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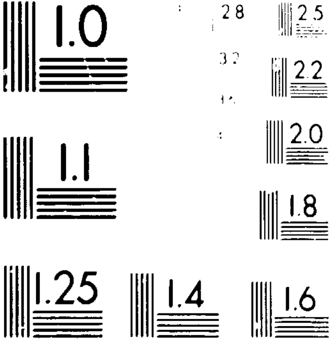

MICROCOPY RESOLUTION TEST CHART

Formulation of Pesticides in Developing Countries

UNITED NATIONS

FORMULATION OF PESTICIDES IN DEVELOPING COUNTRIES

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna

FORMULATION OF PESTICIDES IN DEVELOPING COUNTRIES

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Foreword

Many of the world's 4 billion people are seriously undernourished; some are in fact starving. A dramatic increase in agricultural production will be necessary in order to feed the population of 6 billion forecast for the end of the century. The pre- and post-harvest control of agricultural pests and diseases is a crucial factor in making that increase possible.

Pesticides, although representing only one element of what has become known as integrated pest management, are demonstrably effective in increasing crop yields and in preventing crop spoilage before and after harvest, as well as in public health programmes. Their continued and increasing use seems assured, provided due account is taken of the safety of the user, the consumer and the environment.

The industrial production of pesticidal active ingredients calls for investment in plant and human skills. Developing countries that have a basic chemical industry – and they are relatively few – are capable of undertaking large-scale pesticide production either on their own or with technological and financial assistance. Many of those without a basic chemical industry are at least formulating pesticides from imported active ingredients and packaging and labelling the finished products for their local markets. Developing countries that neither make nor formulate pesticides but rely on imports of finished products, could, with guidance and support, set up the required facilities. In issuing this manual, UNIDO is seeking to fulfil its mandate to offer advice and guidance on particular industrial subjects such as this.

The formulation of pesticides can range from the relatively straightforward production of dusts to the highly sophisticated manufacture of, for example, flowable products. But in all cases, there are specifications to meet and hazards to guard against, because pesticides are, by definition, toxic products. This manual provides authoritative information on such topics for officials in developing countries who must decide whether to establish pesticide formulation plants, those who become directly concerned with planning and operating them and those who must regulate the safe use of the plants' products.

If this manual helps to keep one waterway free from the pollution that could be caused by the careless disposal of pesticides or one worker safe from the hazards of handling pesticides in factory or field, it will have served a useful purpose. If, by encouraging the judicious formulation and use of pesticides in developing countries, it helps to increase crop production and promote public health, it will have achieved the noblest of its aims.

ABD-EL RAHMAN KHANE
Executive Director

Preface

As a result of discussions initiated in 1979 by the Industry Council for Development (ICD) with UNIDO and the Agency for International Development, Washington, D.C. (AID), the latter agreed to make a grant to ICD to enable the present book to be published by UNIDO.

A 1972 UNIDO publication[1] presented a collection of lectures given in 1969 and 1970 at a series of in-plant training programmes sponsored by UNIDO on the theme of industrial production and formulation of pesticides in developing countries.

By 1979, the earlier publication was both out of print and, in certain respects, somewhat out of date. Nevertheless, the theme was seen to be of growing importance.

The present volume, which revises the earlier subject matter, contains much new material, including chapters with an economic and commercial content. Particular stress is laid on aspects of safety to the plant operator, the user and the environment, and a chapter is devoted to labelling and packaging. A final chapter draws attention to the responsibility of officials to regulate the use of pesticides and suggests ways in which this might be done.

Thanks are due to the authors for their contributions and to those officials of AID, the International Labour Organisation, the Food and Agriculture Organization of the United Nations and the World Health Organization who gave their time to read material in draft and used their expertise to propose a number of additions and amendments to the text. With the reservation made concerning the opinions of the authors, the final text remains the responsibility of UNIDO.

The preparation of the book for publication has been in the hands of Alan Maier, Consultant to ICD and formerly a member of the Board of Imperial Chemical Industries, Plant Protection Division, Fernhurst, United Kingdom of Great Britain and Northern Ireland, and of Gunter Zweig, Visiting Scholar at the University of California, School of Public Health, Berkeley, California, United States of America, who was closely associated with the production of the 1972 publication.

[1] *Industrial Production and Formulation of Pesticides in Developing Countries*, vol. I, *General Principles and Formulation of Pesticides* (United Nations publication, Sales No. E.72.II.B.5).

EXPLANATORY NOTES

A full stop (.) is used to indicate decimals.

A comma (,) is used to distinguish thousands and millions.

The following forms have been used in tables:

Three dots (. . .) indicate that data are not available or are not separately reported.

A dash (–) indicates that the amount is nil or negligible.

Besides the common abbreviations, symbols and terms, the following have been used in this publication:

Organizations

AOAC	Association of Official Analytical Chemists
CIPAC	Collaborative International Pesticides Analytical Council
FAO	Food and Agriculture Organization of the United Nations
EPA	Environmental Protection Agency
NACA	National Agricultural Chemicals Association

Technical abbreviations

GLC	gas-liquid chromatography
HPLC	high-pressure liquid chromatography
IPM	integrated pest management
TLC	thin-layer chromatography
ULV	ultra-low volume

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Chapter *Page*

I. The role of pesticides in developing countries[1]

Gunter Zweig and Arnold L. Aspelin***

"... whoever could make two ears of corn or two blades of grass grow upon a spot of ground where only one grew before, would deserve better of mankind and do more essential service to his country than the whole race of politicians put together."

Jonathan Swift, *Gulliver's Travels*

Pesticides are a key input in meeting world food needs and a factor in overcoming the continuing periods of serious food shortage which have occurred since the Second World War. World food production on a per capita basis is slowing, particularly in developing countries, where lagging food production and starvation are endemic. The index of food production per capita in developing countries was the same in 1980 as in 1970 (index of 101 and 100, respectively) [1]. During the same period, food production in developed countries increased by about 11 per cent on a per capita basis. The rate of food production in developing countries is slowing in relation to population growth. The food production index per capita increased from 86 to 95 during the 1950s and from 96 to 101 during the 1960s, compared with no net increase during the 1970s [1].

To make matters worse, the United States of America, a major exporter of food to developing countries, is expected to be transformed from a nation of abundant supplies and excess capacity, as during the 1960s and 1970s, to one of gradually tightening supplies during the 1980s and 1990s [2].

The world capacity to produce food depends on the following factors: the availability and use of land and related inputs; the technology used to increase crops and, to a lesser extent, livestock yields; the weather; and the incentives, economic and other types, offered to producers.

This paper focuses on the role of pesticides in developing countries. Pesticides are a critical factor in increasing crop yields and preventing crop losses before and after harvest in both developed and developing countries. They also play a major

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** Benefits and Field Studies Division, Office of Pesticide Programs, Environmental Protection Agency, Washington, District of Columbia. The opinions expressed in this chapter are those of the authors and do not necessarily reflect the official policy of their employers.

[1] Parts of this chapter have appeared in "The world food problem", paper presented at the 171st meeting of the American Chemical Society, Chicago, Illinois, August 1975 (Dayton, Ohio, C. F. Kettering Foundation, October 1976), pp. 122-143.

part in public health programmes. Consideration will be given to the potential benefits and problems of improved pesticide use in the effort to meet world food needs, and the role of pesticides in public health programmes.

Pesticides: a partial answer to world food needs

A detailed study published in 1967 by Cramer [3] estimated that pests destroy on the average one third of world potential crop production each year. There appears to have been no comparable update of crop losses world-wide since then. The breakdown of estimated losses is as follows:

Cause of annual crop losses	*Percentage of total production*
Insects	12.3
Diseases	11.8
Weeds	9.7
Total	33.8

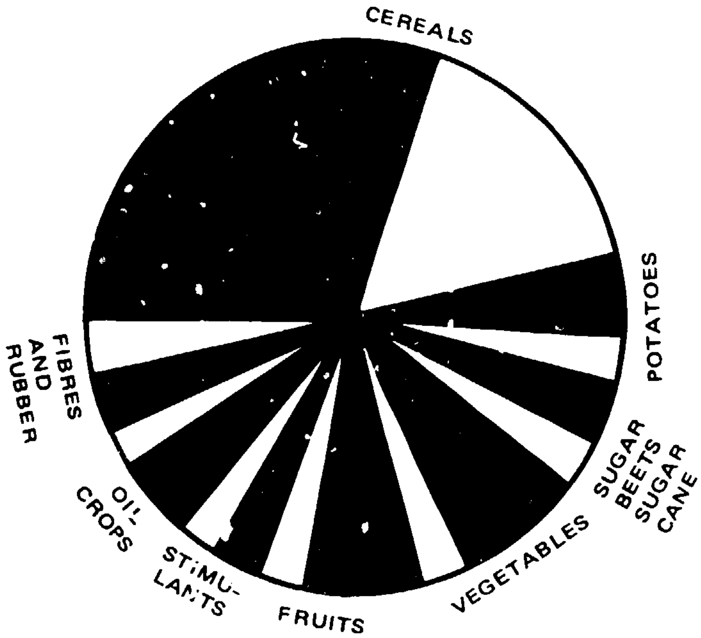
As an example of losses due to crop damage by insects alone, Smith and Calver [4] have reviewed reported rice crop losses. Rice is one of the most important food crops in the world, providing the staple diet of more than 2 billion people. In 1972, there were approximately 131 million ha of land planted with rice and yielding almost 300 million t of crops. Cramer [3] estimated that insect pests destroy over one third of the total rice crop in South-East Asia. The overall extent of losses caused by insects has been demonstrated in experiments conducted at the International Rice Research Institute (IRRI), which showed that plots without insecticide applications yielded only about one-half of the rice crop of a plot treated with the full range of insecticides (3 t/ha as compared with 5.7 t/ha).

The data contained in table 1 show that rather substantial crop losses occur in all regions of the world, including those where pesticides are most widely used. North and Central America, with an annual loss of 28.7 per cent for all pests, rank behind Europe with 25 per cent, and Oceania with 27.9 per cent. Africa and Asia have the highest losses, more than 40 per cent annually. Figure I graphically illustrates pest losses for selected agricultural crops.

TABLE 1. WORLD CROP LOSSES CAUSED BY INSECTS, DISEASES AND WEEDS, AS A PERCENTAGE OF POTENTIAL PRODUCTION [3]

Region	*Insects*	*Diseases*	*Weeds*	*Total*
Africa	13.0	12.9	15.7	41.6
Asia	20.7	11.3	11.3	43.3
Central and North America	9.4	11.3	8.0	28.7
China and Union of Soviet Socialist Republics	10.5	9.1	10.1	29.7
Europe	5.1	13.1	6.8	25.0
Oceania	7.0	12.6	8.3	27.9
South America	10.0	15.2	7.8	33.0
World	12.3	11.8	9.7	33.8

Figure I. Production and pest losses for different crops[a] [3]



[a] Unshaded areas represent pest losses.

The data indicate that pesticide use does not necessarily eliminate pest losses, especially when losses in countries of high and low pesticide use are compared. Pesticides can contribute to alleviating the food problem, but it appears inevitable that some loss of food crops due to insects, disease and weeds will still occur.

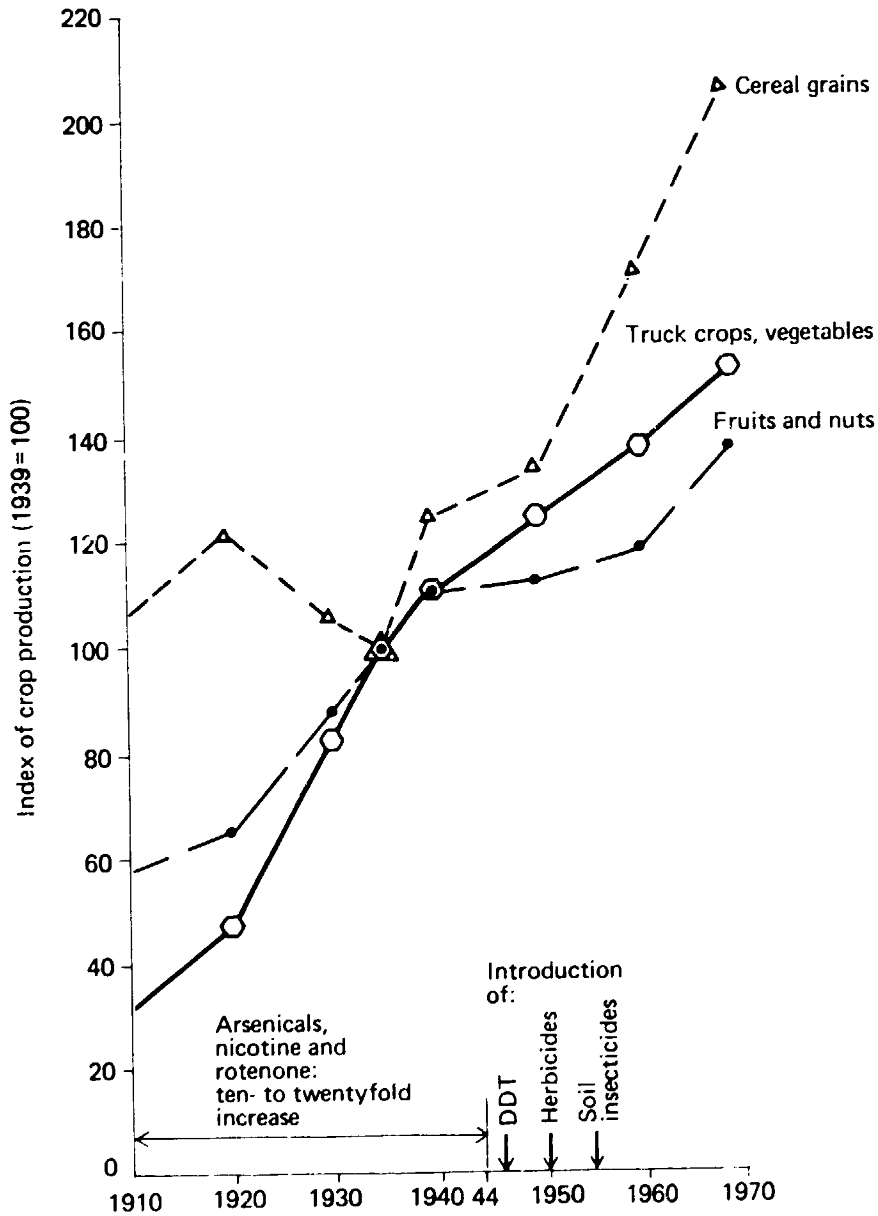
Cramer [3] stated in 1967[2] and it is still valid in 1982 – that "it would, of course, be folly to believe that the problem of supplying sufficient food for the world population could be solved simply by raising the expenditure on pesticides". In 1980, $ 10-12 billion were being spent on pesticides world-wide [5, 6]; of this total, insecticides accounted for 34 per cent, herbicides 42 per cent and the remaining 24 per cent was for fungicides, rodenticides and other minor pesticides. Crop pest losses in 1967 were estimated, world-wide, to be in the range of $ 70-90 billion, which were far in excess of expenditures for pesticides at that time. No doubt there is potential for expanded use of pesticides in crop protection, but it appears that much of the current losses are below the economic thresholds for treatment, that is, cost of treatment exceeds the value of losses to be prevented.

Total pest damage can be expected in case of an epidemic, although much of the damage might be prevented by the judicious use of pesticides. Data assembled in 1982 by the United Nations Food and Agriculture Organization (FAO) [7] indicate that very favourable benefit-cost ratios can be achieved by the use of pesticides in Africa, Latin America and Asia. For example, the benefit-cost ratio for treating maize against stem borers in central Africa was found to be 14. Generally, pesticide benefit-cost ratios in the United States have been calculated to be in the range of 2/1 to 4/1.

[2] But see also the chapter by A. V. Adam in *Pesticides and Human Welfare*, D. L. Gunn and J. G. R. Stevens, eds. (Oxford, Oxford University Press, 1976).

The increase in food supply in developing countries came mostly from expanded acreage rather than greater per-acre yields as recently as the 1960s [8]. Even in India, 60 per cent of additional food was a result of expanded acreage. This contrasts sharply with the situation in the United States, where food production has tripled since 1940, but agricultural acreage declined by about one fifth. At the same time, less than half the world's land which could grow food crops (1.4 billion ha out of 3.2 billion ha) is being used [9]. Much of the uncultivated land, however, is the least productive and requires many social, technical, institutional, and related developments in order to be brought into production.

Figure II. Crop production and pesticide usage [10]



Benefit of pesticides in food production

Statistics [10] show that pesticides have reduced the damage caused by the codling moth in apples and increased the yield of apples and peaches. A correlation has also been found to exist between crop yields during the past 65 years and the increasing use of pesticides, although it appears premature to conclude that a major part of the benefits is due solely to the increasing use of pesticides (see figure II). Another example is cited [10, 11] of an interaction between two inputs – fertilizer and pesticides. When tomatoes were grown in a commercial field separately treated with fungicides to control early blight and with fertilizer, the fertilizer treatment alone led to bigger crop yields. The dollar yield was more dramatically improved by applying both treatments to produce a higher-quality tomato (see table 2).

TABLE 2. YIELD AND CASH RETURN FOR TOMATOES WITH SEVERE EARLY BLIGHT [10, 11]

Treatment	*Yield (tons per hectare)*	*Cash return (US dollars per hectare)*
None (control)	18.76	316.3
Pesticide	26.54	553.5
Fertilizer	34.03	652.4
Pesticide and fertilizer	47.49	1 146.6

TABLE 3. ACREAGE OF MAJOR FIELD CROPS, HAY, AND PASTURE AND RANGELAND GROWN AND TREATED WITH PESTICIDES IN THE UNITED STATES IN 1976[a] [12]

Crop	*Acreage grown[b] (millions of hectares)*	*Percentage of acreage treated with pesticides*				
		Herbicides	*Insecticides*	*Fungicides*	*Other pesticides[c]*	*Any pesticides*
Alfalfa	10.8	3	13	...	...	14
Corn	34	90	38	1	1	92
Cotton	4.7	84	60	9	34	95
Pasture and rangeland[d]	197.6	1	–[d]	...	...	2
Peanuts	0.6	93	55	76	6	99
Rice	1	83	11	...	...	83
Sorghum	7.6	51	27	...	–[e]	58
Soy beans	20.6	88	7	3	1	90
Tobacco	0.4	55	76	30	86	97
Wheat	32.5	38	14	1	–[e]	48
Other grains[f]	12	35	5	2	...	41
Other hay and forage	13.9	2	2	...	...	4
Total acreage	335.7	22	9	1	1	24
Total acreage excluding pasture and rangeland	138.1	56	18	2	2	61

[a] Excluding pesticides used for seed treatment and stored crops and in farmyards and gardens.
[b] Estimate based on *Crop Production*, United States Department of Agriculture, CrPr 2-1 (77), 17 January 1977.
[c] Other pesticides include defoliants, desiccants, growth regulators and miticides.
[d] Estimate based on the *1974 Census of Agriculture*.
[e] Less than 0.5 per cent.
[f] Includes oats, rye and barley.

The interaction of various factors affecting crop yields may be further illustrated by comparing the overall yield of maize grown from 1930 to 1970 [9] with fertilizer tonnage and with the percentage of acreage in hybrids and acreage treated with pesticides (see figures III and IV). It seems clear that the maize yield is improved by all the factors in the modernization of farm practices, but it is almost impossible to single out any one determinant factor.

Use of pesticides on major crops in the United States

As may be seen from table 3, less than one fifth (18 per cent in 1976) of United States food and feed crops are treated with insecticides. Small grains and soy beans are seldom treated with insecticides [12], and about two thirds of the maize and three quarters of the sorghum acreage are not treated with insecticides, which, on a relative basis, seem to be used to a lesser extent than herbicides. While only one fifth of United States cropland is treated with insecticides, more than one half of cropland is treated with herbicides (excluding hay and pasture).

