PESTICIDE FORMULATIONS

Basic Principles of Formulation

LEO R. GARDNER

California Spray-Chemical Corp., Richmond, Calif.

Pesticide formulation consists of much more than a mere mixing of components, and an organized and systematic approach is essential. The first requirement is to determine fundamental properties, such as solubility, grindability, and mammalian toxicity. Next, field requirements must be surveyed for types of formulations needed, concentrations of active ingredients, and equipment. The laboratory process is based on experience, intuition, and ability to evaluate results critically. Some method must be set up for recording data. There is no standard approach, and a shifting line of attack must be used. After a suitable product has been developed in the laboratory, cost, equipment needed, and storage or shelf life must be considered. Package sizes and packaging problems must be evaluated and a plant batch made to see whether the formulation must be changed to fit the equipment available. The final step is extensive field testing under a variety of conditions to determine the best conditions of usage and to collect data needed for registration and labeling.

THE MERE MIXING OF COMPONENTS and laboratory testing of the resultant product by visual means no longer serve the need of pesticide product formulation. A systematic approach to the field is absolutely essential. employing all the modern tools of chemistry and physics.

Statistical methods should usually be employed in the interpretation of test results on new formulations. In general, it is essential to reproduce under laboratory or greenhouse conditions standard tests that will be indicative of field conditions, in order to speed up evaluation of pesticidal formulation developments. Particle size is important and optimum fineness for a given use must be ascertained.

The mere development of a good formula for one area and one type of application condition hardly meets the problem; the art of pesticidal formulations is so complex that one must establish a thorough scientific approach based on comprehensive records and test results, modify the approach in accordance with a knowledge of the art, and shift the line of attack as the occasion demands.

The complexity of pesticidal formulations is overwhelming. To a considerable degree each chemical used presents a new problem, and each technological change in the science of pest control presents new conditions.

Pesticides are normally prepared as one or more of the following types of formulations: oil-soluble concentrate, emulsive concentrate, emulsion, colloidal dispersion, sodium salt, amine, ester, wettable powder, dust concentrate, dust, air-milled powder, coarse powder, granular material, pelleted products, and certain other specialty types.

The properties of the chemical being formulated and the end use to which it will be put determine the type of formulation used. To add to the over-all complexities of this problem, no one chemical is certain to be used alone in modern pest control operations. As many as two to five different pesticides may be mixed in the same spray tank and these pesticides will vary, depending on the area and the purpose for which the product is used. This means that in developing any pesticidal formulation, consideration must be given to its performance alone, in all conceivable combinations, and in different types of water that may normally be encountered in the agricultural areas of the country, ranging from ice-cold snow water, which may be as pure as distilled water, to the hardest

÷

water in Texas, which may carry a large amount of clay.

Basic Principles

The solvents used for the liquid formulations must be nonphytotoxic to the most sensitive plant at the concentration used. This same degree of safety must carry through, whether the material is applied during an early tender growth period or during a late crop maturity period, at which time the foliage and fruit may have hardened sufficiently to withstand phytotoxic agents better. In addition, the solvents must be suitable for repeated application if more than one treatment is required. There must be no cumulative damage effect from the solvent.

Emulsifier In practically all liquid formulations, it is essential that the material be suitable for water dilution to form emulsions and for oil dilution if necessary. This requires that the emulsifiers be soluble in the solvent system as well as in kerosene or Diesel oil and in general the emulsifiers must perform in a uniform manner in the hardest possible water as well as in ice-cold distilled water. The emulsifier system must perform equally well at the minimum and maximum concentrations used, which may vary from 1 part of product to 99 parts of water to 20 parts of product and 80 parts of water. The emulsifier system must make a suitable dispersion of the product in water with either slight or strong agitation and it must not cause excessive foaminess. It must be such that the product can be added to the spray tank at practically any point during filling, as under field conditions the exact point of adding the material to the spray tank is commonly under poor control. The product must be stable to storage and not deteriorate in effectiveness in formulations where, for example, it may be exposed to dilute hydrochloric acid. The over-all system when once diluted with water must be sufficiently stable to permit discontinuance of agitation for 24 hours in case of a motor failure and then after a reasonably short time of agitation, be suitable for field application.

In formulations of pesticides, the formula must be capable of withstanding repeated freezing and thawing from 32° to 0° F. without adverse effect. The material must not break down if exposed to heat of 125° to 140° F. and sunlight for prolonged periods of time. If the material is to be packaged in glass, the product must be exposed to light and heat under normal packing conditions to determine varying rates of decomposition.

In general, the formulated pesticide must be stable for from 3 to 5 years in the specified package, depending on its end use—for certain products a storage life of 3 years would be ample, but for other products, 5 years would be the minimum.

