, and a full physical description.

Over the years, the author has found that pictures are helpful. A sketch or a reproduced photo on the specification page does more to get the right package in the right place than much of the written detail. Also, if there is a need for a special quality control (QC) factor, this paper lets everyone know what it is and what to look for—for example, flash marks on a bottle neck finish can cause leakers. The specification page is the place to record this type of information and let everyone involved know what is important. Appendix III shows a finished specification.

Testing

Testing is a subject which requires more thorough discussion than routine package selection. It cannot be stressed too much that products must be checked carefully. Do not rely on somebody's statement that something is all right.

The author recently had a situation in which the U.S. Environmental Protection Agency (EPA) required a child-resistant closure on a plastic pail for the pesticide calcium hypochlorite. This was a new requirement and probably the first time a closure not only had to be child-resistant (CR), but also had to meet the U.S. Department of Transportation (DOT) regulations for a DOT 35 open-head plastic pail, an outside package. Working with the pail supplier and also with a steel locking ring supplier, we finally arrived at an ar-

rangement which seemed to meet both regulations, and we started the protocol testing. Despite assurances from both suppliers that they understood what was needed, when we rechecked a drop test, the closure did not pass. The ring supplier, in trying to make the closure easier to operate to assist in meeting the CR protocol, had loosened the ring and decreased its efficiency in meeting the DOT requirements. The message of this incident is to check and recheck by actual testing yourself.

Another kind of testing may be of more significance for liquid insecticides, which manufacturers may want to put into plastic containers. Those who are familiar with this area know that compatibility testing has been totally a "seat-of-the-pants" procedure until very recently. It seemed that every company, both formulators and package suppliers, had its own pet methods. Some used panels, others miniature containers, and others full-size containers. Some results may have been good, but standardization of techniques and the correct reading of results was defined nowhere. ASTM Subcommittee D10.24 on Industrial Plastic Containers, a subcommittee of ASTM Committee D-10 on Packaging, is working on the problem, but a finished usable paper seems far down the road.

To fill this gap, a paper (T4101-80) has been developed by the Chemical Packaging Committee of the Packaging Institute U.S.A. covering "Procedures for the Determination of Chemical Compatibility in Plastic Containers." This paper achieves standardized testing conditions, requires standard readouts, is simple enough for most formulators, and yet leaves the pass/fail decision to the packager, who must bear the responsibility for his recommendation. It is of particular note that the test conditions can be selected by the tester and represent a consolidation of all known test parameters and that the test is applicable to any plastic container, including bottles, drums, composites, and other forms in which the product receptacle is plastic. The pamphlet is available through the Packaging Institute U.S.A. in New York.

Trends in Packaging for Agchem Pesticides

Without getting into the closed system situation, this paper will discuss closures, plastic packagings, and, in particular, plastic drums.

The Mitre report[2] did a good job of pointing out the status of packages of 4 litres (1 gal) and over. It is apparent that the industry (for liquid containers) is following a trend toward sizes of 38 mm 400 for gallon jugs, 63 mm 400 for 10-litre (2½-gal) jugs, and 19.05 and 50.8 mm (¾ and 2-in.) National Pipe Thread (NPT) bungs for drums.

Frankly, we applaud this effort, though I am sure it has caused problems for others as well as the Pennwalt Corp. First, concerning the gallon jugs, the

[2] Mitre Corp. under contract to EPA, "Economic Analysis on Container Standardization," Oct. 1980.