Figure III. Comparison of maize yield and use of fertilizer [10]

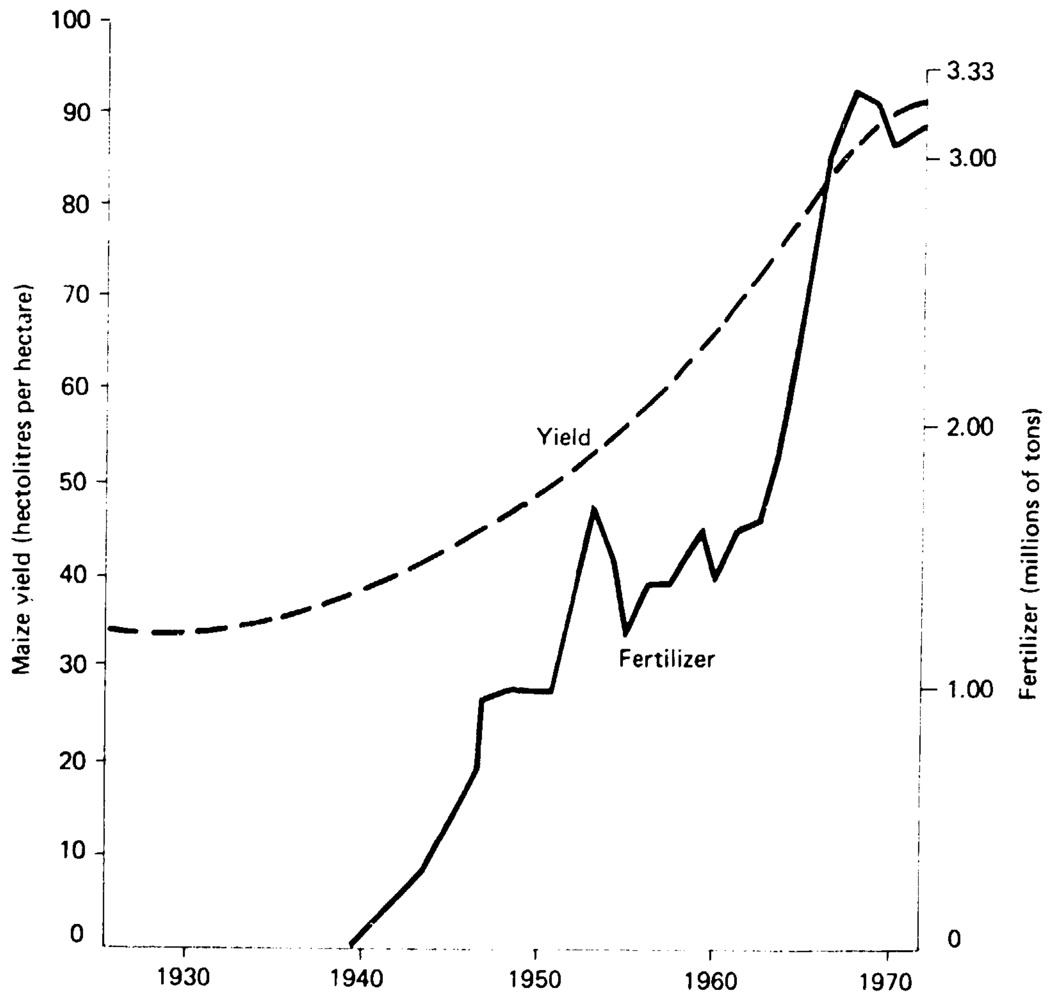
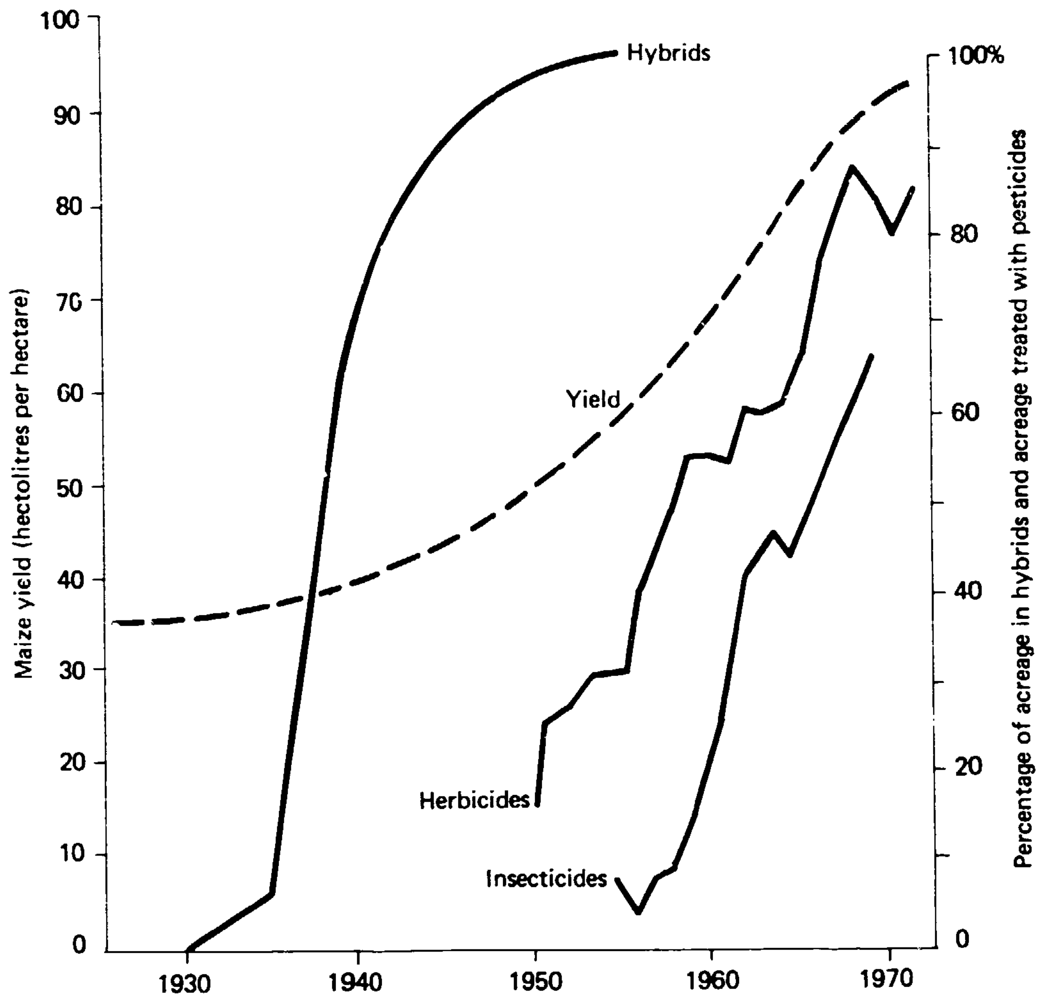


Figure IV. Comparison of maize yield with use of hybrid seed and pesticides [10]



Insecticides are used on about one half of United States cotton acreage and about three quarters of tobacco acreage. Use of insecticides on non-food crops such as tobacco and cotton makes more land and other resources available for the production of food crops.

Maize and soy beans receive the widest herbicide uses (90 and 88 per cent respectively of the 1976 acreage), while only about two fifths of small grains are treated with herbicides. Pastureland is seldom treated (2 per cent). About one quarter of United States crop acreage is treated with herbicides; by excluding pasture treatment, this figure jumps to 61 per cent.

Herbicides greatly add to the productivity of agricultural crops by reducing the competition from weeds for water and soil nutrients and also by saving manual labour in the control of weeds. The production of food and feed crops in the United States is increasingly dependent on the use of herbicides, as shown by the rapid rate of increase of herbicide sales in recent years. This may not be necessarily the case in developing countries, where manual labour for farm work is amply available. Moreover, there is evidence that pesticides are sometimes overused, as discussed below.

Efficient and safe use of pesticides

There has been a tendency in modern farm management to make excessive use of pesticides as a prophylactic treatment without a careful survey of actual and potential pest infestation. Such practices may lead to pest resistance or even a breakdown in cropping patterns when it is no longer economically feasible to control resistant pests.

Over the years, pest resistance to the organochlorine insecticides has developed world-wide, helped to some extent by large and repeated applications of the insecticides. In cotton production such problems have led to the use of alternatives and more effective insecticides and to integrated pest management strategies, where pest populations are carefully studied to determine if and when treatment is justified. These treatments include both chemical and non-chemical methods Such strategies have sometimes led to substantial reductions in pesticide use without loss in output.

The following estimate of excess pesticide use in the United States was made in a 1975 study commissioned by the United States Environmental Protection Agency [13].

Product	*Excess pesticide use (percentage)*
Corn	50
Sorghum	50-60
Apples	20-30

Overuse of pesticides is costly in economic terms and may add to the environmental burden without apparent economic benefits. The above-mentioned study also indicated that excessive use of herbicides and fungicides, on the other hand, was small or negligible for the three crops studied.

Similar problems may arise in developing countries, where pest resistance may ultimately result in heavy losses in crops intended for local consumption or export. Steps are therefore being taken to introduce a system of pest management which does not solely rely on intensive pesticide application [4]. At the same time, it would be a mistake to place too high and too early an expectation of success on purely biological and cultural methods of pest management. The term integrated pest management (IPM) should certainly not be taken to exclude the use of chemical pesticides, as has sometimes been suggested. To place the matter into a more realistic perspective, it may be worth quoting a United States government publication: "... Some think IPM will do away with pesticides. This is not the case. Pesticides will be around for a long time and are essential to producing the food and fiber this country needs. For most crops, pests cannot be managed without the use of highly effective pesticides." [14] Perhaps it would not be inappropriate to suggest that the shorthand term IPM might stand for intelligent pest management.

Developing countries need access to pesticides to improve their crop production. It is forecast that by the end of the 1980s the annual consumption of pesticides in developing countries will total 11 billion dollars [5], as reflected in table 4. This is based upon the 1980 level with an annual 10 per cent estimated increase in dollar expenditures. Technical training must therefore be provided to ensure their effective application and safe use. Programmes devoted to these goals have been sponsored by the United States Agency for International Development.

TABLE 4. WORLD-WIDE SALES OF PESTICIDES: PAST AND PRESENT FARM PRICE LEVELS AND FUTURE PROJECTIONS [5]

(Billions of US dollars)

Region	*1972*	*1980*	*1990*[a]
Eastern Europe	0.27	1.32	6.00
Japan	0.30	1.32	4.00
North America	1.08	3.84	16.00
Western Europe	0 69	3.00	13.00
Rest of world	0.66	2.52	11.00
Total	3.00	12.00	50.00

[a] 1990 estimates are based on 1980 levels with approximately 10 per cent annual inflation.

Probably the most important theme of the pesticide legislation adopted by the United States Government in 1972 was that a registered pesticide, when properly used, will not generally cause unreasonable adverse effects on the environment. Adverse effects have been interpreted to include human health hazards, both to the workers applying the pesticides and to the general public, and effects on endangered wildlife species. Bearing in mind the potential hazards of pesticides, levels of pesticide usage may vary from country to country depending on national goals and needs. For example, crop protection in some developing countries, where the per capita outlay for food may be as high as 80 to 90 per cent for persons on subsistence, should be given high priority. Serious consideration should also be given to the pesticide requirements of agricultural crops intended for export and subject to the pesticide regulations of the importing country. An unintended effect of United States regulatory action is that it may alter pesticide usage in other countries. United States decisions to suspend uses of several pesticides in the United States in the 1970s may have prompted similar action by other countries.

The world food situation is aggravated by vast disparities among countries in the ability to produce and pay for food, to purchase and use modern capital-intensive inputs, and to exploit modern production technology. Despite the green revolution, food production in developing countries has barely kept pace with population, and in Africa has actually fallen behind. Those countries are therefore faced with the prospect of importing food at high prices, using scarce foreign exchange resources which might have other priority uses. Present trends suggest that expanding food production will be necessary to improve the living standards of their people.

The prospects for increasing crop yields in developing countries are good if the record of increasing yields in developed countries may be taken as a basis of comparison. However, in order to exploit new technology, farmers in developing countries will need an entire production and marketing package, including improved crop varieties, fertilizers, pesticides, methods of cultivation, crop insurance, financing and training. Pesticides are highly productive inputs necessary to protect the farmer who makes heavy capital investments in his crops. They may be less important for the less intensive agriculture often found in developing countries.

Basic and applied research on crop biology and extension education for farmers are of prime importance in improving food production in both developed and developing countries.

Incentives to the producer are extremely important in stimulating food production, especially where new and expensive technology is to be used. The producer must have a market incentive in the form of a favourable price. Otherwise, he will produce only for his own needs.

Recognition of the important role of pesticides in contributing to the solution of world food problems led to the adoption of a resolution on pesticides at the World Food Conference held in November 1974. The resolution called on FAO and other United Nations bodies to organize consultations between representatives of member Governments and industry, with a view to recommending ways and means to give effect to the provisions of the resolution [15].

The use of pesticides in public health programmes has historically been of great importance in the control of vector-borne diseases, especially in the campaign against malaria. Indeed, it has been suggested [16] that about 90 per cent of all insecticides used in public health in developing countries is for the control of malaria.

Public health requirements of pesticides probably account for only about 10 per cent by weight of the total pesticide tonnage. Nevertheless, the tonnage used may still be a significant part of the total demand for pesticides in a given country. In forecasting a possible total market for pesticides, those who plan or operate formulation plants should be aware of the contribution that pesticide requirements for public health could make to achieving the fullest and most productive use of installed capacity.

An important difference in the properties required of public health insecticides as opposed to those used in agriculture should be noted. The lack of biodegradability and, therefore, the persistence of the organochlorine-based insecticides, especially DDT and BHC, make them under certain climates unacceptable for agriculture on environmental grounds because of the build-up of residues in soils and in the food-chain. The same property of persistence makes them particularly useful and acceptable for public health programmes. Indeed, it is forecast [16][3] that no less than 30,000 t of DDT and 18,000 t of BHC will be required in 1984 by 103 developing countries for their national vector control programmes. This tonnage of active ingredient represents no less than 74 per cent of the total forecast for that year, compared with 28,000 t (72 per cent) in 1979.

The persistence and safety of organochlorine compounds, especially when sprayed on the inside walls of dwellings, coupled with their relative cheapness, makes them so valuable in public health programmes, primarily in developing countries.

While historically the organochlorine compounds have an unparalleled record of achievement in public health, recent research work has proposed a

[3] Table 12, p. 94.

correlation between persistence and resistance. Though this remains unproven, it strengthens the need for continued research into the formulation of new insecticides, including biological ones. The establishment of cottage industries based on fermentation products of the type of *bacillus thuringensis* has even been suggested.

On the other hand, when pesticide spraying is required on waterways, for example in the control of vector-borne diseases such as onchocerciasis and filariasis, great care must be taken not to pollute the water, especially when it is required for drinking purposes.

The importance of the combination of pesticides for agriculture and public health has been noted above in the context of formulation plant operation. But there is a further sense in which both are linked. Agriculture in developing countries is and, for good socio-economic reasons, should be labour-intensive. Quite apart from general humanitarian considerations, safeguarding the health of the farmer and his family is of major importance for ensuring the productivity of the land and a further reason why the continued and increasing use of pesticides in public health programmes can be foreseen.

Summary

In summary, then, the judicious use of pesticides in developing countries is likely to be an important factor in increasing food production and in public health programmes. Preferably, developing countries with limited foreign exchange would produce an increasing volume of pesticides in locally established formulation plants. The impression should not be given that pesticides are the only factor in increasing crop yield, or that pesticides are the only means of reducing crop losses caused by insects, weeds and plant diseases. However, the careful use of pesticides for both agriculture and public health is, without any doubt, to be recommended. Such use should bring substantial economic and social benefits to developing countries in future. Developing countries, in the application of modern chemical technology, should also be mindful of the need for information and training to exploit the new technology in the most socially cost-effective way.

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II. Principles of pesticide formulation*

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Pesticide formulation is the process of transforming a pesticidal chemical into a product which can be applied by practical methods to permit its effective, safe and economical use. It is not the intent in this chapter to present a compendium of recipes and cookbook procedures whereby different types of formulations can be made. That would be outside the scope of the present publication and totally misleading. There must be a practical and realistic objective and procedure for developing any pesticide formulation. A presentation of the principles and guidelines of pesticide technology will be of practical use to those engaged in the development, manufacture, testing and use of pesticides.

The material presented here is the result of efforts by many workers in Government and private industry. Although synthetic organic pesticides have attained spectacular success since their introduction in the middle 1940s, all specialists in pesticide formulation recognize that the technology is still highly empirical and primitive.

The pesticide formulation

Definitions

A pesticide formulation is a physical mixture of one or more biologically active chemicals with inert ingredients which provides effective and economic control of pests. Because the great majority of all pesticidal chemicals require formulation to be used economically and effectively, the term pesticide throughout this chapter will refer to the finished product rather than to the active ingredient itself. Indeed, to the majority of the users of pesticides, the term pesticide is accepted as the total form of the finished product. Pesticide formulation is the art and technology of developing a formulation of a pesticide. A pesticide formulation plant is a manufacturing facility in which pesticidal ingredients are formulated into a final product.

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Pesticide formulations are classified into two general types according to physical form, namely liquid and dry formulations. There are a number of varying types of formulations within each general classification. A description of these types and their general purposes follows.

Liquid formulation types

Oil concentrates

Oil concentrates are liquid formulations containing, preferably, a high concentration of active ingredients. They are used undiluted for ultra-low volume (ULV) applications or diluted to a convenient low concentration using an inexpensive hydrocarbon solvent such as fuel oil or diesel oil as a diluent.

The concentration may be expressed either in terms of weight of active ingredient per unit volume of concentrate or in terms of per cent by weight of active ingredient. It is necessary that the concentrate be miscible upon minimum agitation with the diluent to be used. Aromatic hydrocarbons such as xylene or heavy aromatic naphtha are generally used as solvents for the active ingredients in oil concentrates. There are pesticide chemicals whose solubility in these aromatics is so limited that they are impractical as solvents. To overcome this limitation, it is necessary to use a more powerful solvent, for example, isopropanol or cyclohexanone. The necessary qualification for the use of any of these polar solvents is that the concentrate is miscible with the diluent oil which will be used.

Emulsifiable concentrates

Emulsifiable concentrates are similar to the oil concentrates, with the exception that they contain a surfactant or emulsifier to permit the dilution of the concentrate with water for practical application. For best results, the solvent system must be immiscible with water. The most generally used solvents are the xylene type, the heavy aromatic naphtha type or, occasionally when the solubility of the pesticidal chemical is sufficient, aliphatics of the kerosene range.

Because of their convenience for the user, emulsifiable concentrates may be considered the most popular form in which pesticide formulations are used. They are expected to perform well under a wide variety of conditions and to withstand a number of extremes of packaging and storage. Although the ideal emulsifiable concentrate is frequently sought, it is seldom attained. It will be shown that either compromises must be made or other useful alternative formulation types accepted as more practical for certain pesticidal chemicals. Functionally, emulsifiable concentrates must disperse spontaneously in waters of all hardness and with the aid of gentle agitation remain uniformly dispersed throughout the spraying period.

Aqueous concentrates

Aqueous concentrates are concentrates of pesticidal chemicals dissolved in water. The most frequently encountered pesticidal type found in this form is the salt of a herbicidal acid. Because the herbicidal acid is the nominal active ingredient, concentrations are generally expressed in terms of amount of acid-equivalent per unit volume. Since these active ingredients are soluble in water, there are generally no problems of miscibility, dispersibility or suspendibility. The exception occurs when magnesium, calcium or iron of natural waters used for dilution may cause an insoluble precipitate; remedies do, however, exist for this situation.

Oil solutions

Oil solutions are ready-to-use formulations containing, generally, a low-odour, colourless solvent of the kerosene type and a pesticide chemical in low concentration. The concentration of active ingredient is usually under 5 per cent by weight. Oil solutions of insecticides are generally used for household or institutional insect control. In addition to low odour, these formulations must preferably be non-staining and have a high flash-point to minimize the fire hazard.

Invert emulsifiable concentrates

Invert emulsifiable concentrates are distinguished from the normal emulsifiable concentrates by the fact that their dilution with water results in an emulsion in which the external or continuous phase of the emulsion is the oil portion, whereas the internal or discontinuous phase of the emulsion is water. These concentrates are used principally in the formulation of oil-soluble herbicidal esters. The solvent is usually an oil having relatively low vapour pressure. Field dilution is generally at a much lower ratio than that used for conventional emulsifiable concentrates and often less than ten parts of water to one part of concentrate by volume. The distinguishing feature of invert emulsions is that they form significantly larger droplets than conventional emulsifiable concentrates when emitted from special application equipment. Because the external phase contains an oil of relatively low vapour pressure, evaporation of the continuous phase is minimized. As a result, there is no reduction in the size of the droplet from the time it emerges from the application equipment until it impinges on the target. The probability of drift of the particle during its fall through the air is, therefore, greatly reduced.

Dry formulation types

The important dry formulation types include dust bases or concentrates, water-dispersible powders, dusts, granules, pellets, flowables, dispersible granules and microcapsules. Dry formulations which may be mixed with water for application include water-dispersible powders, flowables, dispersible granules or microcapsules. Dusts and granules are applied dry. Dust concentrates are mixed with locally available low-cost diluents at a regional formulating plant. In general, the packaging of dry formulations is considered to be less of a problem than packaging of liquid formulations. The characteristic difference of the dry formulations are described below.

Dust bases or concentrates

Dust bases or dust concentrates are dry, free-flowing powders containing a high concentration of active ingredients that varies generally from 25 to 75 per cent. Such products are seldom applied in this concentrated form. They are usually diluted or cut back to a practical concentration with a suitable inert material for final application in the field. Pesticide-fertilizer mixtures are often made by mixing the dust concentrate with the dry fertilizer. If granular fertilizers are being mixed with dust bases, a sticker is often necessary to prevent the segregation of the fine particles of the pesticide base which usually are below 200 mesh (74 µm) size.

Water-dispersible powders

Water-dispersible powders are similar to dust bases except that they are formulated for dilution with water into a final spray. The quality of water-dispersible powders is judged by the rapidity of wetting when mixed with water and suspendibility in water when mixed in practical dilutions for field application. The speed of wetting can be increased by the proper choice of wetting agents which reduce the interfacial tension between the particles and the water. Good suspendibility is attained by reducing the particle size, preferably to below 325 mesh (44 µm). Surfactants of the dispersant class are generally added to water-dispersible powder as part of the regular formulation to prevent the agglomeration of particles and, in turn, decrease the rate of sedimentation, which is a function of particle size. Exceptionally fine particle size which further improves suspendibility is sometimes attained by air-milling the product to a particle size of 10 µm or less. Water-dispersible powders are frequently used for the slurry treatment of seeds as well as in a variety of spraying techniques.

Dusts

Dusts are very finely powdered, dry pesticides. They are formulated to field strength which may vary from 1 to 10 per cent active ingredient depending upon the potency of the pesticide and the rate of application. Dusts must be free-flowing so that they can be accurately metered in application equipment. Particle size may vary, although it is usually under 200 mesh (74 µm). For aerial application of dusts, the avoidance of drift is important; therefore, a moderate particle size and uniform distribution are necessary. Dust formulations applied by air or ground equipment are extremely advantageous when treating mature crops with dense foliage. This advantage is the inherent property of billowing around the foliage and covering the undersides of the leaves and the stems of the plant.

Granules

Granular pesticides are distinguished from powdered pesticides according to mesh size range. It is generally accepted that a granular pesticide is a product which is limited to a range of from 4 mesh (United States standard sieve series) to 80 mesh. For any given material (for example, a product labelled 30/60), at least 90 per cent of the finished product must be within this specified mesh range, and the remaining 10 per cent may be distributed on either side of the specified mesh sizes. The presence of fines which may become airborne by a crosswind during application is generally considered to be objectionable in a granular product.

To be useful, granular pesticides must be non-caking during storage. To permit accurate application in metered application equipment, the granules must be free-flowing. Depending upon the field requirements, the granules may have fast or slow disintegration characteristics in the presence of moisture. The disintegration characteristics of granules after entering the soil have a direct bearing on the release rate of the pesticides.

The concentration of active ingredient in granular pesticides may vary from as little as 1 per cent to as high as 42 per cent depending upon the properties of the active ingredients, the characteristics of the carrier or upon other factors such as the potency of the insecticide and the desired rate of application of the finished product.

Flowables

Flowable formulations have also been identified as suspension concentrates or water-dispersible concentrates. They consist of a fine dispersion of a water-insoluble pesticide in water. The particle size of the particulate is generally of a narrow size distribution in the range of 2-3 μm. Flowables generally contain greater than 40 per cent solids by weight per unit volume of dispersion. They are designed to be very stable with little sedimentation and are easily dispersed in additional water. Stabilization of the dispersion is effected by a combination of a water-soluble polyelectrolyte and a non-ionic surface agent. The flowable formulation may be used directly, as in a ULV-type application, or diluted with appropriate amounts of water.

Pellets

Pesticide pellets are dry pesticide formulations in which the particle size is larger than that specified for granular pesticide, for example, greater than 4 mesh. There are no established maximum sizes for pellets but, in practice, diameters may be as large as 0.6 cm and possibly 1.3 cm. Pellets are generally formed by mixing the active ingredient with a suitable inert ingredient plus a binder, if necessary. The mixing is followed by pan-granulating to the desired size or extruding (and crushing, as required) to the desired size. Concentrations of active ingredients may range from a fraction of a per cent as in the case of baits, in which an attractant, inert ingredient is used, to as high as 20 or 25 per cent, if fertilizer is added.

Dispersible granules

Dispersible granules are formed from finely divided solid materials that are compressed into granules during the compounding and manufacturing process. When placed in water, the granules tend to swell and break up into the original finely divided particles. The requirements of a good dispersible granule formulation include: good dispersibility, good break-up to particles that will pass screens and nozzles during the spraying operation and a stability of physical properties during temperature cycling and aging processes. The particular advantages of dispersible granules include a high pesticide concentration per unit weight of the product, relatively dust-free formulation and a comparatively large unit sales package.

Other formulation types

A number of other possible formulation types are used for special purposes. These are better classified by themselves rather than with the familiar types because of their unique physical form or their unusual application. Both liquid and dry formulation types are encountered.