Wettable powders must be conditioned to prevent lumpiness or fusion of the originally finely divided active agents. Many of the active agents have a tendency to re-form on standing under pressure with heat, which may completely nullify the value of fine grinding. Without adequate conditioning agents, such materials may be rendered less effective.

Systemic insecticides and fungicides must be formulated to give the maximum penetration of the active agent into leaf and plant. It is important in the case of systemics that the formulation have the minimum phytotoxic effect, because the objective is to obtain plant penetration through the foliage, bark, or root.

Insoluble fungicides must have extreme particle fineness—for example, an average particle size of 2 microns with no particles larger than 12 microns. Where contact and leaf coverage are essential, fineness of particles is extremely important, especially in the case of fungicides of the insoluble type, which must come in contact with the area to be effective.

Pesticide formulations of all types must be designed to deposit the active agent selectively on the plants and must provide adjuvants where possible to cause the particles to adhere to the plants, seeds, and other areas being treated. A quick-breaking oil emulsion might be cited as one example where proper formulation rendered a 2% oil spray as effective as a 5% stable oil emulsion.

Special Formulations

Specific pesticidal formulations must be developed for certain types of application equipment including, for example, airplanes, air atomizers, mist sprayers, concentrate ground sprayers, conventional power machines, and hand equipment, where the design of the equipment is such that ordinary formulations would be entirely unsuitable. Mist sprayers require a separate line of products. Certain other equipment can be used with a number of products, but frequently special formulations must be made for all types of equipment. Airplanes require different dust formulations in many instances than do ground dusters, because airplanes must have a dust that will not drift excessively on application, and they must have a dust formulation that will permit an effective pay loadthat is, a dense rather than fluffy dust and a dust with high concentration of active agents to be applied at low poundage per acre.

As a further complicating factor to the principle of pesticidal formulation, it is necessary to adjust products from year to year to meet the requirements of new application equipment and new methods of application.

Chemicals that partially or slowly decompose on dilution with water require special treatment and must be protected from water during application. By the development of an inverted emulsion with an oil protective film, it may be possible to retard product decomposition during application. Chemicals sensitive to light decomposition may be protected in part through the use of pigments. Chemicals that are more effective under conditions of greater heat may be colored with pigments to take advantage of heat absorption.

The diluents in product formulation should not cause build-up of secondary pests, such as red spider mites, or result in poor color of the crop. They should be free from corrosive or abrasive substances and from large particles that might damage delicate crops when applied as a very high pressure spray—for example, under 500 to 700 pounds pressure.

The formulation must be such that the treated crop can be rendered fit for human consumption. It might be possible to formulate a material and cause it to adhere to the plant as tenaciously as paint, but if the residue on the plant rendered the crop unfit for human consumption, the formulation would be useless. Product formulation must provide for an effective deposit and effective adhesion of the chemical on the plant and permit removal of the residue from the mature crop where necessary.

The formulation should take advantage of any possible synergistic combinations, such as might be obtained by combining special solvents or special active agents.

The product must be such that it can be packaged through conventional facilities and sold to normal marketing channels in standard package equipment.

Safety

Maximum safety to the operator and to the plant worker as well as to the user of pesticides is essential, and the formulation should be designed with this in view.

A number of specifications have been developed for product formulation, the most prominent of which are the World Health Organization (WHO) standards. In general, the major defect of the WHO formulations is that they are designed for use in hand equipment and are not suited for the modern spray equipment of the United States and Canada. In general, the WHO formulations are very well worked out for conditions in Europe and in certain other parts of the world where the material is applied with hand equipment and at a minimum gallonage per acre. Where such formulations are used under American conditions material is likely to be wasted, as a large percentage of the active agent runs off onto the ground because of excess wetting agents in the formulation. This demonstrates the difference in the basic principles of formulation due to the equipment through which the material is to be applied. In America the chemicals are available at an extremely low price and labor is costly, whereas in Europe the chemicals are very costly and labor is frequently available at an extremely low price. For this reason, the tendency in Europe is to design formulations for use in small hand equipment.

Conclusions

Pesticidal formulation consists of much more than developing a suitable mixture in the laboratory. It requires a complete understanding of the use and handling of the product under all types of conditions and must be backed up by sound laboratory testing methods, supplemented by extensive field testing. Product formulation is in part an art, but fortunately today all the precision tools of modern science are finding application here.

Received for review March 4, 1953. Accepted June 12, 1953. Presented before the Division of Agricultural and Food Chemistry, Symposium on the Formulation of Pesticides, at the 123rd Meeting of the AMERICAN CHEMICAL SOCI-ETY, Los Angeles, Calif.