Aerosols

Since their development for insect control during the early years of the Second World War, aerosol insecticides have become a familiar form of pesticide formulation. As generally understood, aerosols are solutions of an active ingredient in a suitable solvent plus a propellant which is a gas dissolved in the insecticide solution or contained under pressure within the aerosol dispenser. The type of spray pattern and particle size of the spray are controlled by the design of the nozzle which is used and by the pressure in the container which forces the concentrate through the nozzle. The internal pressure is determined by the properties of the propellant gas. There are many different approaches to the formulation and packaging of an aerosol pesticide product including both non-aqueous and aqueous solvent systems. In formulating an aerosol it may be wise to check local laws and regulations regarding propellants allowed to be used. Many countries ban the use of fluorinated hydrocarbon propellants believing that excess use tends to deplete stratospheric ozone layers.

Seed dressings

Seed dressings may be either a liquid or a dry type: and there are variations within each type. Two of the most important requirements of a seed dressing are that the seed dressing must not interfere with the plantability of the seed; and that the seed dressing must not diminish the viability of the seed. In addition, it is most desirable, however seldom achieved, that the seed dressing is non-toxic and does not constitute an adulteration if the seed is later to be fed to livestock. Seed dressings must often contain a dye which colours the seed to indicate the chemical treatment. Certain seed dressings have been developed in dry concentrate form for the addition to seed grains in a planter box as controls of insects or diseases from the time of planting until after the seed has germinated. Water-dispersible powder types of seed-treating formulations are used for the slurry treatment of feed as well as liquid types of certain emulsifiable concentrates and water-dispersible concentrates. The concentration of the active ingredient in seed-dressing formulations follows the same rules and limitations as other liquid and dry formulations.

Poison baits

Poison baits are special formulations designed to attract and kill certain types of foraging insects and rodents. Poison baits are designed preferentially to lure and poison these pests near or in their natural environment. They are frequently used as a barrier to intercept the migration of insects such as locusts into grain fields. In orchards, rodenticide baits are placed around the tree trunks to prevent their attack by rats. Another form of bait is used in the so-called bait trap for the control of Japanese beetles in orchards or gardens and for the control of the Mediterranean fruit fly in citrus groves. Rodenticide baits in pellet or meal form are widely used for municipal and residential rat control and for the control of mice and rats in farm buildings and grain storage areas.

Poison baits have numerous physical forms and composition. Where applicable, they have a distinct advantage in agricultural pest control by effectively reducing damage to agricultural crops by insects and rodents without the hazard of leaving a residue on the plant or crop to be protected.

Capsulated formulations

The encapsulation of pesticides is a relatively new development with the principal objective of providing a controlled release rate for specific types of pesticide action. An encapsulated pesticide is essentially a very small mass of a pesticidal composition surrounded by a continuous shell or envelope of a coating material. Two factors to be considered in the selection of the coating material are the chemical inertness of the material toward the active ingredient and the ability of the material to dissolve or disintegrate at a controlled rate by the action of certain environmental factors such as moisture or soil micro-organisms. Particle diameter varies from a few μm to 0.3 cm or larger. Theoretically, the concentration of the active ingredient contained in the shell wall varies from a fraction of 1 per cent up to and approaching a 100 per cent active ingredient. Although the shell thickness may be very small in comparison to the diameter, the percentage of the encapsulating shell material increases as the particle size decreases. Similarly, the cost of an encapsulated pesticide ingredient varies inversely with the per cent of concentration.

Functional properties and characteristics

The formulation of pesticides is a property-oriented technology. To the formulation chemist, the physical properties of the pesticidal chemicals are of greater concern than their chemical structure or their biological activities.

Active ingredients

The active ingredients are those portions of a formulation which possess biological properties. All other ingredients in the formulation are used to facilitate the application of the active ingredients to the desired target. For a given type of formulation, the physical properties of the active ingredients limit the choice of formulation ingredients.

Physical state

The physical state of a pesticidal chemical defines the form in which it occurs under normal ambient temperature conditions of shipping and storage. The physical state provides the first clue to the preferred method of handling the technical pesticidal chemical in the formulation process.

Pesticidal chemicals in their technical form may be encountered as liquids, fine crystals, powdered flakes, solid cakes or small lumps. The fine crystalline or powdered material is generally preferred when dust bases or wettable powders are to be made by dry-blending followed by grinding. For the preparation of liquid concentrates, any form of pesticide may be used. Heat is generally applied in dissolving solid pesticide for liquid formulations to increase the rate of solution. Because spray impregnation is the simplest and most effective way of preparing granular pesticides, the solid pesticidal chemicals are generally dissolved in a solvent to facilitate spraying. Some low-melting solids, however, are heated sufficiently above the melting point and sprayed through heated lines and nozzles to obtain proper spray characteristics.

Some technical pesticidal chemicals in their normal state are waxy or semi-solids and are most suitably packaged in thin-gauge metal containers or special leakproof, lined or coated fibre drums. Pesticidal chemicals are removed from their containers by stripping away the container walls or by melting them and then pumping or pouring out the contents. Waxy or semi-solid materials are processed by dissolving them in a suitable solvent through heating.

Melting- or setting-point

The melting-point normally refers to the temperature at which a pure substance becomes a liquid. The setting-point of a pesticidal chemical is the temperature at which a molten or liquid pesticide becomes a solid as a result of withdrawing heat from the system. The melting- or setting-point of a pesticidal chemical defines its physical state at room temperature.

The melting- or setting-point suggests the ease of grindability of the material; the grindability generally improves as the melting-point of the pesticide increases. Materials with melting- or setting-points between 60° C and 90° C can often be ground with the addition of dry sorbent carriers. However, care must be taken, especially with lower-melting materials, to avoid a build-up of heat in the mill. Materials which melt below 60° C are more conveniently processed after melting or by dissolving in an appropriate solvent.

Boiling-point

Most pesticidal chemicals have relatively high boiling-points. In processing pesticide formulations, it is unlikely that temperatures will be encountered which approach the boiling-point of the active ingredient.

Specific gravity or density

The specific gravity of a substance is a measure of the relative weight of a substance relative to the weight of an equal volume of water at the same temperature. Liquid and molten pesticides are pumped and metered into formulation equipment on a weight basis by applying the specific-gravity factors with temperature corrections. In this way, materials-handling and weighing problems can be greatly simplified. In the development of liquid formulations such as emulsifiable concentrations, the probable concentration of the active ingredient in the finished product can be reasonably estimated from the specific gravities of the active ingredients, solvent and surfactants.

In the design or preparation of liquid formulations such as emulsifiable concentrates, the volume of active ingredient or solute and the volume of solvent are not additive. Therefore, it is necessary to compute the volume of the active ingredient on the basis of its apparent solution density which has been shown in some cases to decrease with dilution.

Studies of the sorptivity of dry carriers and diluents indicate that the maximum quantity of liquid which can be held by a dry solid is a function of the volume of liquid rather than its weight. Therefore, when the volumetric sorptivity limits of a given carrier are known, the probable maximum weight percentage of the active ingredient which can be absorbed by the carrier can be estimated.

Viscosity

The viscosity of a pesticidal chemical is a functional characteristic which must be considered in all handling operations. Although viscosity is usually associated with liquid products, it is likewise an inherent characteristic of molten and solid chemicals. In the transference of technical pesticidal chemicals from their bulk containers into processing equipment, the power requirement at a given rate of flow increases as the viscosity increases. For pumping highly viscous materials, the use of a gear pump or a positive displacement pump (with a bypass) is preferred rather than the use of centrifugal pumps. This is especially true in cold weather when the temperature of the liquid may be relatively low.

In the spray impregnation of powdered or granular carriers for the preparation of dry formulations, a low viscosity is generally required for a good spray pattern. To reduce viscosity in the operation, it is necessary to warm the liquid to a suitable viscosity or to add a solvent which is miscible with the active ingredient. If heat is used to decrease the viscosity of the liquid being sprayed, the heat loss in the transfer lines from the spray kettle to the nozzle should be minimized by insulation so that the proper viscosity will be maintained throughout the entire spraying operation.

The viscosity of a pesticidal chemical is significant in emulsifiable concentrates; as the concentration of the active ingredient in emulsifiable concentrates increases, the viscosity increases. In general, the dispersibility of an emulsifiable concentrate in water improves as the viscosity of the concentrate decreases.

Solubility

The solubility of a pesticidal chemical is an inherent characteristic dependent upon its molecular structure and molecular weight. Although it is possible to set forth certain rules of solubility relating to molecular constitution, in practice it is necessary experimentally to determine the solubility characteristics of each new pesticidal chemical in representative solvents. In liquid concentrates, the solubility of pesticidal chemicals is usually expressed in terms of grams of active ingredient or grams of technical pesticide per 100 ml of solution. Other units such as weight of active ingredient or technical material per volume or per weight of solvent may be used, but practical application of these units requires additional calculation based upon density or apparent density.

The solubility of a pesticidal chemical is of high economic significance. It is normally desired that each pesticidal chemical has a very high degree of solubility, so that high concentrations can be prepared in low-cost solvents, such as kerosene. If the solubility is low, more expensive solvents may be required and even then only low concentrations may be attainable. If the cost of producing a liquid concentration becomes excessively high because of poor solubility properties, and if a spray-type formulation is required, alternative formulation types, such as water-dispersible powders or flowable concentrates, should be considered.

Stability

The stability of a pesticidal chemical is its ability to withstand the degradative effects encountered in storage, formulation and the environment to which it is subjected after application. The principal concern is the stability of the molecule under all stresses rather than its stability under lowered temperatures or its persistence as a residue.

Although many organic molecules may decompose spontaneously during storage, this cannot be tolerated for a pesticidal chemical. If there is a tendency to decomposition, a stabilizer must often be added to the technical pesticide significantly to retard the decomposition process. Heat and the presence of impurities such as certain metallic substances or oxides may occasionally cause breakdown of pesticides. When this is the case, stabilizers are necessary or the impurities must be removed. During many formulation processes, the application of heat is often necessary to dissolve the pesticidal chemical or to reduce its viscosity. Therefore, the heat stability of the active ingredients must be studied. Regardless of the type of formulation to be made, the chemical compatibility of the formulation ingredients must be studied for prolonged periods of time. To accomplish this, it is necessary that sensitive and specific methods of analysis be developed prior to the initiation of the study.

Some pesticidal chemicals are subject to decomposition in varying degrees by acids or bases. In formulation, this type of decomposition might be encountered with mineral carriers and diluents or, in certain cases, with the particular surfactants which are used. When working with pesticidal chemicals which are sensitive to strong acids or bases, care must be taken to avoid formulation ingredients with these properties. Other organic chemicals are very sensitive to hydrolysis by the action of water. If the rate of hydrolysis is too great or cannot be controlled, a serious limitation is placed upon this chemical for use in emusifiable or any aqueous spray formulations. After application, the persistence of such a chemical is of such short duration that pest control is not provided. The ability of a pesticidal chemical to withstand degradation by air or light may be a factor to consider and the use of antioxidants or light-screening agents may be helpful, although they generally provide only temporary relief.

Other properties

Two other characteristics of pesticidal chemicals are odour and colour. Although colour is of no importance in agricultural applications, odour and colour may be significant for household or institutional sprays. The avoidance of colour in spray formulations of insecticides may be accomplished in some cases by the removal of impurities through decolourizing processes in the technical product of the formulation. Where colour develops after formulation, a search is made for formulating ingredients which will not react with certain impurities in the technical material. Odour can sometimes be removed or greatly diminished by processing of the pesticidal chemical. However, it is generally more expedient to find a suitable aromatic masking agent to make the inherent odour of the formulation less obnoxious.

Powdered carriers and diluents

The most important dry carriers and diluents used in pesticide formulations are inorganic materials principally of natural origin (see table 1). They include minerals such as diatomite, vermiculite, attapulgite, montmorillonite, talc, pyrophyllite and kaolinite. They are processed for use in pesticide formulations by many techniques ranging from simple drying and pulverizing to washing, air-floating and calcining. Their properties are imparted by the crystalline and molecular structures as well as by the composition. The properties of these carriers and diluents are often enhanced by unique processing conditions. The properties of powdered carriers and diluents are described below.

Particle size

The powdered carriers and diluents are distinguished from the granular carriers and diluents principally on the basis of particle size. Most pesticidal carriers and diluents are finer than 200 mesh (United States standard sieve series). In general, dry carriers and diluents are used for the formulation of dusts, dust bases and water-dispersible powders. Generally, the finer the particle size, the more suitable the material will be for water-dispersible powder formulations because the suspendibility in water of a water-dispersible powder is inversely proportional to the particle size. For this type of product, a minimum of 95 per cent of the carrier or diluent should pass through a 325 mesh (44 μm) screen.

Sorptivity

Relative sorptivity is the usual measure for distinguishing between dry carriers and diluents. Sorptive carriers are necessary when liquid or low-melting pesticidal chemicals or solutions are to be formulated as dust bases or water-dispersible powder concentrates. For the formulation of dusting powders of pesticides, sorptivity is of minor significance for all practical purposes.

Sorptivity may be defined as the capacity of a powdered inert material to maintain the addition of a liquid in a quantity up to but not exceeding the

TABLE 1. GENERAL PHYSICAL PROPERTIES OF CARRIERS AND DILUENTS

Carrier or diluent	*Specific gravity*	*Loose pack density (kg/m³)*	*Packed density (kg/m³)*	*Oil sorptivity (g/100 g)*	*Sorption index*
Attapulgite	2.3-2.4	256-400	465-577	100	135-237
Calcium carbonate	2.7	640-881	1 282-1 538	5-18	. . .
Diatomaceous earth	1.8-2.1	96-160	160-272	100-220	187-272
Kaolinite	2.4-2.7	240-272	609-1 282	5-54	69-184
Mica and vermiculite (expanded)	2.2-2.7	128-737	160-737	38	. . .
Montmorillonite	2.3-2.8	256-865	288-1 025	23-70	80
Pumice	2.6	481	721-769	. . .	78
Pyrophyllite	2.6-2.8	449-561	833-993	25-50	76-90
Silica	1.9-2.7	48-641	400-640	25-09	64
Talc	2.6-2.9	449-737	449-1 009	24-40	73

Carrier or diluent	*Maximum flowable concentrate (per cent)*					*pH*	*pK*	*Approximate deactivation required for pK 1.5*
	Heptachlor	*Chlordane*	*Endrin*	*Methyl parathion*	*Ethyl parathion*			
Attapulgite	25	40-50	75	25	25	5.2-8.0	< 1	6-10
Calcium carbonate	5	5	75	5	5	9.0-9.2	> 3.3	0
Diatomaceous earth	50	70	75	50	60	5.5-7.0	1	1-5
Kaolinite	. . .	20-40	75	10-15	15	4.2-9.4	< 1	0-3
Mica and vermiculite (expanded)	25-40	55-60	75	. . .	. . .	6.9-7.1	. . .	1-3
Montmorillonite	5-25	5-40	75	5-25	5-40	4.5-9.4	< 1	4->9
Perlite	25	40	75	25	40	. . .	. . .	0
Pumice	15-20	20-25	75	15-20	20-25	5.4-8.1	. . .	0-1
Pyrophyllite	5-10	5-10	75	5-10	5-40	6.0-7.0	3.3	0-1
Silica	5-60	5-75	75	5-60	5-75	4.5-10.0	. . .	0-10
Talc	5-10	5-10	75	5-10	5-10	6.8-9.6	3.3	0-1

transition point between dryness and plasticity of the total mass. One laboratory has adopted the term "sorption index" as the weight of technical material which can be absorbed by 100 g of the inert powdered mineral up to the point of plasticity as defined above (see table 1). The method for determining the sorption index is similar to the method used in the paint industry for determining the oil absorption value of pigments.

In practice, the quantity of liquid pesticide added to a carrier never approaches the quantity which is designated by the sorption index, for to do so would probably produce a highly non-flowable mixture. For example, diatomaceous earth which has a sorption index of around 270 may be used with care to produce a chlordane 50 per cent dust base. The dust base consists of 50 per cent technical chlordane and 50 per cent diatomaceous earth. If this 50 per cent concentration of chlordane is exceeded, the product becomes increasingly heavier and less flowable, which makes it more difficult to dilute with an inert diluent. It is often necessary to add other ingredients such as solvents, liquid deactivators and surfactants; all these additional ingredients have a great tendency to reduce the available sorptivity of the inert carrier portion.

Table 2 lists a number of typical carriers and diluents according to their sorption index. It shows that synthetic silica, diatomite and attapulgite have high sorption indices, whereas pyrophyllite, talc and powdered limestone (calcium carbonate) have very low sorption indices and are, therefore, classified as diluents.

TABLE 2. SORPTIVITY OF MINERAL TYPES COMMONLY USED AS PESTICIDE CARRIERS AND DILUENTS

Mineral	*Typical sorption index*[a]
Carrier	
Silica (synthetic)	400
Diatomite (salt water)	270
Vermiculite (expanded)	250
Attapulgite	230
Diatomite (fresh water)	200
Perlite	200
Montmorillonite (non-bentonoid)	190
Kaolinite	160
Diluent	
Pyrophyllite	90
Bentonite	80
Pumice	78
Talc	73
Silica (natural)	64
Limestone ($CaCO_3$)	50
Gypsum ($CaSO_4$)	50

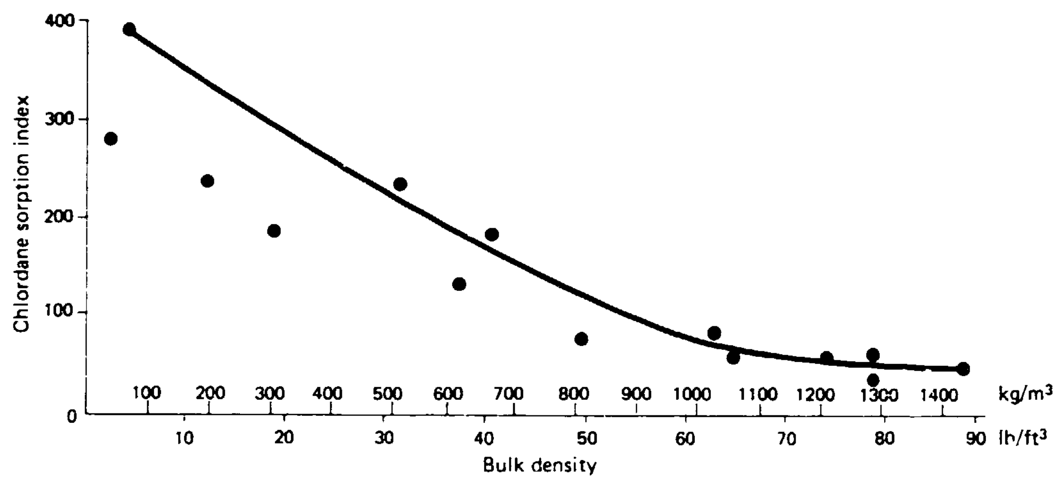
[a] The quantity of chlordane absorbed in the rub-out method (g/100 g of powdered material).

If the sorptivity of a carrier is determined as mentioned above by using liquids of varying densities, it will be found that the sorptive capacity in terms of the weight of material absorbed varies inversely as the density of the liquid. The linseed oil absorption of many minerals used as carriers and diluents is frequently given by the suppliers. If the linseed oil absorption value is known, the chlordane absorption or sorption index, for example, can be estimated through multiplication by the ratio of the higher to the lower density.

Bulk density

Bulk density generally varies inversely as the sorptivity of the carrier or diluent. Therefore, diluents tend to be heavier than carriers. This is illustrated in figure I, where bulk density for a random selection of carriers is plotted in relation to the chlordane sorption index. The bulk density of carriers and diluents can be measured by two different techniques.

Figure I. Sorption index as a function of bulk density



The loose-packed (or aerated) bulk density technique gives the bulk density in its fluffed-up form as determined with a volumeter. This is a measurement of randomly oriented particles that are allowed to fall a minimum distance and to settle without orientation. It is a useful index in estimating the maximum amount of carrier or diluent which might be added to a dry blender. When a blender is in operation, the powdered material which it contains is continually being circulated so that aeration and disorientation are at a maximum.

The packed bulk density technique gives the weight of a volume of powdered material after it has been vibrated to maximum orientation. The material has been completely deaerated and the particles are permitted to settle in their most stable geometric alignment. Packed bulk density is the index of the greatest weight of the powdered material which can be packed in a container of any given size (see table 1). The ratio between the loose-packed density and the packed bulk or vibrated density varies from material to material according to specific gravity, particle shape and particle size distribution.

Surface acidity and chemical compatibility

Surface acidity is a common characteristic of most naturally occurring mineral carriers and diluents but varies in degree depending upon the crystalline and molecular structures of the mineral. Surface acidity may be defined as a disproportionate distribution of electric charges in the mineral to produce a surface with positively charged centres. These centres are referred to as acid sites or electrophilic centres. The strength of these positively charged sites can vary depending upon the composition of the surface and the degree of distortion in the structure which brings about the disproportionate distribution of the electrical surface charges.

The acidity will, in turn, affect reactions with other chemicals. The strength of the acid centres may be measured by certain sensitive dyestuffs known as Hammett indicators which change colour at very specific acid strengths. These dyes form conjugated bases with the nucleophilic acid centres at different surface acidities which are defined as the pK with a numerical system ranging from +7 to −8. Consequently, the pK is a measure of acid strength (i.e. the affinity for electrons) of the average acid site.

In practice, the strength of the acid site is of importance as well as the number of acid sites in a given mass or weight of the mineral. For example, the most active acid sites of kaolinite probably have a pK equal to −8; kaolinite has only about one third as many acid sites as montmorillonite for a given weight of material. The surface acidity of a mineral carrier or diluent is of great importance for the stability or rate of decomposition of the active ingredient in the finished formulation.

Pesticidal chemicals vary greatly in their susceptibility to decomposition as the result of the catalytic activity of the acid sites. Fortunately, these acid sites can be deactivated with certain organic chemicals which preferentially share their electrons with the mineral to form a covalent bond which is stronger than bonds formed between the pesticidal chemical and the acid centre itself. Compounds containing oxygen in an ether linkage or amine derivatives are effective for this use.

For surface active minerals, deactivators should be tested for compatibility with the pesticidal ingredients in the entire system. Although urea and hexamethylenetetramine are excellent deactivators for formulating some materials such as aldrin and endrin, respectively, they are not suitable for use in heptachlor formulations where a different decomposition mechanism is encountered. For heptachlor and chlordane, diethylene glycol and similar neutral substances perform well as deactivators without encountering any degradative reaction with the active ingredient.[1] Usually 6 or 8 per cent of the deactivator material is added. Its use increases the cost of formulation. When other properties and characteristics of the carrier and diluent are satisfactory for a given formulation, an inert material with the least surface acidity should be selected.

The acidity or alkalinity of carriers and diluents may cause the decomposition of certain pesticides. Consequently, only those inert ingredients which in

[1] M. A. Malina and others, *Journal of Agricultural and Food Chemistry*, vol. 4, 1956, p. 1038.

accelerated storage tests do not affect the active ingredient should be considered in the formulation. The acidity inferred here is the more classical acidity and not surface acidity discussed above. This acidity can be determined by measuring the pH of a 10 per cent slurry of the mineral in water.

Furthermore, the presence of metallic impurities such as iron oxides in certain clays can have a deleterious effect upon the active ingredient. If the pesticidal chemical is sensitive to metallic impurities, materials should be selected which do not contain extractable iron salts.[2]

Flowability

The flowability of a powdered carrier is the rate at which the material can be poured, moved or displaced; it is dependent upon particle shape, density and to a lesser extent, particle size. Its significance in the formulation process is that as flowability increases, the power requirement for blending or working the material decreases. This is a significant factor in field application because, as flowability increases, the flow through the dusting hopper and the meter improves, and the rate is more easily controlled.

Dustability

Dustability is a characteristic of powdered diluents relating to the ability to flow through the air, to be transported by air currents within a limited area of application and to cling to the surface of the crop after application. There are no precise laboratory methods for testing the dustability other than practical application under actual or simulated conditions of use.

Abrasiveness

Abrasiveness is the property of certain carriers and diluents to cause wear of processing equipment, metering devices and orifices of application equipment. Water-dispersible powders prepared from abrasive carriers and diluted in water can cause the continued enlargement of fine orifices of spray nozzles through the abrasive process. This action significantly changes the flow characteristics of the nozzles thereby increasing spray volume rates. The spray pattern is changed and the resulting applications are inaccurate. Abrasive materials include pyrophyllite, pumice, silica and diatomite, while non-abrasive materials include kaolinite and talc.

Granular carriers

Granular carriers are particulate materials which form the basis for most granular pesticides. These carriers may be of mineral or vegetable origin.

Popular carriers include the mineral carriers of attapulgite and montmorillonite and the carrier of plant origin derived from maize cob grits. Granular cobs have the desirable physical properties of being lighter per unit volume than

[2] H. L. Holler and others, *Industrial and Engineering Chemistry*, vol. 37, 1945, p. 403.

mineral carriers and having less of a tendency to create dust particles through attrition than mineral carriers. Maize cob grits do, however, have a smaller sorptive capacity than mineral granules.

Because granular pesticides are most conveniently prepared by impregnating the granular carrier with the pesticidal chemical, sorptivity is a desirable property.

Particle size

An unofficial designation of a granular carrier is that it must have a particle size lying within the range of 4 mesh to 80 mesh (4 mesh is approximately 4,460 μm; 80 mesh is 177 μm). In practice, this broad particle size range is not used. Much narrower ranges are conventionally used for purposes of product uniformity, minimum segregation, accurate metering and optimum particle distribution. These size ranges may be of the following designations: 8/15, 16/30, 20/35, 20/40 and 30/60. A number of suppliers of granular carriers have adopted the standard that at least 90 per cent of all particles in a given designation shall fall within the stated mesh range. As an example, the designation 16/30 states that 90 per cent of the particles should lie within the range of 16 and 30 mesh, and that the remaining 10 per cent may be distributed on the 16 mesh screen and through the 30 mesh screen.

A 16-mesh screen has a size designation of 1,190 μm, whereas a 30-mesh screen is equivalent to a 590 μm opening. The 16/30 designation, however, does not define the distribution of the particles in this range. Indeed, the majority of particles can be in the 18 to 20 mesh range for one product and in the 20 to 25 mesh range for another product. Yet, both products would meet the 16/30 designation or specification as indicated in table 3. Where the finer particle size distribution is

TABLE 3. VARIATION IN DISTRIBUTION OF PARTICLES IN A GIVEN MESH RANGE OF TWO CARRIERS

	Carrier (%)	
Designation	*A*	*B*
20/25	10	20
25/30	30	40
30/35	40	30
35/40	20	10

encountered and the distribution is skewed toward the 25 or 30 mesh designation, there will be more particles per gram than if the skewness is in the opposite direction or towards the larger particle size. Table 4 illustrates the mesh size and number of particles per gram. It may be argued that better distribution in application may be obtained by a granular product having skewness toward the finer mesh range. However, there is no evidence of practical benefit. Field research has shown that this factor is of little significance. The number of particles per gram of a granular product is dependent upon the particle size, distribution of particle size and the bulk density of the granular carrier.

TABLE 4. THE RELATIONSHIP BETWEEN MESH SIZE AND PARTICLES PER GRAM OF FLOREX ATTAPULGITE GRANULES

Mesh size	*Particles per gram*
16/30	2 668
18/35	5 137
25/50	20 282
30/60	24 802

Sorptivity

The sorptivity of granular carriers has the same functional purpose as the sorptivity of powdered carriers. It is a function of both the crystalline structure and the available surface area of the material. For granular carriers of minerals such as attapulgite and montmorillonite which have a relatively high pore density, the sorptivity approaches that of the respective powdered carriers. Granular pyrophyllite and granular limestone have relatively low pore density so that sorptivity is principally a surface phenomenon. As particle size increases, surface area decreases; therefore, for the latter class of granular carriers, sorptive capacity is relatively low.

Attapulgite is often extruded in the process of manufacturing granules to improve sorptivity. The extruded granules are then calcined, thus affecting the moisture content, catalytic activity, hardness and tendency of the granules to break down in water. The following designations are used to identify the type and degree of processing:

A	unextruded
AA	extruded
RVM	(regular volatile matter) uncalcined, rapid water breakdown
LVM	(low volatile matter) calcined, resists disintegration in water

Granular vermiculite is a laminar mineral which can be expanded by heat to produce a sorptive material. Its sorptive properties are caused by the capillary spaces between the layers. The general acceptance of granular vermiculite as a carrier has been limited, however, by its low bulk density.

Granular materials of vegetable origin include maize cob grits and ground walnut or pecan shells. The sorptivity of maize cob grits approaches that of the attapulgite or montmorillonite granules. The sorptivity of maize cob grits varies with the source and the process used. Walnut and pecan shells have less than half the sorptivity of the attapulgite granules.

Bulk density

The bulk density of granular carriers is a weight-limiting factor for a granular pesticide which is loaded into the hopper of the application equipment. Because sorptivity varies inversely as the bulk density, a lower weight of the sorptive granules can be loaded into the hopper of application equipment than the same volume of heavier but less sorptive granules. For practical purposes, attapulgite granules are acceptable on the basis of both bulk density and sorptivity. The process of impregnating attapulgite granules with liquid pesticides or liquid pesticide solutions does not change the shape or the size of the particle. During the impregnation process, the liquids are absorbed by the particle structure so that the weight of the particles increases without a significant change in volume.

Granular application flow rates are controlled by volumetric metering through adjustable and calibrated orifices in the application equipment. Therefore, it is necessary that the bulk density of the finished product be controlled. In addition to the effect on bulk density (assuming no attrition of the particles), as the weight of solvent increases and the weight of the granular carrier decreases, the number of particles per pound of finished product decreases likewise.

Surface acidity

The mineral types used for granular carriers are the same as those used for powdered carriers and diluents. Consequently, they have the same type of surface acidity and must be treated accordingly.

Mechanical strength

The mechanical strength of a granular carrier is its resistance to attrition under mechanical stress during the formulation process, packaging, shipment and use. When attrition does occur, the granules undergo a reduction in particle size with the generation of undesirable fines. Montmorillonite and attapulgite (especially the RVM grades) generally have sufficient mechanical strength that the formation of fines through attrition is minimal. Materials of vegetable origin, such as maize cob grits and pecan and walnut shell granules, are resistant to attrition.

Water breakdown

The release of the active ingredient from most granular pesticides is made possible by the disintegration of the granular particles by the action of water. Granular clays such as attapulgite and montmorillonite (especially of the bentonite type) have the property of breaking down or swelling as a result of hydration. This phenomenon makes possible the release of the active ingredient. Pyrophyllite and calcium carbonate do not behave in such a manner. The swellable clays are also useful as a partial component of dispersible granules.

Solvents

Because most pesticidal chemicals are insoluble in water, it is necessary to use some form of organic solvent for the preparation of liquid formulations or liquid concentrates used for the impregnation of dry formulations. The different types of solvents for pesticide formulations are classified by composition, chemical type, structure or function. In pesticide formulation work, it is convenient to classify the solvents as polar or non-polar. Among the non-polar solvents, the most important economically are the hydrocarbon and petroleum distillate solvents.

The polar solvents include ketones, esters, glycols, glycol ethers and acid amides. The hydrocarbon and petroleum distillates are further classified as aliphatic or aromatic types for a functional, as well as an economic, distinction.

The formulation chemist may encounter water-miscible and water-immiscible types among the polar solvents. Although there may be a broad choice of available polar solvents, the question of water miscibility, together with other factors including economics, will influence the choice. The important functional properties of the solvents used in formulating pesticides are discussed below.

Distillation range and boiling-point

The distillation range or boiling-point of a solvent is an indication of the volatility of the solvent under formulation or application conditions. For pure solvents, the boiling-point is the temperature at a given pressure where the liquid phase is in equilibrium with the vapour phase of the material. The normal boiling-point usually refers to the temperature measured at atmospheric pressure.

The hydrocarbon solvents and petroleum distillates normally used in pesticide formulation are mixtures of hydrocarbons, each of which has its own boiling-point. To determine the boiling-point range, it is convenient to distil the material and record the temperatures from the initial drop received in the overhead and through fractional points as volume per cent, until no further material from the sample is distilled (this is sometimes known as the Engler distillation). Typical hydrocarbon solvents used in pesticide formulation are the xylene-type solvents which distil over a range from approximately 133° C to 165° C. The heavy aromatic naphthas normally distil in the range from 117° C to approximately 287° C. Aliphatic hydrocarbon solvents are used in large quantities; they are principally of the kerosene type and distil in the range from 190° C to approximately 475° C.

Polar solvents are usually of relatively high purity as compared to the hydrocarbon solvents, and their distillation range is seldom greater than 12° C. In selecting a polar solvent, those with boiling-points higher than the range from 94° C to 99° C are preferred. In special cases involving solubility or phytotoxicity, materials with lower boiling-points may be used with caution.

Specific gravity (density)

The specific gravity of a solvent is the weight of a given volume of the solvent relative to the weight of an equal volume of water at a standard temperature. The density of the solvent is usually expressed in units of grams per millilitre (g/ml). When defining the temperature at which the density was determined, the density becomes an absolute value. Of the hydrocarbon solvents used in pesticide formulation, the aliphatic types such as kerosene have the lowest density values ranging from 0.76 to 0.79. The xylene types have intermediate density values in the range from 0.85 to 0.88. The density of heavy aromatic naphthas range from 0.92 to 0.97.

Kauri-butanol value

The kauri-butanol value (sometimes called the KB) is a measure of the solvency of a given solvent. It is a relative number compared to that of toluene (= 105). For most aromatic hydrocarbons used in pesticide formulation, the KB value is nearly equivalent to the volume per cent of aromatics available in the solvent.

Aromatics content

The aromatics content of a hydrocarbon solvent such as those used in pesticide formulation is measured in terms of volume per cent. As a general rule, the solvency power of the solvent increases as the aromatics content increases. The cost of the solvent increases as the aromatics content and solvency increase. The aromatics content of xylene type solvents and heavy aromatic naphthas range from 85 per cent to more than 95 per cent.

Specification sheets for solvents furnished by suppliers usually include inspection data for a typical batch or lot of a solvent. Occasionally, the typical aromatics content of a solvent will be listed as around 95 per cent with a minimum specification given as 90 or 91 per cent. When developing emulsifiable or oil concentrates with pesticides having limited solubility at low temperatures, the formulation chemist should perform cold stability tests using samples of solvents having KB values and aromatics percentages as close as possible to the lower limit of the specification for a particular solvent.

Flash-point

The flash-point of a solvent is an indication of the flammability of that solvent. Numerically, it is the temperature of ignition when tested under closely prescribed conditions using standard test apparatus. In selecting a solvent for pesticide formulation, a solvent should be chosen with the highest flash-point consistent with other desirable properties. For most liquid formulations, the minimum flash-point should be 27° C. Any liquids determined by the Tag Open-Cup flash-point method[3] as having a flash-point below this temperature should be packaged in a container carrying a Bureau of Explosives red caution label for flammable liquids as prescribed in the regulations of United States Department of Transportation (USDT). If solvents having a lower flash-point are used, extra precautionary measures must be used to avoid fire hazards during both formulation and shipping.

Solvency

Solvency is the ability of a given solvent to dissolve a specific material or class of materials when tested under prescribed conditions. The solvency of solvents

[3] M. B. Jacobs and L. Scheflan, *Chemical Analysis of Industrial Solvents* (New York, Interscience Publishers, 1953), pp. 109-111.

used in pesticide formulations usually increases in the order of aliphatics, aromatics to polar compounds. Even though this is a broad generalization, it is reliable for formulation chemists and permits a few tests of new pesticidal chemicals with the minimum number of test solvents of each class.

The solvency requirements for the different classes of pesticidal chemicals vary considerably. Indeed, even within a given class of pesticides, such as the diene chlorinated hydrocarbons, there is a wide-range of solvency demand. For example, any ordinary kerosene, which is one of the poorer solvents, will dissolve an infinite weight of technical chlordane. However, endrin has a very limited solubility in the aromatics and is seldom formulated at concentrations higher than 20 per cent by weight or 19.2 g per 100 ml.

Solubility may be expressed in a number of units such as the weight of the solute in grams per 100 g of solvent, the per cent by weight of the solute in grams per 100 g of solution and the weight of the solute in grams per 100 ml of solution. Solvency tests cover a range of temperatures usually extending to $-16°$ C. Where extreme cold weather conditions are encountered, cold-stability tests are sometimes performed at temperatures as low as $-39°$ C.

Water miscibility

In preparing emulsifiable concentrates, it is important to choose solvents which are relatively insoluble in water. The aliphatic and aromatic hydrocarbon solvents meet this requirement; however, the problem becomes more acute when the polarity of the solvents is increased, since it is usually accompanied by increasing solubility in water. Although solvents such as cyclohexane and isophorone are slightly soluble in water, they can often be used effectively, particularly when combined with aromatic hydrocarbons. Solvents of increasing polarity such as glycol ethers and amide solvents may be used usually only sparingly in mixtures with hydrocarbon solvents.

Viscosity

The viscosity has a minor, yet real, effect upon the quality or characteristics of an emulsifiable concentrate. As the viscosity of a solvent used in an emulsifiable concentrate increases, the rate of crystallization decreases when the temperature of the concentrate drops below the solution saturation point. Therefore, caution must be exercised during cold-stability studies performed during a minimum period of time to avoid determining solubility at a given low temperature when, in fact, the formation of crystals in the concentrate is only delayed. A high viscosity apparently retards the molecular and crystal alignment. Seeding (the addition of a very small quantity of the crystalline material to the solution) may sometimes accelerate the rate of crystallization by providing nucleating surfaces for further crystal growth from the supersaturated solution.

The ease of dispersibility in water of an emulsifiable concentrate is inversely proportional to the viscosity of the concentrate. Therefore, non-viscous concentrates are best prepared with a solvent having as low a viscosity as possible while maintaining the most desirable solubility characteristics.

Toxicity

It is essential that both mammalian toxicity studies and plant phytotoxicity studies be conducted on pesticide formulations. Solvents may modify (either enhance or retard) the human dermal penetration of pesticides, may affect the toxicity of the composition to the human eye, etc. Consequently the results of comprehensive safety evaluations must be incorporated into a label and appropriate material safety data sheets to ensure the safety of all who come in contact with the composition (see chapter X).

Solvents also affect the degree of phytotoxicity of plant protection compositions. The hydrocarbon solvents are generally more phytotoxic than other solvent types. The higher boiling hydrocarbons are more phytotoxic than the lighter solvents.

Colour

The colour of a solvent has no practical significance when it is used for agricultural formulations. For household and institutional pesticide formulations, however, the colour of a solvent may stain walls and furniture. Therefore, if the formulation is to be used in the home or in other areas where staining of the applied surfaces is objectionable, the solvent should either be colourless or very light in colour. Most of the petroleum companies, which supply aliphatic solvents, provide special kerosene-type, so-called odourless and colourless insecticide base oils especially for the pesticide industry.

Odour

The odour of a solvent used for agricultural formulations is of minor significance; however, most hydrocarbon solvents have a characteristic odour. Gross changes in the odour of a solvent may be due to a change in composition and should be checked for possible effect on phytotoxicity as well as on the solvency of the material.

The odour of a household or institutional formulation must be kept to a minimum to avoid offending consumer sensitivities. The aliphatic solvents marketed as odourless insecticide base oils are generally satisfactory in this regard. Occasionally, special fragrances or masking agents are added to the formulation for a more pleasing odour. Most of the major essential oil and perfume supply houses have developed products especially for this use.

Surfactants

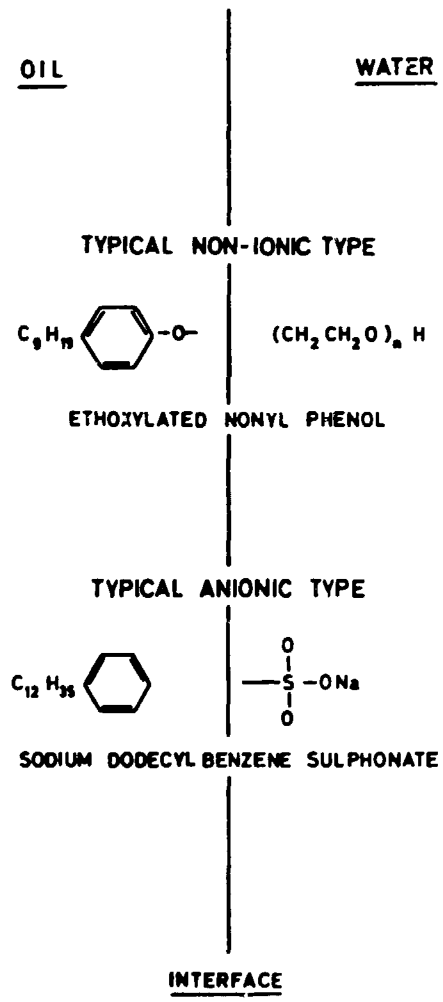
Surfactants reduce the interfacial tension between immiscible liquids or between liquids and solid surfaces. There are a number of functional classifications depending upon the predominantly surfactant characteristics. In pesticide formulation the surfactant characteristics of greatest interest are wetting and dispersing for water-dispersible powders and emulsifying for emulsifiable concentrates.

A surfactant is used for the management of systems containing two immiscible phases. The molecular structure of a surfactant, therefore, should consist of one portion oriented toward one phase, while the other portion of the molecule is oriented toward the second phase of the system. If the system is oil and water, one portion of the molecule should be soluble in oil and the other in water.

Chemical types of surfactants

Surfactant molecules are anionic, non-ionic and cationic chemical types. In formulating agricultural pesticides, the anionic and non-ionic surfactants are the most important. Figure II shows the schematic function of these two surfactants. Although the cationics hold theoretical interest, they have not been used practically to any significant degree. A fourth type is the amphoteric surfactant that combines the properties of the anionic and cationic surfactants and functions as either type depending upon the pH of the total emulsion. The non-ionic emulsifiers are compatible with either anionic or cationic emulsifiers. Cationic emulsifiers and anionic emulsifiers are, however, incompatible with each other.

Figure II. Schematic function of surfactant molecules



The wetting agents used in water-dispersible powders are usually of the anionic type; of these the largest number are probably the sodium salts of alkyl benzene sulphonates. Dispersing agents used in addition to the wetting agents in water-dispersible powders function by imparting the same electrical charge to all particles in suspension. The effect is that the individual particles repel each other and, consequently, resist flocculation and agglomeration. Dispersants used in the formulation of water-dispersible powder pesticides may be of the lignosulphonate type with cations such as sodium or calcium or the sodium or calcium sulphonates of polymeric phenols. Dispersants are generally dry, powdered solids which facilitate their incorporation in water-dispersible powders.

Solubility and miscibility

In order for a pesticide emulsifiable concentrate to be a completely homogeneous liquid, all components must be soluble in each other in the complete system under all conditions of storage and testing. In the development of an emulsifiable concentrate, the first step is to find a suitable solvent for the toxicant which is to be formulated. Then the emulsifier is selected which gives the best dispersibility and emulsion performance. Subsequently, storage tests are performed to establish the solubility and compatibility of the emulsifier with the toxicant-solvent system. Normally, and especially when aromatic-type solvents are used, surfactant systems will remain miscible in the formulation. However, when the solvent is aliphatic, such as kerosene, and the concentration of the active ingredient is relatively low, such as 20 per cent chlordane, the emulsifier system may separate from the concentrate. This separation can be avoided by working with emulsifier systems which are soluble in or miscible with kerosene or by partial or complete substitution of the kerosene with a xylene or other aromatic solvent.

Compatibility

In selecting an emulsifier for an emulsifiable concentrate, tests must be performed to verify that a chemical reaction is not taking place between the emulsifier and the active ingredient. Such degradative action may result in a loss of toxicant strength in the formulations as well as a loss in the emulsifiability of the system. Special caution should be taken in the use of emulsifiers containing amine salts of anionic emulsifiers which may react with certain chlorinated hydrocarbons or with phosphate-ester active ingredients. A clue to this type of interaction may be shown by a rapid darkening of the system. Furthermore, the interaction is found by assays and emulsifiability tests after accelerated storage tests.

Stability

The anionic and the ether-type non-ionic emulsifiers used in pesticide formulations are for all practical purposes stable. On the other hand, ester-type non-ionic surfactants may decompose under long-term or accelerated storage conditions. The presence of free hydrogen chloride from the dehydrochlorination of certain chlorinated hydrocarbon pesticides may cause a hydrolysis of the ester linkage. The cationic surfactants or emulsifiers used in pesticide formulations are for all practical purposes stable.

Physical state

The surfactants used in pesticide formulation are solids or liquids. There are no known volatile surfactants for the formulation of emulsifiable concentrates. For their formulation, liquid surfactants are the most convenient. They can be easily pumped or metered into the mixing tanks and blended with normal agitation.

For water-dispersible powder formulations, solid or dry wetting agents and dispersants are preferred. For the most efficient mixing by a dry blender, the particle size should be reasonably small (less than 100 mesh) to facilitate uniform blending.

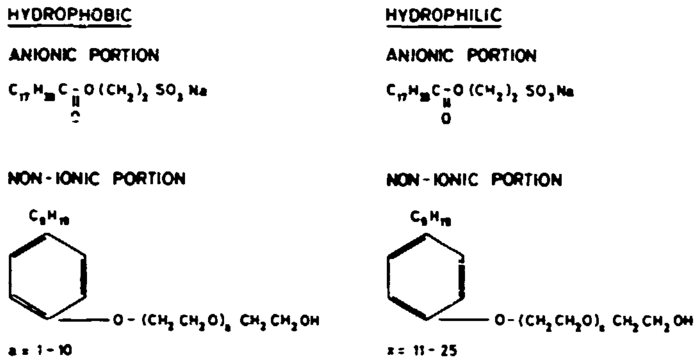
Some liquid emulsifiers used in pesticide formulation may show partial crystallization after lengthy storage. When crystallization occurs in packing drums, it is advisible to warm the drum and to mix the contents by rolling or tumbling the drum before it is emptied. This technique will ensure a uniform composition of the contents. To avoid normal crystallization, some emulsifier manufacturers add a small quantity of solvent to maintain a homogeneous liquid product.

Paired emulsifiers

The very large number of different molecular structures and compositions of pesticidal compounds causes large variations in emulsifiability. Furthermore, the varying solubility of pesticidal chemicals in different solvents is another complex factor in the selection of the proper emulsifier for a system. A further complication is that the final concentrate must perform equally well in water of varying hardness ranging from very soft to very hard. Indeed, even the temperature of the water which is used for the dilution of the concentrate in the field may have an important effect on the emulsifiability.

As the number of pesticide formulations and different products demanded for field use increased, the logistics of maintaining a specific emulsifier or emulsifier blends for each new product became unmanageable. This was particularly apparent in purchasing, inventory control and warehousing. To meet the need for simplification in emulsifier selection, manufacturers developed paired-emulsifier systems. Figure III illustrates one of these systems. The paired-emulsifier system consists of two products; each is based on a blend of anionic and non-ionic emulsifiers with different hydrophilic and lipophilic characteristics (i. e. one member of the pair will have emulsifying characteristics suitable for pesticide-solvent blends which are lipophilic in nature, and the characteristics of the other member will favour the emulsification of the hydrophilic pesticide-solvent system). These systems can be used for 90 to 95 per cent or more of the formulation requirements by simple determinations of the proper ratio and quantity which should be blended with the solvent-pesticide mixture to be emulsified.

Figure III. A paired-emulsifier system



Because of variations from lot to lot of solvent or from batch to batch of the pesticidal chemical, adjustments may be required in the hydrophile-lipophile balance of the emulsifier system in order to obtain uniform emulsification in the finished product. The adjustments are greatly implemented by the use of the paired-emulsifier system. When satisfactory performance cannot be obtained with the existing paired-emulsifier system or with either one of the pair separately, the manufacturer supplies a supplementary emulsifier, which is usually required on the hydrophilic side of the hydrophile-lipophile balance. This supplementary emulsifier together with the paired-emulsifier system extends the versatility of the paired-emulsifier concept.

Adjuvants

Adjuvants are added to pesticidal formulations to improve quality or performance characteristics. Because the objectives of the pesticide formulations are optimum effectiveness, safety to desirable crops and case of application, adjuvants may be different types and perform different functions. A few of the more important types, their usage and available materials for these uses are described below.

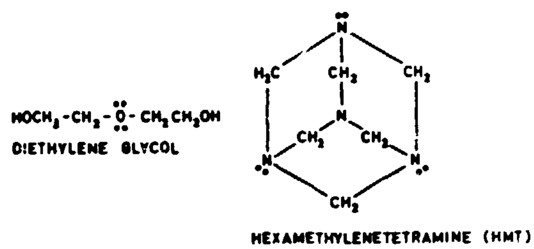
Penetrant aids

There are two significant factors that affect the biological activity of a pesticidal formulation, namely the penetration of the formulation through an outer protecting lipid membrane of the pest and the rate of reaction of the pesticide with a vital reactive site. The penetration of a protective lipid membrane is frequently not optimized in a given formulation. Penetration may be enhanced or reduced by the addition of non-ionic surface active agents to the formulation depending upon the surface properties of the surfactant. Whether or not a given surfactant will be effective in enhancing penetration may be checked by adding a hydrophobic surfactant to one solution, a hydrophilic surfactant to another, and then comparing the resultant biological activity of the solutions with the original solution. Penetrant additives should be present at a sufficient concentration that the final spray solution will contain greater than 0.5 per cent by weight of penetrant aid. By virtue of the addition of a non-ionic surfactant, the apparent biological activity may be found to be as much as twice as effective.[4]

Deactivators

Many of the clays, minerals and inorganic substances used as carriers and diluents for dry formulation have the property of surface acidity, which catalyzes the decomposition of many organic pesticidal chemicals. The surface acidity must be neutralized to overcome the catalytic activity. The deactivators are usually organic compounds which share or contribute a pair of electrons to the acid sites of the catalytically active substance. These organic compounds are ethers, glycol ethers, ketones, esters, amines, acid amides or sulphoxides.[5] Examples of paired electron compounds shown in figure IV are diethylene glycol and HMT. It is not sufficient, however, to select the organic compound at random, because pesticidal chemicals may have different mechanisms for decomposition and structural characteristics that are incompatible with the potential deactivators.

Figure IV. Deactivators for pesticide formulation



Study of the effect of oxygenated materials, such as ketones, glycols and alcohols, as deactivators for heptachlor formulations (prepared upon attaclay (an attapulgite), Barden clay (a kaolinite) and other minerals) showed that all of the compounds functioned effectively as deactivators for heptachlor-clay systems with the effectiveness diminishing in those materials having a relatively high volatility.[6] Urea is an effective deactivator for many of the clays and minerals used in aldrin formulations.[7] Attempts to use urea in a similar manner for heptachlor formulations were not equally effective; there seems to be incompatibility between the system heptachlor-urea and the acid sites of the clays.

Other work has shown that hexamethylenetetramine (HMT) is a preferred deactivator for endrin formulations. However, when endrin is formulated with methyl parathion, a neutral-type deactivator such as diethylene glycol gives the best results. Fatty acids, such as tall oil acids, are effective deactivators for methyl parathion on attapulgite.[8]

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[4] Weed Society of America, "Adjuvants for herbicides" (Champaign, Illinois, 1982).

[5] F. M. Fowkes and others, *Journal of Agricultural and Food Chemistry*, vol. 8, 1960, p. 203.

[6] Malina and others, *loc. cit.*

[7] Fowkes and others, *loc. cit.*

[8] E. Jr. Sawyer and J. Plon, "United States patent 2,962,418" (20 November 1960).

Anti-caking agents

When dust concentrates, water-dispersible powders and granular formulations are prepared in concentrations close to or at the saturation point of the carriers, caking occurs in storage when the individual particles of the formulation become stuck or fused together to form lumps or a solid mass which resists minimal physical effort to break it. When dry formulations of liquid pesticidal chemicals show a tendency toward caking, it is because the surface film of the liquid forms an adhesive bond. Caking of dry formulations of normally solid pesticidal chemicals (especially those prepared by impregnation of a solution or molten pesticidal chemical) often occurs after the mass has cooled and crystallization takes place at the particle interfaces.

The addition of anti-caking agents to a formulation will prevent the formation of an adhesive or a physical bond between the particles. In the formulation of dry pesticides, diatomaceous earth and microfine synthetic silica and silicate are often used as anti-caking agents. Finely divided clays such as attapulgite are often useful for this purpose. The requisites for the anti-caking agent are low bulk density and high sorbency. Fine particle size and high surface area are significant. Anti-caking agents should furthermore be insoluble in any of the organic or liquid phases of the formulation.

Temperature cycles will produce caking if the dry formulation contains a water-soluble material and a significant amount of water (about 1 per cent or greater). Contained moisture solubilizes the water-soluble ingredients. Subsequent evaporation leaves the water-soluble material behind. As it precipitates, it tends to cement particulate materials together. Water absorbers or coating of particles by less hygroscopic materials may be beneficial in this case.

Dry lubricants

Dry lubricants improve the flow or the slip characteristics of the formulations. Although anti-caking agents may assume part of this function, there are applications for dry, seed-treatment compositions where the use of the formulation must not interfere with the plantability or flow of the seed from the seed hopper through the metering orifice. Materials useful as dry lubricants in pesticide formulation are powdered graphite, soapstone talcs and certain metal stearates.

Protective colloids

Protective colloids are used in liquid formulations or aqueous dilutions of water-dispersible powder formulations to inhibit the agglomeration and sedimentation of dispersed particles. They generally have high molecular weight or are polymeric materials that are soluble or dispersible in the continuous phase of the suspension. They function by one or both of the following two mechanisms: by increasing the viscosity of the continuous phase and by imparting a similar electrical charge to all of the dispersed particles. Typical materials used as protective colloids are polyvinyl pyrrolidone, sodium carboxymethylcellulose, methylcellulose, blood albumin and collagen. The water-swelling bentonites, such as the type mined in Wyoming, United States of America, are inorganic protective colloids.

Stickers

Stickers are adjuvants which can be added to a formulation concentrate, although more commonly, they are added to a spray tank prior to application. They prevent the run-off of spray solutions when applied to crops. After the evaporation of water or solvent, stickers retard the wash-off of the pesticide deposit on the plant by wind or rain. Although many protective colloids and gelling agents, such as blood albumin, are used as stickers, other preparations, such as polyethylene polysulphide (PEPS) can be used. A number of proprietary compositions are used as stickers, but they are generally intended for tank-mix application and not for incorporation in the formulation concentrate.

Anti-dusting agents

Anti-dusting agents reduce the dustiness of water-dispersible powder and granular formulations. They are generally liquid substances which cause extremely fine particles of dry materials to adhere to each other, thus making them less susceptible to air flotation and drift.

Many water-dispersible powders contain active ingredients which are extremely hazardous to operators who handle them. These hazardous materials can include thiophosphates, which are used in orchard sprays, or mercurial fungicides, which are often used in seed-treating formulations. In order to protect the operator, these materials are treated with a liquid agent (frequently a water-soluble material such as glycerine) to suppress the dustiness. After adding the formulation concentrate to water, the anti-dusting agent should not interfere with the efficacy of the product.

Granular pesticides, which are usually shipped in multiwall bags, are frequently subjected to mechanical attrition during handling or shipping; a resulting fine powder is caused by erosion from the edges and corners of the granular particles. Such fines are undesirable because they may become airborne during application and drift upon adjacent fields. This drift can result in possible injury to the adjacent crop if the granular pesticide is a herbicide or leave undesirable residues as with insecticides. Water-soluble materials, such as glycerine or petroleum oil (diesel oils, motor oil (viscosity SAE 30) or crankcase drippings) may be used to minimize dustiness from fines.

Anti-foaming agents

Anti-foaming agents are surfactants which suppress the tendency of foam formation by other surfactants used as emulsifiers or wetting agents when the formulation is diluted with water. Foam is undesirable in spray tanks, especially those using a bypass agitation, because it interferes with the development of sufficient pressure at the nozzles for proper spraying. To overcome the tendency of excessive foam, anti-foaming agents are added to the concentrate or to the spray tank. The anti-foaming agents are proprietary compounds, such as liquid silicone or aliphatic alcohol of eight to ten carbon atoms in length.

Formulation design and evaluation tests

The large range of physical and chemical properties of different pesticidal chemicals has been discussed previously. Therefore, the cost of preparing a given type of formulation will vary according to the properties of the pesticidal chemical. When a given pesticidal chemical cannot be formulated inexpensively as an emulsifiable concentrate for spray application, an alternative choice would be a wettable-powder formulation. Similarly, some chemicals do not lend themselves readily to the formation of impregnated granules; therefore, an alternate technique, such as extrusion or pan granulating, should be considered. The cost of pesticide formulation reflects the properties of the pesticide and the performance characteristics of the formulation required for optimum control of the pest.

Liquid formulation

Liquid formulations are among the most popular formulation types. As a general group, recommended dosages of liquid formulations are easily computed and dispensed. When realistically conceived, emulsifiable and similar liquid concentrates are economical formulations since they can be readily diluted with water and conveniently applied. Regardless of type, liquid formulations all have one requirement in common, i.e. the solvent or the fluid diluent must be physically compatible with the active ingredient under all conditions of storage. Experimental procedures for developing liquid formulations are described below and in their relative order of importance.

Emulsifiable concentrates

Emulsifiable concentrates consist of the toxicant, the solvent and the emulsifier. The solubility characteristics of the pesticidal chemical determines the solvent or solvent type to be used and the concentration which is permissible for meeting certain storage conditions. At any given concentration, the physical nature of the combination of pesticidal chemical and solvent determines the type of emulsifier and emulsifier balance to be used. The selection of solvent and emulsifier is the initial phase of emulsifiable concentrate development.

Solvent selection and solubility determination

The first step in the formulation of an emulsifiable concentrate is to estimate the solubility of the toxicants in suitable solvents. A solvent from each of the following classes should be tested: kerosene, xylene-range solvent,[9] heavy aromatic naphtha and cyclohexanone.

Because commercial solvents vary in their properties, it is desirable to know precisely the density, boiling range and percentage of aromatics of a test solvent. A simple procedure for approximate solubility determination is described, in which the quantities are fairly small to conserve the toxicant, but other suitable units may be substituted. The following equipment is required:

[9] Such as xylene 5° or xylene 10°. Range refers to boiling-point range; the smaller the range, the purer is the solvent.

Burettes (5 to 25 ml) or pipettes (2 ml)
Balance with sensitivity of 0.01 g
Five medium-sized test tubes
Hot-water bath
Refrigerator

The experimental procedure is as follows:

(a) Weigh 1.20 ± 0.02 g of a representative sample of the toxicant into each of five test tubes;

(b) With a pipette transfer 2 ml of solvent into each test tube;

(c) Each test tube is warmed gently, if necessary, to effect solution;

(d) To test tubes where solution does not occur, add another 2 ml of solvent and repeat the mixing and warming process;

(e) To test tubes still containing undissolved solute, additional increments of solvent are added as in step *(d)* until 10 ml of solvent are consumed. If the solute is still undissolved, abandon further testing and choose another solvent;

(f) Place tubes containing dissolved solute in refrigerator set at 0° C. Observe evidence of any crystallization or stratification after four hours. Add seed crystals of toxicant to tubes which have remained clear;

(g) Add additional 2 ml increments of solvent to those tubes that have precipitated solute and repeat step *(f)* until 10 ml of solvent are consumed.

The results of the experiment are reflected in table 5.

This test is the basis for more exact solubility measurements with the most suitable solvents.

TABLE 5. SOLUBILITY TEST RESULTS

Number of 2 ml increments added	*Minimum solubility*	
	g/ml	*lb/gal*
1	600	5.0
2	300	2.5
3	200	1.67
4	150	1.25
5	120	1.0

Laboratory preparation of emulsifiable concentrates

It is important that a representative sample of the technical pesticide be used for all trial formulations prepared for cold stability or emulsification tests. The presence of impurities can seriously effect the solubility and cold-stability properties, density of the finished formulation and selection of the emulsifier balance.

To facilitate formulation measurement, a multitoxicant calculation system has been designed for fairly precise estimates of weight percentages of formulations.[10]

Emulsifier selection

In selecting the appropriate emulsifier for the concentrate, the formulation chemist must have the co-operation of the biological field research worker or the potential user to answer the following questions:

(a) At what dilution rate will the formulation be applied?

(b) What water hardness range must be considered?

(c) Is the water diluent temperature likely to be unusually warm or cold?

(d) Will agitation of the emulsion be available?

(e) Are any specific properties such as rapid spontaneous dispersion, long stability or excellent reconstitution particularly important?

The selection of an emulsifier or an emulsifier blend for an emulsifiable concentrate is one of the least understood aspects of pesticide formulation. There are many variables which can affect the performance of an emulsifier during the act of emulsification or dilution with water. The following questions may be asked:

(a) Why is not one emulsifier as good as another in a given formulation?

(b) After finding a good emulsifier blend for a particular formulation, cannot the emulsifier be used with equal success in another formulation?

The answer to these valid questions is that a good or well-balanced emulsion involves the selection of an emulsifier blend whose average structure reflects the polarity of both the discontinuous (oil) and continuous phases (water). Both toxicants and their solvents vary considerably in their polarity; in the terminology of the formulation chemist, they are more or less hydrophilic (water-soluble) or lipophilic (oil-soluble).

The following lists of solvents and toxicants rank them from lipophilic to hydrophylic properties:

Solvent	*Toxicant*
Refined kerosene	Malathion
Kerosene (plant)	Parathion
AR solvent (methylated naphthalene)	Heptachlor
Heavy aromatic naphtha	Aldrin
Espesol 3B	Chlordane
Espesol 5	DDT
Xylene 5°	BHC
Toluene	Lindane
Ketone (isophorone)	Dieldrin

A simple explanation of the mechanism of emulsifiers is that they reduce the interfacial tension between oil and aqueous phases, thus permitting one of the phases (usually the oil) to disperse into very fine discrete particles within the continuous (water) phase. If all other factors are equal, the better the reduction of the interfacial forces, the smaller will be the average size of the discrete oil

[10] P. Lindner, *Farm Chemicals*, April issue, 1966, pp. 50-57.

particles. The size of these oil particles governs the relative rate of undesirable creaming of an emulsion. For example, the larger the average oil particle size, the more rapid will be the rate of creaming.

The second function of the emulsifier is to surround each particle with a similar repellant electrostatic charge and to prevent these small discrete particles from colliding and recombining into larger particles, accelerating the rate of creaming and eventually coalescing into a second continuous phase or "oiling out". In reality, no such sharp distinction exists between these two functions, but it helps to explain some anomalous behaviour of emulsions. For example, an emulsifiable concentrate may show excellent, spontaneous dispersion but poor stability on standing. Other emulsions seem to produce much creaming but never oil out, while still other emulsions oil out with little prior evidence of creaming.

These theories would be more helpful if they aided in the selection of effective emulsifiers on the basis of prior calculations of interfacial tension, polarity or the hydrophile-lipophile balance. Although impressive attempts have been made to use the theories, the selection of emulsifiers remains a trial-and-error process.

The development of paired-emulsifier systems is an aid to efficient formulations. Paired emulsifiers roughly reflect the approximate hydrophile side of a class of toxicants. Each member of the pair differs sufficiently in the hydrophile side, however, so that proper blending of the two enables the formulation chemist to produce a balanced formulation of virtually any of the toxicants in the class at any concentration and with any of the more commonly used solvents. There are a number of paired systems marketed, which the formulation chemist should have available for testing work.

The simplest approach to determine the appropriate balance of an emulsifier pair is the preparation of two samples of the test formulation. Each sample should contain a member of the pair in an arbitrarily selected quantity (usually 5 per cent). Blends in ratios of 0:5, 1:4, 3:2, 2:3, 4:1 and 5:0 are tested preferably at practical dilutions in one or a series of water samples of varying but precisely known hardness. After this initial screening is complete, more exact ratios may be derived for optimum performance. Although the standards are somewhat arbitrary, it is generally unsatisfactory for a formulation to oil out within a two-hour period, and the rate of creaming should not exceed 3 to 5 per cent of the emulsion. In selecting the proper emulsifier pair, it is wise not to select a combination that is too sensitive to slight shifts in the ratio of the pair. In any production sequence, the quantities of toxicant, solvent and emulsifier will vary. The system must be able to handle these variations without large changes in performance. It is more desirable to reduce performance factors in favour of a more adaptable system.

A word of caution concerning the accuracy of the emulsion tests is extremely important. The tests must be performed consistently, especially in regard to water temperature, the manner of adding the concentrate to the water, and the type and duration of agitation. If not carefully controlled, all of these factors cause a significant variation in the results obtained in the test.[11]

[11] R. W. Behrens and W. C. Griffen, *Journal of Agricultural and Food Chemistry*, vol. 1, 1953, p. 720.

Occasionally, it may be necessary to correct the balance of an already prepared batch or to make other adjustments. It is helpful to know in which direction to proceed. The following generalizations may be helpful in such cases:

Effects of increasing the ratio toward the lipophilic side	*Effects of increasing the ratio toward the hydrophilic side*
Improved performance in soft water	Improved performance in hard water
Increased tendency to oil out	Increased tendency to heavy creaming
Better stability provided at higher dilution rates	Improved stability at lower dilution
Improved performance in cool water	Improved performance in warm water
Improved spontaneity	Increased aging stability

Storage stability

The useful product life of an emulsifiable concentrate depends on the mutual compatibility of toxicant, emulsifer, solvent, container, dissolved mineral salts, the moisture which may be present in small quantities and the over-all resistance to oxidation. All toxicants deteriorate after a certain time. They usually release acidic products, which, in turn, may accelerate the degradation of the emulsifier or the container. The storage life can sometimes be prolonged by the use of stabilizers such as epichlorohydrin.

Since it is usually impractical to wait several months or years to establish the shelf life of a product before marketing it, the formulation chemist performs storage tests at elevated temperatures. Ideally, the accelerated storage tests are run at series of elevated temperatures; if the reaction order remains constant throughout this range, the stability can be predicted with a fair accuracy at ambient temperatures through the use of the Arrhenius equation. The more usual practice, however, is to make a working assumption regarding the relationship of storage at one elevated temperature to actual shelf life. For example, a commonly used relationship is that one month at 50° C is the equivalent of two years at ambient temperature.

Storage tests should be carried out in the proposed container with control samples in glass containers. At the conclusion of the test, the toxicant assay, emulsification properties and acidity should be determined and compared with data obtained from a freshly prepared sample. The formulation should be examined for stratification or precipitation, and the container should be checked for corrosion.

Tests of cold-storage stability should be run concurrently with the accelerated storage tests. For cold-storage testing, small glass bottles or vials of approximately 4- to 5-dram (16-20 ml) capacity are fitted with tightly closed stoppers. Approximately 8 to 10 ml of trial formulation is placed in each test vial. The studies should be carried out at temperatures of $-24°$, 0°, 7° and 20° C. The samples are seeded at the end of the third day and checked on the tenth day. If crystallization is noted at one temperature but not at the next higher temperature, the solubility is satisfactory at some temperature between those limits. If there is slight crystallization at 0° or $-24°$ C, it is sometimes possible to find a solvent (if xylene or heavy aromatic solvents are being tested) with a higher percentage of aromatics or a higher kauri-butanol number. If the higher-grade solvents are not satisfactory, the solvency of the system may be upgraded by the addition of small quantities of cyclohexanone.

Many formulations are unstable in the presence of iron or are themselves of a corrosive nature and degrade the container causing leakage. As a consequence, the steel pails and drums commonly used for emulsifiable formulations are lined with protective coatings, which are mixtures of phenolic and epoxy resins. Coatings with a high phenolic content are more resistant to acidic corrosiveness than those formulated on the epoxy side, but they suffer the drawback of being very brittle. This characteristic results in the breaking of the coating frequently when the pail or drum is dented and exposes the steel. Therefore, it is economical to select a lining with the highest epoxy content that the corrosiveness of the concentrate will permit.

Oil concentrates

Oil and emulsifiable concentrates have similar concentrations. They are intended primarily for dilution with a low-cost miscible oil such as kerosene, diesel oil or fuel oil before field application, and do not require an emulsifier. Occasionally, the oil concentrates are used to mix pesticides with dry fertilizers or to impregnate dust or granules.

The procedures for solvent selection with oil concentrates are the same as those for emulsifiable concentrates. Acceptability is based upon cold stability at a reasonable or practical concentration. When intended for field dilution with an oil, the ease of miscibility with typical oils should be tested at practical dilution rates. Although the formation of a precipitate after dilution is seldom, its presence indicates that the solvent lacks sufficient coupling power or that the concentration of the active ingredient must be reduced.

Normally, oil concentrates are not as corrosive to container linings as the emulsifiable concentrates. They should, however, be tested with strips of mild steel or tin plate under accelerated storage conditions. Functional characteristics of specific gravity and flash-point should be determined.

ULV formulations

Ultra-low-volume (ULV) oil concentrates are usually sprayed without dilution. Spray volumes are 1 to 4 l/ha with application from either low-flying aircraft or ground-based sprayers.

Of primary importance to the ULV formulator is the volatility and particle size distribution of the spray during the application process. Factors that affect these parameters include volatility of the solvent, viscosity and surface tension of the formulation, application equipment, distance of the nozzles from the spray target and climatic conditions at the time of spraying.

In general, a liquid of moderate viscosity should be used. Low viscosity tends to give spray droplets that are too fine. Increasing viscosity tends to increase the diameter of the spray droplets. Table 6 below shows cases in which 100 μm droplets are most desirable. The least volatile solvent should also be used.

TABLE 6. HALF-LIFE HEIGHT FOR VARIOUS SOLVENTS AT 20° C
(Metres)

Solvent	*Boiling-point (°C)*	*Initial droplet sizes* 50 μm	100 μm	200 μm
Water	100	0.04	0.5	4.6
Cyclohexanone	156	0.05	0.6	5.3
Butyl cellosolve acetate	188	0.5	5.5	41
Hexylene glycol	196	3.5	37	270
Dimethyl phthalate	282	110	990	6 400

Source: A. Grubenmann and F. Neuenschwander, *Advances in Pesticide Science*, H. Geissbuhler, ed. (Oxford, Pergamon Press, 1979), p. 813.

ULV formulations should be applied with a mean droplet size of approximately 100 μm (volumetric mean diameter). Considerable loss of the spray due to drift will occur if the size of the spray droplets is reduced to 50 μm. If the droplet diameter is in the range of 200 to 400 μm, coverage is much poorer and the danger of phytotoxicity to foliage is considerably increased.

The boiling-point of a solvent is a good measure of the volatility of the solvent. The higher the boiling-point, the lower the volatility. As table 6 shows, the more volatile solvents will lose 50 per cent of their volume during relatively short distances of fall.

Candidate formulations should be evaluated for potential drift (formation of fine particles that are carried away from the target by wind) by adding an oil-soluble dye to the formulation, spraying the formulation in a downward direction, placing a clean white target downwind from the spray and observing the amount of dyed fine particles that impinge on the target. The best formulation will have the least spray on the downwind target. If there is little or no wind, one may wish to use a fan that would blow a wind across the spray pattern.

Aqueous concentrates

Aqueous pesticide concentrates are water solutions of salts of organic acids (usually herbicides, which include dicamba, 2,4-D and 2,4,5-T). They are mainly dimethylamine salts, although sodium, potassium or lithium salts are sometimes used.

Solvents

Because water is the solvent used for aqueous concentrates, there is a definite solubility limitation to the concentration of active ingredient contained in the solutions depending upon the cation. The dimethylamine salts generally give adequate cold stability as well as good performance in the field.

Effects of hard water

Some organic carboxylic acids, such as 2,4-D, 2,4,5-T and MCPA form insoluble salts in the presence of cations, such as calcium and magnesium found in hard water. Dicamba does not present this problem. Water hardness, however, can be overcome by the use of chemical sequestering agents added to the concentrate or to the tank at the time of field dilution. Among the sequestering agents are sodium polyphosphate, ethylenediamine tetracetic acid and its derivatives, and citric acid salts. Some lignosulphonates have been used as sequestering agents to prevent precipitation of the active agent by hard water. When iron is present in the water in quantities exceeding several parts per million, sequestering agents related to ethylenediamine tetracetic acid are used.

Acidity and pH

The addition of base to the herbicidal acids in stoichiometric quantities will produce solutions having different pH values that are usually alkaline because the acid strength, ionization constants and acidic impurities of herbicidal acids vary. The stronger the acid, the closer the pH value is to 7. If dimethylamine is used as the base of the salt, an excess will result in a product with an objectionable amine or fish-like odour.

Storage and stability

The herbicidal acids are generally quite chemically stable in aqueous concentrates of their salts; however, accelerated storage tests should be run for any new herbicidal acid or aqueous concentrate in the normal manner at 50° C for periods up to 90 days. The packaging of aqueous concentrates of herbicidal acid salts in metal containers often presents problems of corrosion. For pails and drums, however, pigmented, high-baked phenolic linings as well as modified epoxy linings overcome some of the difficult problems of container corrosion. For small packages up to 4 l in size, high-density polyethylene bottles and jugs are satisfactory.

Evaluation of functional characteristics

Aqueous concentrates may be characterized by a specific gravity determination. Aqueous concentrates are subject to freezing at very low temperatures. Banvel 4S is the 48 g/100 ml concentrate of dicamba dimethylamine salt; it will freeze at approximately −20° C. However, when warmed to room temperature, the properties of the formulation are unchanged.

Dry formulation

Dry formulations include dust bases, water-dispersible powders, flowables, dusts, granules, dispersible granules and capsules. Dry formulation of a new pesticide chemical requires prior study of its compatibility with typical carriers and diluents.

Dust bases

Dust bases must be dry, finely divided and flowable powders; capable of easy dilution with a variety of inert powdered diluents to produce a uniform dusting powder; sufficiently high in concentration to permit economical storage and shipment while allowing simple calculations for the dilution process; non-caking and flowable under all conditions of storage; and chemically stable in storage for several years under normal storage conditions. If deactivation is carried out as above to permit 5 per cent or less decomposition for 90 days under accelerated conditions, the last requirement is generally met.

Stability studies and deactivation

A practical method is to prepare a 5 per cent dust formulation of a number of typical mineral carrier and diluent classes such as diatomaceous earth, attapulgite, montmorillonite, kaolinite, pyrophyllite, talc and calcium carbonate or powdered limestone. A convenient quantity to handle is 250-500 g of the finished product. The active ingredient can be mixed in a beaker of suitable size by a slow-speed paddle stirrer or simply with a flat metal spatula. If the pesticidal chemical is a liquid, a porcelain mortar from 15 to 20 cm in diameter and a matching pestle generally provide good mixtures. The crude mixtures thus prepared are ground further in a laboratory grinding mill. After grinding, the pulverized product is blended in a jar tumbler or in a 0.5 or 1 l twin-shell blender. The material is then separated into several portions and a small quantity sufficient for the initial chemical analysis is withdrawn.

One portion of the preparation is precisely labelled and subjected to room-temperature stability studies. The other portions are placed in a constant-temperature oven at elevated temperatures for accelerated storage tests. After 7, 14 and 28 days from the beginning of the accelerated storage tests, small samples of the 5 per cent dust formulations are withdrawn and analysed for active ingredients. The results of analysis are compared with the results of the initial assay of the formulation and the rate of decrease in active ingredient content after each storage period to indicate chemical incompatibility. If decomposition at the end of the 28-day period is less than 1 or 2 per cent of the active ingredient initially present, accelerated storage tests are continued for two or three months.

Decomposition proceeds at a faster rate with the more absorbent clays such as montmorillonite and attapulgite. Some of the less absorbent materials contain highly surface-active impurities that cause rapid decomposition. Diatomaceous earth, even though generally more absorbent than attapulgite and montmorillonite, does not normally possess the surface acidity associated with the clays; catalytic decomposition, therefore, occurs at a lower rate.

The decomposition of pesticides incorporated with dry mineral carriers occurs by one or more of the following principal mechanisms: catalytic decomposition resulting from surface acidity, the acidity or alkalinity of the carrier or diluent and thermal effects. If the rate of decomposition follows approximately the absorbency of the carriers or diluents (with the exception of diatomaceous earth), catalytic surface acidity is certainly involved in the decomposition rate. However, if the rate of decomposition is greater for the attapulgite or montmorillonite carriers, the pH value of the carrier is involved.

Attapulgite is slightly alkaline and montmorillonite is acidic. Therefore, if the rate of decomposition with attapulgite is greater than that with montmorillonite, the active ingredient is very probably sensitive to mild alkaline reactions. If the active ingredient decomposes at a very low rate or not at all with talc and pyrophyllite but at a significant rate with montmorillonite and attapulgite, the catalytic surface acidity is involved. If, however, the rate of decomposition with talc and pyrophyllite is significant and nearly equal to that found with diatomaceous earth as well as with kaolinite, attapulgite and montmorillonite, the active ingredient is thermally unstable at least at the elevated temperature of the tests. An additional cause of decomposition or decreasing assay is hydrolysis in the presence of moisture or volatilization.

Volatilization is usually a minor factor which can be minimized by conducting the storage tests in small, tightly closed containers. The effect of moisture can be verified by preparing a 5 per cent dust on a carefully dried sample of talc or pyrophyllite and conducting parallel tests with the same diluent to which small increments of 0.5 per cent or more of moisture have been added.

A word of caution concerning the accuracy of the assay method of testing is advisable at this point. Because laboratory stability studies must be based upon chemical assay methods, it is necessary that all aspects of the assay method be fully developed before chemical compatibility and stability studies are undertaken. Most assays of dry formulations are based upon the analysis of a solvent extract of the active ingredient from the carrier or diluent. This extract is then usually analysed by chemical, infra-red or other spectro-chemical methods or gas chromatography. In these steps of the assay procedure there is seldom any great difficulty. However, the accuracy of the assay procedure is dependent upon the accuracy of the extraction procedure. Difficulties often can be encountered because the extraction solvent must be capable of dissolving a significant quantity of the active ingredient, and the solvent should be capable of displacing any active ingredient which has been absorbed by the diluent or carrier particles. It has been observed that polar molecules such as dicamba are very strongly absorbed by some clays such as attapulgite. Therefore, in order to displace them, a more strongly polar solvent such as acetone or alcohol may be necessary to effect a complete extraction.

In all stability studies, it is desirable to determine the identity of decomposition products when instability of the active ingredient is observed after accelerated storage tests. A complete analysis of the experimental formulation to obtain a material balance follows. If an experimental formulation is found by assay to contain only 70 per cent of the initial active ingredient, the remaining 30 per cent of decomposition products should be identified and measured quantitatively.

Carrier selection and concentration limits as a function of physical properties

The most important physical properties of a technical grade pesticidal chemical which determine the selection of the carrier used in dust bases are the physical state, the melting point and the specific gravity. The simplest materials to handle are the powder or crystalline pesticidal chemicals with melting points of approximately 90° to 100° C. Among the most difficult materials are low-melting solids because their waxy nature prevents convenient handling of them as solids. Although the liquid pesticidal chemicals can be incorporated with absorbent carriers by a straightforward spray impregnation method, the necessary equipment is more complex to install and control than the equipment for dry, powdered pesticidal chemicals.

The most important properties of a carrier for dust bases are sorptivity, pH and surface acidity. When formulating powdered, high-melting pesticidal chemicals, however, sorptivity is of little or no importance because the active ingredient can be combined with the carrier by a simple dry-blending process and the mixture reduced to the desired particle size by mechanical grinding. There is generally no serious problem in attaining high concentrations of the active ingredient in dust bases with pesticidal chemicals having melting points above 100° C. Indeed, with such materials even less sorptive diluents such as talc and pyrophyllite may be used. Fortunately, these diluents of low sorptivity generally have a low surface acidity so that only small quantities of deactivator are necessary. These diluents are fortunately much lower in cost than the more absorbent carriers. Pesticidal chemicals having high melting points can be readily and more economically formulated than liquid or low-melting, solid pesticidal chemicals.

It was pointed out earlier that the sorptive capacity of a mineral carrier is inversely proportional to its bulk density, and that the sorptivity of a given liquid in per cent by weight of finished formula is directly proportional to the density or specific gravity of that liquid. In other words, a clay which can be used to formulate a dust base having 40 per cent chlordane of specific gravity 1.6 can only contain up to 25 to 30 per cent of a liquid pesticide having a specific gravity of 1.5 to 1.2. Therefore, the chlordane sorption value of the carrier should be known as well as the density of the liquid pesticide with the carrier relative to that of chlordane. To determine the chlordane sorption value, the "rub-out" sorption test may be used.

Two additional factors that limit the percentage of active ingredient which can be formulated with absorbent carriers in dust bases are the assay or active equivalence content of the technical pesticide and the quantity of solvent which must be combined with the technical pesticide efficiently to incorporate the active ingredient with the carrier. For example, technical methyl parathion normally contains 80 per cent active ingredient. Therefore, to prepare a 25 per cent dust base, it is necessary to use the ratio 25/0.80 or 31.25 per cent of technical methyl parathion in the formulation. Similarly, to prepare a 25 per cent heptachlor dust base from a technical heptachlor assaying at 74 per cent, it is necessary to use 33.8 per cent of the technical heptachlor. Because technical heptachlor is a low-melting waxy solid, it is convenient to melt it and add a small quantity of solvent to improve handling and spraying characteristics. Thus the quantity of liquid to be sprayed upon the carrier is increased to between 37 and 40 per cent.

Technical chlordane, on the other hand, is a liquid used on a 100 per cent active ingredient basis. Its sprayability can be improved by slight warming to reduce the viscosity. Because of its high specific gravity, chlordane can be readily formulated up to a 40 per cent active ingredient concentration on absorbent carriers, such as attapulgite or diatomaceous earth.

Chlordane and toxaphene are among the few liquid or low-melting, solid pesticides which can be formulated in concentrations of 40 per cent or higher on simple carriers such as attapulgite. The reason is their high specific gravity and the fact that they are liquids or very low-melting solids with a high degree of solvency or miscibility in solvents such as kerosene. If a high concentration such as 40 per cent active ingredient is required for pesticides as in heptachlor, it may be necessary to use diatomaceous earth and to supplement the absorbency of the carrier by the addition of highly absorbent material such as synthetic silica. Such a formulation prepared from technical heptachlor and using an auxiliary solvent will contain 65 to 70 per cent liquid. Because synthetic silica is a relatively expensive material, it is seldom used as a primary carrier but is frequently used to upgrade the absorbency of natural clay.

Storage stability

Accelerated storage stability should be determined on the finished formulation by placing the sample in a sealed container in an oven maintained at 50° C. Assays should be made on the initial sample and after 30 days' storage. Duplicate analysis should be made of both the initial and the aged samples. The average loss in 30 days determined by an assay should be less than 2 per cent.

It is important that the formulation exhibit non-caking tendencies when stored at 50° C for 24 hours under a static pressure of 25 g/cm^2. This is determined by measuring the percentage of the powder retained on a 100 mesh (United States standard sieve series) or 149 µm screen using a Tyler Ro-tap sieve analysis machine.[12] The quantity retained on the 100 mesh screen should be less than 5 per cent of the quantity that is retained on a sample of the same formulation which has not been subject to accelerated storage tests.

Water-dispersible powders

Water-dispersible powders generally have the same concentration units (percentage by weight) as the dust bases of the same pesticide. Water-dispersible powders are similar in appearance and have approximately the same bulk density, but there are functional differences in their use. Dust bases are generally diluted with a dry, powdered inert such as talc or pyrophyllite, while water-dispersible powders are primarily diluted with water for a spray formulation. Although it is possible to dilute a water-dispersible powder with talc, pyrophyllite or other inert material to make a dust formulation, the water-dispersible powders have additional functional ingredients and more rigid specifications which make them more expensive than dust formulations.

Stability studies and deactivation

Because water-dispersible powders are special forms of dust concentrates, the procedures for determining stability and the necessary quantity of deactivator to prevent decomposition are the same as for the dust concentrates. Certain wetting agents can function as deactivators. However, they are used in small quantities and only partially deactivate the formulation.

Carrier selection and concentration limits as a function of physical properties

The formulation of water-dispersible powders is similar to the formulation of dust bases since absorbent attapulgite, montmorillonite or diatomaceous earth carriers must be used for liquid and low-melting pesticides. For the medium to

[12] Ro-tap is the registered trade mark of the W. S. Tyler Co., Cleveland, Ohio, United States. A description of this machine is given by World Health Organization, *Specifications for Pesticides*, 2nd ed. (1961), p. 521.

high-melting pesticides, however, highly absorbent clay or material with low absorbency such as talc, kaolinite and pyrophyllite must be used as diluents. The detailed discussion of these points for dust bases is applicable to water-dispersible powders.

Storage stability

It should be tested by accelerated storage. The suspensibility and toxicant stability of a water-dispersible powder should be controlled after the storage test.

Wettability and suspensibility

The wettability of the powder is the time required for a given weight of the formulation to be completely wet and submerged beneath the water surface. The shorter the period of time (in seconds) required for wetting, the better is the wettability of the formulation. In addition, a water-dispersible powder must remain uniformly suspended and free of nozzle-plugging agglomerates in the mixing tank throughout the application period.

The stability of a suspension of solids is dependent upon a balance of several forces. Stokes' law indicates that stability is favoured by increasing the viscosity of the suspending medium or by reducing the size of the particle. Therefore it is desirable to reduce the particle size as much as possible by a suitable milling operation. Unfortunately, as the size of a particle is reduced, the small attractive forces on its surface become significant with respect to the particle's mass. This effect causes the joining together of several particles into larger agglomerates, which settle more rapidly because of the increased size and thereby plug nozzles. Occasionally, this behaviour results in the formation of a flocculent curd in the suspending medium.

To prevent agglomerate formation, surface-active materials are introduced into the formulation as suspending or dispersing agents. They surround each particle with a like electrostatic charge and cause a reorientation of the molecules surrounding the particle into an electrical double layer. This layer develops a potential with respect to the rest of the system, which wards off collisions with other particles. Wetting agents reduce the interfacial tension between the powder and the suspending medium.

The suspension characteristics of the formulation may be improved by increasing the viscosity of the medium. In practice, sodium carboxymethylcellulose, polyvinylpyrrolidone and other water-soluble polymers are added to water-dispersible powders. However, when added to water, these materials have little effect upon the viscosity because of their low concentration. Certain formulations benefit from their addition possibly due to the formation of a protective colloid around the particles to prevent agglomeration and settling.

Surfactant selection

This is primarily an empirical process. Surfactant systems used in the formulation of water-dispersible powders usually consist of a wetting agent and a dispersant. Wetting agents are generally sodium salts of alkylbenzene sulphonic acids, although non-ionics such as the polyethylene oxide derivatives of alkyphenols may sometimes be used. Other anionics such as alcohol sulphates and sodium sulphosuccinates provide good wetting performance. In some systems, however, these materials show excessive foaming tendencies. A number of trials are necessary before a satisfactory wetting agent is found. The dispersants are generally anionic materials and are frequently salts of lignosulphonic acids and sulphonated polyphenols. The quantity of wetting agent and dispersant generally used varies from 1 to 1.5 per cent each. Their ability to perform satisfactorily with a specific carrier pesticide combination is often very selective. The choice of the proper pair and ratio is based upon the results of selective testing of each wetting agent in combination with each dispersant. For example, if four wetting agents and four dispersants are selected from a number of typical compounds, 4 × 4 or 16 individual wettability and suspensibility tests are performed for the surfactant system at the same concentration level.

Procedure for evaluating wettability

Weigh one half of the experimental formulation on a 10 cm piece of glazed paper. Pour the powder rapidly but gently on to the surface of 100 ml of water contained in a 100 ml graduated cylinder. Measure the time with a stop watch from the moment the powder is placed on the surface of the water until 90 to 95 per cent of the material has become wet and submerged below the surface of the water. The time (in seconds) is the wetting time of the formulation.

Flowables

Flowables are basically concentrated water-dispersible powders that are dispersed in a liquid medium. The formulations require all the conventional physical properties of water-dispersible powders, but have, in addition, a requirement of remaining dispersed or suspended in the liquid for long periods of time and through a variety of temperatures.

This maintenance of dispersibility, or lack of agglomeration, requires that the particles remain separated, one from another, and remain suspended without aggregating into a sludge on the bottom of the container. Because most flowables tend to sediment and require some degree of mixing (comparable to normal problems of latex paint formulations), the formulations are usually not packaged in greater than one liter quantities.

Maintenance of physical separation of particles requires two additional additives, one, a hydrophilic colloid to coat the individual particles and increase the viscosity of the medium, and a second additive, a combination of surfactants and polyelectrolytes to effect a high surface charge on the suspended particulate.

The surface charge on the particulate is frequently identified as the zeta potential. This refers to an electrical potential at the solid surface due to a charge separation between the surface and counter ions in the suspending medium. One manner of building up the zeta potential to a high enough value to effect stability is to add a mixture of a nonionic surfactant and a phosphate derivative of an anionic surfactant. The nonionic surfactant tends to adsorb at the interface while the phosphate builds up the charge on the surface by a charge transfer mechanism.

The flowable formulations should be checked for dispersibility and ability to pass through fine screens after the compositions have been aged for several weeks at 35° C and have gone through several temperature cycles between 5° and 35° C.

Dusts

Pesticidal dusts are dry-powder formulations for application in the field without further dilution. Dusts are identical in appearance and general form to dust bases or concentrates. However, dusts contain a much lower concentration of active ingredient which may vary from 1 to 20 per cent. Pesticidal dusts are prepared by the dilution or cut-back of a dust or concentrate with a suitable inert powdered diluent or by directly combining the active ingredient with the diluent in the desired concentration.

A cut-back procedure requires a minimum of processing detail to obtain a uniform product. The cut-back process is preferable when dusts are made from pesticidal chemicals which are liquids or low-melting solids, or when powdered or high-melting, solid pesticidal chemicals are present in low concentrations of 1 to 3 per cent of the active ingredient.

If dust formulations are made directly from liquids or low-melting solids, a solvent is usually necessary to improve the spraying quality. The sorptivity of the diluent should be greater than that of the talc, pyrophyllite and calcium carbonate that is used. Possible absorbent diluents are attapulgite and montmorillonite, or kaolinite, which is somewhat less absorbent. One disadvantage of preparing dusts on absorbent carriers by impregnation is that often relatively large quantities of a deactivator are necessary to prevent decomposition of certain pesticidal chemicals, such as heptachlor and methyl parathion. If talc, pyrophyllite or calcium carbonate is the diluent in the cut-back procedure, deactivation of the carrier often is unnecessary, or at the most only 1 to 2 per cent may be required. A further advantage is that the low-sorbency diluents are frequently less than one-half as costly as absorbent carriers.

If pesticidal dusts are to be made directly from solids or high-melting pesticidal chemicals, the active ingredient should be as finely powdered as possible. Furthermore, after deactivation and during the blending operation, representative samples should be withdrawn from various sections of the blender. The samples should be analysed for uniformity by assaying the active ingredient in each sample. Following blending by cut-back or direct blending, the finished mixture is ground by a suitable mill such as a Raymond mill or a micropulverizer and discharged into a blender to assure uniformity. As most diluents consist of very fine-sized particles, the grinding operation is not for particle size reduction but for obtaining a very thorough mixture of the active ingredient with the diluent to minimize segregation during storage and to assure a uniform product during the application.

Diluent selection

There is no generally accepted standard for the particle size or particle size distribution of diluents. The size generally ranges from 140 mesh (105 μm) to 270 mesh (53 μm); 90 to 95 per cent of some of the finer diluent products may even pass through a 325 mesh (44 μm) screen. However, for aerial application, the coarser dusts are generally more suitable because of lower drift than the extremely fine powders. For ground application to crops with a very dense foliage, a very fine dusting powder should be used to obtain a uniform coverage of all plant surfaces. Pyrophyllite is probably the most widely used diluent for pesticidal dusts. It is followed in popularity by talc and calcium carbonate. A number of other low-cost mineral-type diluents are used, for example dolomitic limestone and kaolinite, which have good sticking properties on plant surfaces. The low cost or local availability of diluents frequently affect the choice. The suitability of any diluent, however, should be determined by comparative field tests in the areas intended for their use.

Stability studies and deactivation

Even though many of the diluents, such as talc and pyrophyllite, have less surface activity and fewer acid sites than the more absorbent clays, their use in dilute dust formulations provides a relatively large number of active acid sites per unit of active ingredient. Consequently, the deactivation of the diluents to prevent decomposition during storage is necessary.

Evaluation of physical characteristics

To perform efficiently in dust application equipment, the flowability of the formulation is important. Generally, the flowability of a formulation prepared by liquid or low-melting, solid formulations either by cut-back or direct impregnation, decreases as the concentration of the active ingredient increases. The addition of 0.1 to 0.5 per cent of colloidal pyrogenic silica pigment improves the flowability. Because pesticidal dusts are metered volumetrically when applied by field dusting equipment, the bulk density of the product is important and must be controlled.

Granules

Most granular pesticides are produced by the spray impregnation of a pesticidal chemical or a solution of a pesticidal chemical upon an absorbent granular carrier. The maximum quantity of active ingredient which can be incorporated in this manner depends upon the sorptivity of the granular carrier and the purity and density of the pesticidal chemical or the density and the concentration of the active ingredient.

Pesticidal chemicals that have too low solubilities for formulation by impregnation may be processed into granular form by techniques based upon extrusion, pan-coating and pan-rolling. Although these techniques are used to some extent, they require specialized equipment that is not available to many formulators.

The two most important characteristics of granular pesticides are concentration and particle-size range. Although the maximum concentration is limited by the physical properties of the pesticidal chemical and the carrier, it is as low as 1.5 per cent for an endrin granule to as high as 40 per cent for a chlordane granule when granular attapulgite is the carrier. The particle size or particle-size range is normally based upon the selection of the properly sized carrier. Although granular pesticides range from 4 to 80 mesh, typical sieve size designations are 16/30, 20/40 and 30/60. One granular carrier used for special purposes is 20/25 attapulgite.

Other desirable characteristics of granular pesticides are storage stability, resistance against attrition, resistance against caking during storage and good flowability. The rate at which the granule releases the pesticide is difficult to control with impregnated pesticides. It is usually an inherent characteristic of the pesticidal chemical itself and the carrier. In actual practice, the release rates for different uses vary; each use must be treated individually.

An important requirement of granular pesticides is the uniform distribution of the active ingredient on all particles. To accomplish this by spray impregnation, spray nozzles must have an extremely low discharge rate. Rotary or tumbling mixing equipment should be used to minimize attrition of the particles.

Several types of equipment which are suitable for the laboratory development of granules are the double cone blender, the Patterson-Kelly twin shell blender and the Nauta mixer. They can be obtained in capacities of 57 l or less and can be fitted with an internal spray attachment. The liquid handling system consists of a spray tank with a capacity of 1 to 2 l with an agitator and heating facilities. The liquid is carried to the spray nozzle either by a small gear pump or in a closed spray tank; it is pumped to the nozzle by compressed air or nitrogen. The liquid system should be capable of operating at pressures of 1.3-4.0 bar. To prepare formulations for which the spray liquid must be heated, all spray lines and the pump must be heated to prevent a drop in temperature of the spray liquid and to avoid crystallization. A fine filter with a particle size retention capacity less than that of the diameter of the nozzle is installed between the pump and the nozzle. To protect the pump from foreign particles, a 140 to 200 mesh basket strainer is placed between the spray tank and the pump. The positive-displacement gear pump should have an adequate by-pass circuit and a throttling valve for pressure regulation and control.

Carrier selection

The principal carriers used in the formulation of impregnated pesticide granules are granular attapulgite and non-swelling montmorillonite. Kaolinite, pyrophyllite, talc and calcium carbonate have been tested as granular carriers, but they are generally too soft (suffering attrition during the impregnation process) or too low in absorbency. Swelling bentonite, which is a montmorillonite, is useful when high absorbency is not required. Granular vermiculite has many desirable properties for granular pesticides. However, because it has a relatively low bulk density, hoppers must be reloaded more frequently than is necessary for formulations based upon attapulgite or montmorillonite with the same concentration of the active ingredient.

Vegetable materials which have been studied and used to a limited extent are maize cob grits and crushed walnut and pecan shells. Maize cob grits have many desirable characteristics such as inertness, fair absorbency, resistance to abrasion and a bulk density of about 448-480 kg/m^3.

The absorbency and catalytic surface acidity of all potential granular carriers should be studied. Because the sorptivity of a granular carrier is difficult to measure on a small scale, the carrier can be pulverized in a laboratory grinder and then the sorptivity is determined by the rub-out method. The sorptivity for granular pesticides is close to the chlordane absorption value as determined by the rub-out method. The catalytic surface acidity and the necessity for deactivation are determined by using the same test methods as for other dry formulations.

Typical particle-size ranges normally used for pesticide granules are 16/30, 20/40 and 30/60. These carriers should be tested to ensure that 90 per cent of the particles fall between the upper and lower limits of the particle-size range and the remaining 10 per cent are distributed randomly on either side. The maximum quantity permitted to pass through the finest screen should be specified because further attrition of the particles might conceivably occur during processing, bagging, shipping and handling, and result in undesirable fines. It is recommended that a maximum of 1/10 of 1 per cent be permitted to pass a 100 mesh (149 μm) screen.

The bulk density of a granular carrier is an important property because it determines both the size of a batch which may be produced in a blender of a given capacity and the size of the bag which is to be used for the container. Because the formulation of impregnated granular pesticides involves the absorption of all liquid ingredients, the volume of a given weight of formulation is the same as that of the unimpregnated carrier which it contains. Table 7 shows properties of typical granular carriers.

TABLE 7. PROPERTIES OF TYPICAL GRANULAR CARRIERS

	Bulk density (kg/m^3)	*Relative sorptivity*	*Relative hardness*
Inorganic			
Clays and minerals			
Attapulgite	449-577	High	High
Montmorillonite	881-1 041	Low	High
Diatomite	320-481	High	Medium
Vermiculite	128-192	High	Low
Organic			
Botanical			
Maize cob	352-513	Medium	Medium
Nut shell	561-721	Low	Medium

The use of solid pesticides in dust and granular formulations may cause caking depending on the concentration of the toxicant, the volume of liquid solvent and the handling conditions. Attapulgite and montmorillonite vary in their particle size and sorptivity, and these properties are critical to caking in border-line formulations. Because carriers adsorb and absorb differently, the time of pesticide distribution is critical for certain carriers.

The semi-solid pesticides such as heptachlor and aldrin have more problems with caking than the high-melting pesticides such as dieldrin and endrin. Liquid pesticides seldom cause caking on granules or dusts.

Deactivator requirements

The stability and deactivator level studies for granular pesticides are the same as those for the powdered dry formulations. Initial stability tests may be satisfactorily carried out on a small scale and at concentrations of 5 per cent active ingredient. Because it is not convenient or practical uniformly to impregnate granules in small quantities, the granular carrier may be pulverized for these tests. The quantity of deactivator required for each mineral type is nearly the same as the quantity required for dust bases and concentrates. If the quantity has been previously determined, additional experiments with the powdered granular carriers can be held to a minimum.

In formulating granular pesticides which require deactivation, every particle of the carrier must be uniformly deactivated. For pesticidal chemicals which are extremely sensitive and have an initial rate of decomposition which is more rapid than the rate of deactivation, it is necessary to deactivate the carrier prior to the spray impregnation of the active ingredient. If the deactivator is a solid, such as HMT or urea, it is dissolved in a minimum amount of water or other suitable solvent and sprayed directly onto the carrier. Alternatively, solid deactivators of this type are finely pulverized and blended with the carrier prior to spray impregnation. The spraying of a solution of a deactivator is generally preferable. Liquid deactivators are spray-impregnated directly upon the carrier with or without addition of water to attain a more uniform distribution.

If the rate of decomposition of a pesticidal chemical on a surface-active carrier is reasonably less than the rate of deactivation, the deactivator is dissolved or mixed in the concentrated spray solution to permit simultaneous deactivation and spray impregnation. Generally, this is a desirable procedure because the large volume of liquid sprayed onto the carrier increases the probability of a uniform distribution of the active ingredient and the deactivator.

Solvent selection

Spray concentrates used for the impregnation of granular carriers are normally prepared in batches at the time of formulation. Because the spray operation is carried out at any temperature from ambient room temperature up to 82° C, there are no limits to the cold-solution stability as there are for emulsifiable concentrates and oil bases. The solvent portion of a granular formulation has the following three principal functions to maintain the pesticidal ingredient in a liquid condition so it can be sprayed, to provide sufficient volume for uniform distribution of the pesticide (and deactivator) upon the carrier, and to reduce the viscosity of the liquid or molten pesticidal ingredient for good atomization from the spray nozzle. Heat is applied to the spray liquid to maintain a temperature at which crystallization cannot occur and to reduce the viscosity for improving sprayability. The viscosity of the spray mixture at the spraying temperature preferably should be below 10 cP (10 mPa.s). Generally, the effectiveness of atomization increases as the viscosity decreases.

For economic and safety reasons, hydrocarbon solvents such as kerosene, xylene and heavy aromatic naphtha are preferred. These low-cost solvents have flash-points of 27° C or higher. When hydrocarbon solvents are unsatisfactory because of poor solubility, polar solvents such as cyclohexanone, diacetone alcohol and normal propyl alcohol are used. Volatile solvents, such as methylene chloride, are used with suitable allowance for their evaporation from the formulation. It is essential that evaporative systems be designed with worker safety as a primary concern. The higher-boiling solvents, which evaporate more slowly, are included in the final weight of the formulation.

For the simultaneous impregnation of the deactivator and the toxicant-solvent system, all materials are combined in the spray tank, which should be heated if necessary to bring them to the proper temperature for complete solution and viscosity reduction. If the deactivator or deactivator mixture is immiscible with the toxicant spray solution, an efficient agitator in the tank keeps all material uniformly dispersed. If extremely high concentrates of pesticidal chemical and solvent are to be sprayed at elevated temperatures, all spray lines, filters, pumps and nozzles must be heated to prevent a loss of heat and possible crystallization during the spray cycle.

The position of the nozzle in the blender must place it directly in the centre of the plane of granules when the blender is in motion. The axis of the nozzle should be exactly perpendicular to this plane, and the orifice should be at a sufficient distance from the plane of granules so that maximum coverage of the surface is attained just within the outer periphery of the spray pattern hitting the walls of the blender. A spray nozzle giving a full cone pattern with a 120° spray angle is effective.

Sieving and attrition tests

A necessary condition for the spray impregnation and blending process is that the attrition of the particles to produce fines be minimal. A sieving test on both the finished product and the untreated granular carrier indicates excessive attrition; for example, if the number of particles passing the finest screen designation of the nominal particle size increases by 5 per cent of the total weight of the formulation. The problem can be overcome in the following ways: select a carrier which is harder or less subject to attrition; select a carrier which is more skewed toward the larger particle size of the distribution; decrease the blending cycle; or redesign various steps in the loading, blending and discharging process. Attrition that takes place in the handling of the granule by equipment such as a screw elevator can be substantially reduced by the use of bucket elevators or pneumatic conveyors.

Stability and storage tests

Experimental granular formulations of the chlorinated hydrocarbons should be tested for storage stability by accelerated ageing at 50° C. The samples are placed in tightly closed jars and kept at the elevated temperatures for periods up to 84 days. To begin the tests, each sample is analysed for active ingredient immediately after preparation. The samples in accelerated storage conditions are reassayed after periods of 7, 14, 28, 56 and 84 days. A maximum loss of 5 per cent active ingredient in 84 days is acceptable.

Dispersible granules

Dispersible granule technology combines the know-how of both water-dispersible powders and granules to yield this new type of formulation. With the large number of diversified formulation ingredients, particular care must be taken to select components that do not significantly interact with one another during long-term storage. Reaction between ingredients is particularly evidenced by loss of dispersibility of the granules after storage at an elevated temperature of 50° C for 84 days.

Granules are frequently formed using pellet mills similar to those used in catalyst manufacture. Pelletization is aided by adding a small amount of water to the mix; the amount will vary depending upon the sorptivity of the diluents used. Following pelletization the granules are dried under conditions that do not decompose the toxicant.

Break-up of the granules into dispersed particulates (that is, like a water-dispersible powder) is accomplished by adding a swellable type clay such as bentonite or a combination of a solid acid and a carbonate. When bentonite swells it obviously creates a force that disrupts the granular structure facilitating the dispersion of the fine individual particles. When an acid and a carbonate are present and the material is placed in water, the acid and base react giving off carbon dioxide and water. The release of the gaseous carbon dioxide aids in the break-up and dispersion of the fine particles.

Capsules

Microcapsules have proved advantageous where the environment may adversely affect the stability of a pesticide or where a controlled release (that is, gradually making a pesticide) available to the environment over an extended period of time is desired. Much of the technology was developed in the late 1950s and 1960s[13], and many of the original patents (United States 2,800,457 and United States 2,800,458, 23 July 1957) have now expired.

There are many processes of encapsulation. One of the most popular involves the concept of coacervation, which is a phase separation that occurs when negatively and positively charged colloids neutralize each other. If an oil solution (which may contain a pesticide) is present, it may act as a nucleating agent whereby the neutralized colloids coat the dispersed oil phase as they go through the phase separation process.

The coacervation process is exemplified by the following quote from United States 2,800,457:

> "A sol is made of 20 grams of gum arabic dissolved in 160 grams of water. Gum arabic in water always forms negative ions, it not being amphoteric, regardless of the pH. Into this is emulsified 80 grams of trichlorodiphenyl. A second sol of 20 grams of pork skin gelatin, having its iso-electric point at pH 8, and 160 grams of water is prepared, and this second sol is mixed with

[13] A. Kondo, *Microcapsule Processing and Technology*, J. W. Van Valkenburg, ed. (New York, M. Dekker, 1979).

the emulsion. A volume of water then is added slowly to the mixture drop by drop, or by spray with constant stirring until coacervation starts and is continued until the particle size of the oil droplets on which the coacervate material is deposited is as large as desired, the less water used the smaller the particle size. All of the foregoing steps are carried out with the ingredients at 50 degrees centigrade. The resulting coacervate mixture is poured into water at 0° C, enough water being used to bring the total weight of ingredients to 3,960 grams. The mixture is agitated and thereafter is allowed to stand for an hour at not over 25° C. The formation of the capsules is now completed, and they may be used in suspension as a coating for surfaces or for other use as a fluid, or they may be dried and comminuted."

Prior to the isolation of dry discrete capsules it is advisable to harden the polymeric shells through the use of aldehyde cross liners.

III. Technical and environmental aspects in siting, construction and operation of a pesticide formulation plant

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In the planning, design, construction and operation of a pesticide formulation plant, the following logical sequence of steps occurs: preparation of flow diagrams of raw materials to finished products; planning packaging operations; meeting storage requirements; choice of plant equipment; deciding plant lay-out and the physical structure of the building; and construction.

Chapters IV and V cover the feasibility of planning based on an economic analysis of the market and product range. However, the physical properties of the products themselves mainly determine the design and construction of the plant. In addition to the purely technical factors, consideration must be given to potential occupational hazards and environmental pollution in the operation of a pesticides formulation plant. All those factors taken together influence the site selection, design, construction and operation of the plant.

Site selection

Site characteristics

Choice of location

Whatever decision is taken on the products to be formulated, certain technical and environmental requirements for the site will not vary. The plant should be located on level ground not subject to flooding, ideally away from towns or, at least, not on the windward side, and accessible to a source of labour. The shape and area of the site should lend itself to further expansion.

Soil structure

The soil structure should be capable of withstanding the weight of heavy machinery such as mixers, pulverizers and packing machines. Piling or other extensive foundation work on soft or swampy land will greatly increase construction costs.

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Climate

The climate also plays a part in site selection. Locations with a mild climate will keep down the cost of equipment and building. Extreme heat or cold or excessive humidity have serious effects on the efficient operation of a plant. Because many active ingredients and other chemicals are not compatible with, for example, humidity, protection against the elements may be needed. For sites unavoidably located in hot and damp climates or in areas adjacent to salt water, maintenance costs will tend to be high. The painting of metalwork with salt- or chemical-resistant paint, although more expensive, may in the end prove to be cost-efficient.

Services

Although the available services must include electric power, fuel and water supply, demand will be less critical for a formulation plant than one manufacturing basic chemicals. Pesticide formulation processes consist mainly of mixing operations, and chemical reactions are usually not involved. If formulation, as normally is the case, is by batch process, the operation can safely be stopped at any time.

Waste disposal[1]

Serious consideration must be given to the disposal of waste materials, especially of toxic wastes. Although the amount of by-products or wastes tends to be small in a formulation plant, since the main process is mixing not accompanied by chemical reactions, the site must have settling tanks for wastes or a lagoon or pond of appropriate size diked against overflows, together with incineration facilities.

The advantages offered by the evaporation pond as compared with other methods of waste-water disposal include minimizing the contamination of nearby water and food supplies, simplicity of construction and operation, and optimum use of local resources. This disposal method requires significantly more land than other methods of disposal, a condition found unattractive where land value is high, but particularly suitable in many developing countries.

Almost all non-organic soils, such as clay, sand and gravel, are satisfactory materials for an evaporation pond. However, porous materials or materials incompatible with waste-water require a clay or synthetic liner to prevent leakage.[2] With the exception of the synthetic liner, the pond can be constructed by untrained workers with minimum supervision. Installation of a synthetic liner would require direct supervision.[2]

[1] This section was primarily contributed by George Jett, Environmental Protection Agency, Washington, D.C., and Al Dettbarn, ESE Corp., Miami, Florida, United States of America.

[2] David W. Schultz and P. Michael Moklas, "Assessment of liner installation procedures", in *Proceedings of the Sixth Annual Research Symposium*. Reference material available free of charge from the Agency for International Development, ST/AGR, SA-18, Washington, D.C., 20523, United States of America.

The thickness of the clay liner depends on the type of clay available and the durability required, but would generally be 0.5 m thick.[3] The selection of a synthetic liner depends on the properties of the waste-water. Synthetic liners are manufactured sheets approximately 6 m in width and require installation by trained workers to ensure that the liner is properly installed and all seams are properly sealed.

Concrete may be used for construction of the pond in organic soils, or as an alternative to a synthetic or clay liner. As a liner, concrete is reinforced with steel mesh and laid in a thickness of approximately 0.1 m. In organic soils, the concrete would compensate for the instability of the soil. Installation would require skilled workers.

The critical factor in an evaporation pond is size, which is a function of local climatic conditions and the volume of waste-water received by the pond. The volume of waste-water per unit area that can be evaporated from the pond is termed net evaporation, which is defined as the total evaporation from the pond minus the total rainfall into the pond. Under optimum conditions, the total evaporation should exceed rainfall. Under less than optimum conditions, heat may be added to increase evaporation, or the pond may be covered to prevent rainfall from entering the pond.[4] Table 1 gives the approximate depth and pond surface area required for each cubic metre of waste-water discharged on an average day.[5]

TABLE 1. AVERAGE DAILY PERFORMANCE OF EVAPORATION PONDS

Net evaporation rate (m³/a)	*Approximate depth[a] (m)*	*Surface area per unit volume of daily discharge (m²/m³)*	
		Open pond	*Covered pond*
50	0.8	730	970
100	0.9	360	490
150	1.1	240	320
200	1.3	180	240
250	1.4	150	190
300	1.6	120	160

[a] Assumes precipitation is equal to evaporation over a four-month period.

Annual precipitation and evaporation records are necessary for the design of an evaporation pond. Other considerations are knowledge of local resources, structure of the soil and volume of waste-water to be disposed of.

A variety of materials are available for roofing the pond, ranging from polyethylene film to corrugated fibreglass panels.[5] Polyethylene film is of low cost

[3] R. Willinkinson, "Pesticides disposal research" (Kansas City, Midwest Research Institute, September 1978).

[4] Environmental Science and Engineering, "Revised contractor technical report for BAT, PSES, NSPS and BCT in the pesticide industry" (Gainesville, November 1980).

[5] Richard E. Egg and Donald L. Reddell, "Design of evaporative pits for waste pesticide solution disposal", in *Proceedings of the Sixth Annual Research Symposium*. Reference material available free of charge from the Agency for International Development, ST/AGR, SA-18, Washington, D.C., 20523, United States of America.

but has a life expectancy of only three years. The cost of fibreglass sheeting is approximately 12 times that of polyethylene, but it has a 20-year life expectancy and is more durable than the film and essentially maintenance-free. Both types of structure are relatively simple to construct. The roof structure can be either built on site if suitable materials are available locally, or shipped to the site prefabricated. Because of the long spans of the roof structure, on-site construction requires direct supervision. The net evaporation rate from a covered pond would be approximately 75 per cent of the total local evaporation rate.[5]

The simplicity and effectiveness of the evaporation pond makes it an attractive method of disposal of toxic and hazardous waste-water. The pond can usually be constructed with local resources and workers and effectively dispose of waste-water even in unfavourable climates.

Solids will eventually accumulate on the floor of the pond and require periodic removal (approximately every 10 years). These solids are typically disposed of in a secure landfill or by high-temperature incineration. Maintaining a secure landfill involves putting in impermeable soils or liners to prevent leachings from entering ground water, collection and treatment of precipitation run-off or construction of a roof as described above, and establishing a final cover when closing the site. In addition, wells should be installed around the landfill and monitored periodically to detect ground water contamination.

Environmental factors

Odours and gaseous or fine powdery wastes are also serious and of increasing environmental concern, especially if the plant is unavoidably located near a town. Attention should be given to whether the area has local zoning restrictions. Even if none exists at the time the plant is established, it does not follow that such a situation will necessarily continue. The relevance of environmental considerations to the formulation of two typical products is seen in the following examples:

(a) Plants formulating dusts need large sites for production and storage. Equipment to provide protection against noise from jet or hammer mills and from dust pollution is essential if the plant is located near a town. Such equipment adds substantially to production costs;

(b) Emulsifiable concentrate formulation plants require large amounts of organic solvent, usually xylene, which involve the hazards of fire, explosion, and toxicity. Before selecting a site, it is particularly necessary to be aware of legal restrictions covering these hazards. Such restrictions are becoming of increasing importance in all countries.

The potential environmental hazards from pesticide formulation plants are air and water pollution, both of which may cause damage to health and crops. Odour and excessive noise are considered nuisance factors. Special consideration should be given to the abatement of noise arising from mills or pulverizers and to possible unpleasant odours. Water pollution by organic solvents or active ingredients may cause extensive fish kill or pose human health hazards if the recipient water is a source of public water supplies.

Most of the environmental problems can be reasonably controlled by proper engineering techniques and good plant management. If, however, an accident does occur, the effect of the release of toxic pesticides upon the community may be very serious. The site must therefore be chosen to take account of such an accident and to minimize the hazards. Contamination of underground shallow wells and aquatic sites recharged by run-off from the watershed area upon which the formulation plant may be built will almost certainly occur if special precautions are not taken with regard to disposal of all solid and liquid wastes produced by the plant. A disaster plan should form part of the precautions of any prudent works manager. Although it did not involve a pesticide formulation plant, the incident which occurred at Seveso, Italy, in July 1976, involving the explosion of trichlorophenol production facilities and the release of a highly toxic vapour which caused serious harm to people, animals and crops over a large populated area, demonstrated the critical importance of the site selection process.

In conclusion, a properly sited, well-laid-out and well-operated plant that minimizes environmental pollution will have a good relationship with the local community, especially if it provides local employment. Open days to enable the local community to see the plant are a useful way to dispel anxieties.

Design and construction

The following four factors determine the characteristic feature of pesticide formulation plants:

(a) The physical type of products, which could be emulsifiable concentrates, water-dispersible powders, dusts or granules;

(b) The physical and biological hazards, since pesticides are by definition toxic and many become flammable because of the solvent used;

(c) Production tends to be by batch rather than continuous, and frequently is a multi-product operation;

(d) Usage is seasonal, and this affects the amount of product to be made, stored and transported.

All these factors influence both the layout and construction details of the plant. There must be space to handle bulky materials and to minimize fire risks. A strong perimeter fence is necessary for security, especially since toxic materials will be stored both as raw material and finished product.

The following sections were prepared with particular reference to equipment and layout requirements, and are accordingly illustrated by block-type process and equipment flow sheets.

Outline of formulation plant operations

Handling of incoming raw materials

Liquid raw materials such as solvents are generally delivered to the plant by tanker and stored in storage tanks in the open. The solvent is transferred to the mixer through a pipeline by means of a pump. Drum deliveries are stored in the warehouse. Provision therefore should be made for several solvent tanks, appropriate pipework and a warehouse with reasonable space for drum storage.

Raw materials in powder form (active ingredients and carriers) are usually contained in paper bags or drums. The handling and emptying of bags or drums presents problems of hygiene, which are referred to in chapter X.

Inert carriers, which are used in large amounts, can be fed direct into silos in the plant from the delivery vehicle without problems of hygiene. The construction of a silo will depend on the quantities used.

Weighing and proportioning

The next operation common to most formulations is to proportion the correct amount of technical materials, carriers and other additives. For this purpose a small storage hopper with bottom-discharge outlet is a convenient means of holding the materials at a common central point. Below this, a variable-speed feeder is located for individual control and feeding of the materials into a centrally located weighing machine. Accurate weighing is achieved by the constant and reliable flow of materials from the storage hopper to the discharge feeders. The hopper must have the maximum valley angle and maximum discharge opening that can be accommodated by the discharge feeders and the best shape to assist the flow of materials.

In order to avoid blockages, many devices are available, such as bolt-on vibrators, aeration pads and pulsating rubber diaphragms. Similarly, there are electric vibrating tray feeders, or screw feeders with live vibrating screws and feed cones, with multiple ribbon worms mounted in the feed inlet, and also those of a rotary type.

Mixing and blending

In order to mix active ingredients with the carriers into a homogeneous state, the common ribbon or paddle type of mixer is generally used. Impregnation into carriers can also be effected during mixing. Metering pumps or metering valves incorporated in a pump system may be utilized to apply liquid ingredients or solutions of solid ingredients. The macroscopically uniform dispersion of active ingredients to form a properly blended and homogeneous product can be achieved by using various kinds of blenders, for example, ribbon mixer, drum and cone blenders. Henschel-type mixers and ploughshare mixers are also available. The selection of mixing or blending machinery may determine or be determined by plant requirements and layout.

Milling

For milling solid active ingredients or formulated products, various types of conventional mills can be used. Among them the following mills are available:

High-speed hammer pulverizer

Pin mill (horizontal and vertical type), pin-disc mill and stud mill

Screenless Victoria hammer mill utilizing a separate pneumatic classifier and operating in conjunction with a product filter collector

Aspirated beater-type mill

Blast mill

Universal mill

Fluid energy mills utilizing compressed air as the grinding energy medium

The selection of a mill depends on its availability, the quality of the product, the relation to plant requirement and layout. Fluid energy mills are generally used to make finer products or for the final milling. They require compressed air for their operation. Air supply can be from standard compressors working in conjunction with air receivers of suitable size, intermediate air coolers and controls.

Packing

Manual packing of liquid and solid formulations presents problems of hygiene and safety to the plant operator, which, together with the more general problem of hazards from vapour and dust explosion, are covered in chapters IX and X.

Specific formulation processes and selection of equipment

Emulsifiable concentrates

Emulsifiable concentrates are formulated simply by mixing active ingredients, emulsifiers and solvents. Minimum essentials are mixing tanks and mixers. A block-type process flow-sheet and equipment flow-sheet for emulsifiable concentrates are shown in figures I and II, respectively. Usually the mixing tank is a closed system and each component is put into the tank by the use of

Figure I. Block-type process flow-sheet for emulsifiable concentrates

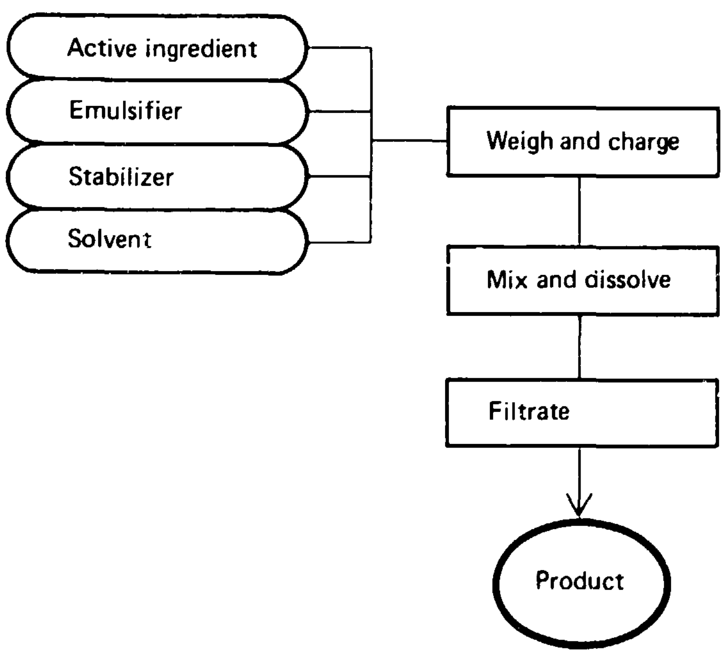
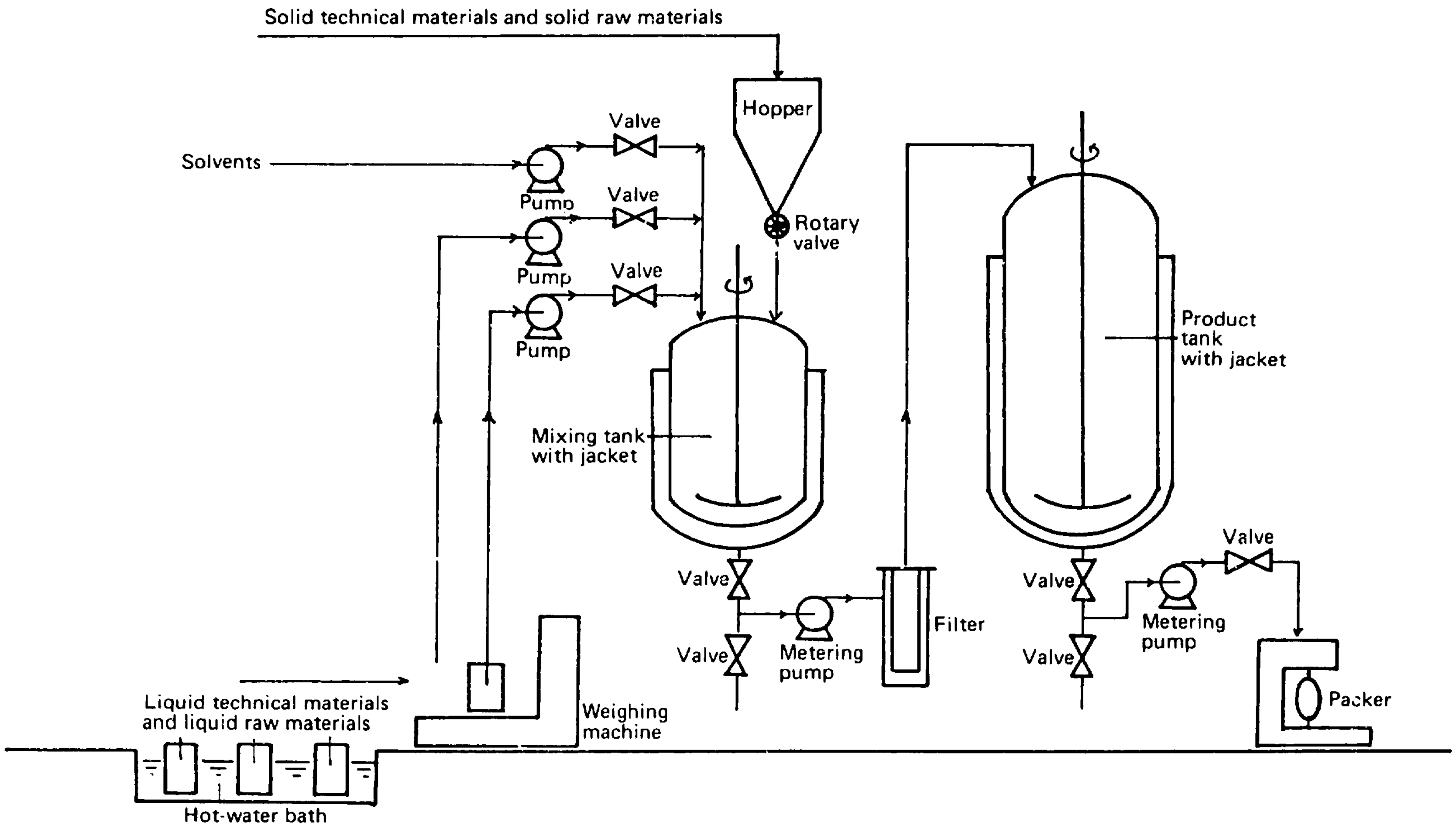


Figure II. Equipment flow-sheet for emulsifiable concentrates



pumps. Solvents used frequently and in large amounts are better stored in outdoor tanks and supplied to the mixing tank by pipeline. A flow meter is used for measurement of the volume to be added. The emulsifiable concentrate formulation is filtered prior to packing. It is recommended that mixing tanks be provided with steam jackets around them in order to keep the contents liquid. Xylene, a typically used solvent, has a flash-point of about 27° C. Fire-proof equipment is therefore recommended. Good ventilatior is also necessary in order to avoid air pollution by solvent vapour.

Some emulsifiers are very viscous and hard to extract from the drum. Placing the emulsifier drum in a hot-water bath will reduce the viscosity. Other viscous technical materials can be treated in the same way or held at a high temperature (80° C) before use.

Dusts

Dusts are formulated by mixing 0.1 to 5 per cent of active ingredients with inorganic carriers under 300 mesh. Dust concentrate, which is a mixture of the active ingredients at high concentration is normally made first, followed by subsequent dilution with carriers. The reasons for this procedure are as follows:

(a) It is best to mill a mixture of a solid technical material with the carriers because melting and sticking will take place if the technical material is milled by itself;

(b) Liquid technical materials can be handled as powders when mixed with oil-absorbent carriers;

(c) It takes longer to obtain a uniform mixture in the case of a high-dilution ratio. It is best therefore to mix twice with a low-dilution ratio. For example, when 1 per cent dust is wanted, it is better first to make a 20 per cent dust concentrate by mixing with a 1:4 ratio followed by mixing with a 1:19 ratio, rather than direct mixing with a 1:99 ratio.

When liquid technical materials are used, the first mixing is carried out by using the ribbon blender equipped with a spray, then milling with an impact mill, such as a pin mill, in order to break the coagulations in the mixture. Final reblending is effected by using the ribbon blender. The block-type process flow-sheet and the equipment flow-sheet of dust containing liquid active ingredients are shown in figures III and IV, respectively.

When solid technical materials are to be milled to fine particles, an impact mill such as a micron mill or an atomizer is generally used. If the technical materials are very hard or require milling to several micrometers, a jet mill is recommended.

Dilution mixing of the dust concentrate with the carriers is simply carried out by using the ribbon blender.

Efficient mixing is possible by the process of first mixing and milling with a pin mill, followed by reblending, rather than by a single mixing in the ribbon blender, which takes longer.

As is shown in figure IV, the ribbon blender, disintegrator, screw feeder, powder pump, bucket elevator, scale and packer etc. are necessary. In these sequential processes, it is possible to install each machine on the same level, but

Figure III. Block-type process flow-sheet for dusts (liquid active ingredient)

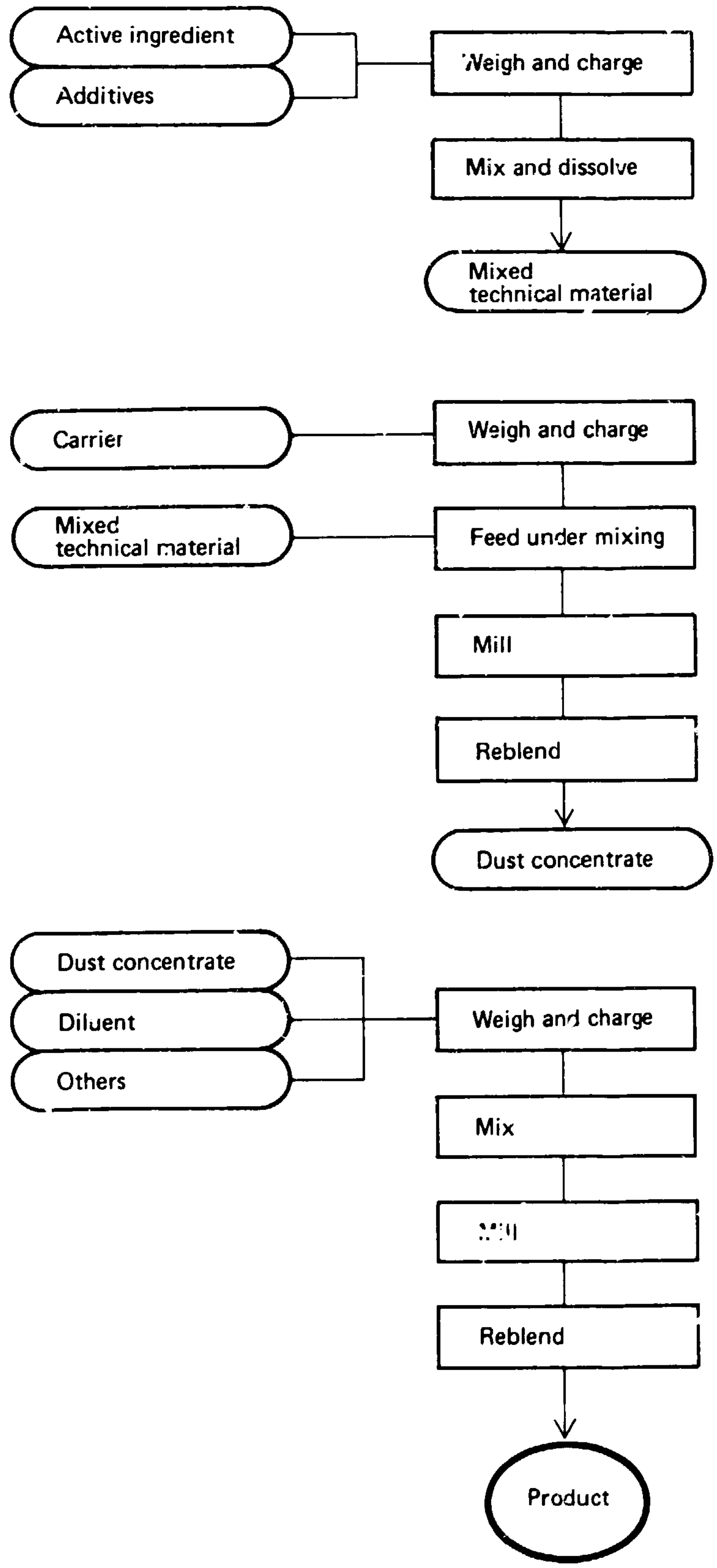
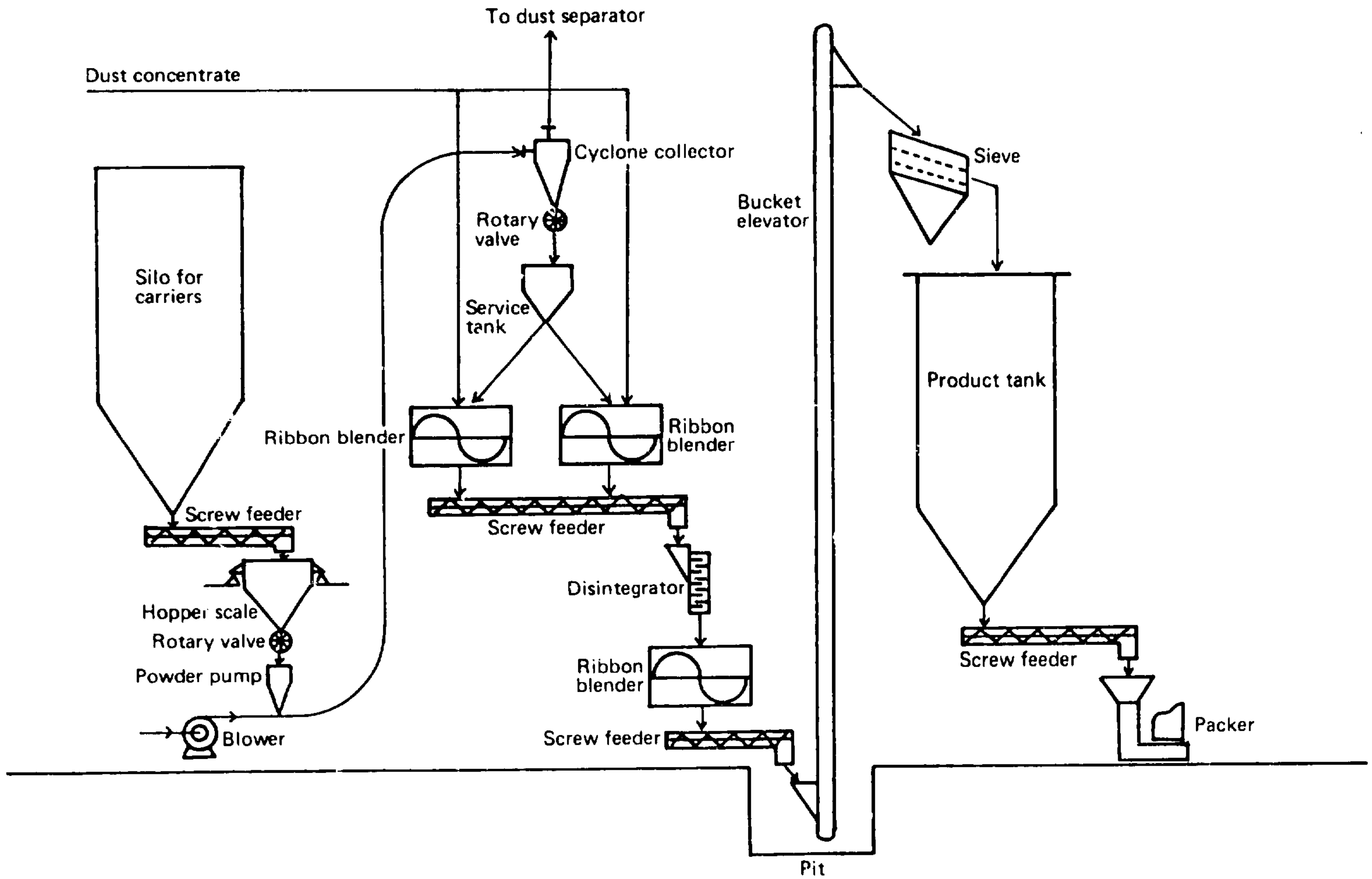


Figure IV. Equipment flow-sheet for dusts (liquid active ingredient)



this demands more space. If space is at a premium, the individual items of plant equipment may be installed one above the other, making use of gravity to move the material. A closed and interlocking system is recommended for these sequential processes from the viewpoint of safety.

If feeding of the powder is carried out manually instead of automatically, a hood should be installed above the feed inlet in order to extract floating dust and to avoid hazards to workers. At the feed inlet a sieve of about 3 mm is provided to remove foreign substances. Magnets are also used to take out tramp metal.

Good ventilation is essential for manual filling and packing of the dust, which should in any case be handled as far as possible automatically or in a closed system.

Water-dispersible powder

Water-dispersible powder is formulated by mixing technical materials and dispersing agents with carriers. The block-type process flow-sheets for water-dispersible powder containing liquid and solid active ingredients are shown in figures V and VI, respectively.

Formulation processes are similar to those for dusts, but content of active ingredient in this formulation is usually between 50 and 90 per cent. Since water-dispersible powder is used as a suspension in water, it is necessary first to mill the solid technical materials with the carriers as pulverizing aids for the formation of very fine particles of about 1 to 5 μm per cent of pulverized technical material. The milling process for water-dispersible powder is therefore very important, and for this purpose a jet mill is the most suitable. The equipment flow-sheet of milling is shown in figure VII. The final product is made by subsequent mixing of the pulverized technical materials, additives and carriers. When liquid technical materials are used, milling may be carried out by using a micron mill, atomizer or hammer mill, as in the case of dust formulation. The equipment flow-sheet of water-dispersible powder and dust concentrate is shown in figure VIII. In the case of handling water-dispersible powder, the same precautions as for dust formulations are necessary.

Water-dispersible powder can also be formulated by single mixing in a Henschel-type mixer or ploughshare mixer.

Granules

There are two methods of formulating granules, namely the extrusion and the spray methods.

Extrusion method

Granules are formulated by extrusion after kneading the mixture of technical materials, inorganic carriers, binder and water. The block-type process flow-sheet is shown in figure IX. First, diluent carriers (for example, clay, talc, bentonite and calcium carbonate), as pulverizing aids, and technical materials are mixed and milled to fine particles to make pulverized technical material. An aqueous solution of binders such as lignosulphonate and polyvinyl alcohol is added to the mixture of pulverized technical material and carrier, and the mixture is kneaded. A continuous kneader or vertical screw mixer is used for this purpose. There are many kinds of extrusion granulators. In pesticide formulation, the most usual type consists of a die or cylindrical screen set round a screw axis. Screws may be set vertically or horizontally. Production efficiency depends on the kind of carriers and quantity of water added. The extrusion diameter is generally 0.7 to 1.0 mm. The larger the diameter, the better is the production efficiency, but at the cost of biological efficacy.

Extruded granules are dried by a band or fluid bed drier. The drying temperature is determined by the stability and volatility of the technical materials. After drying, disintegration is carried out in order to reduce the size of longer extruded granules. Sieving them produces granules of proper particle size. The equipment flow-sheet for granule production is shown in figure X.

Figure V. Block-type process flow-sheet for water-dispersible powders (liquid active ingredient)

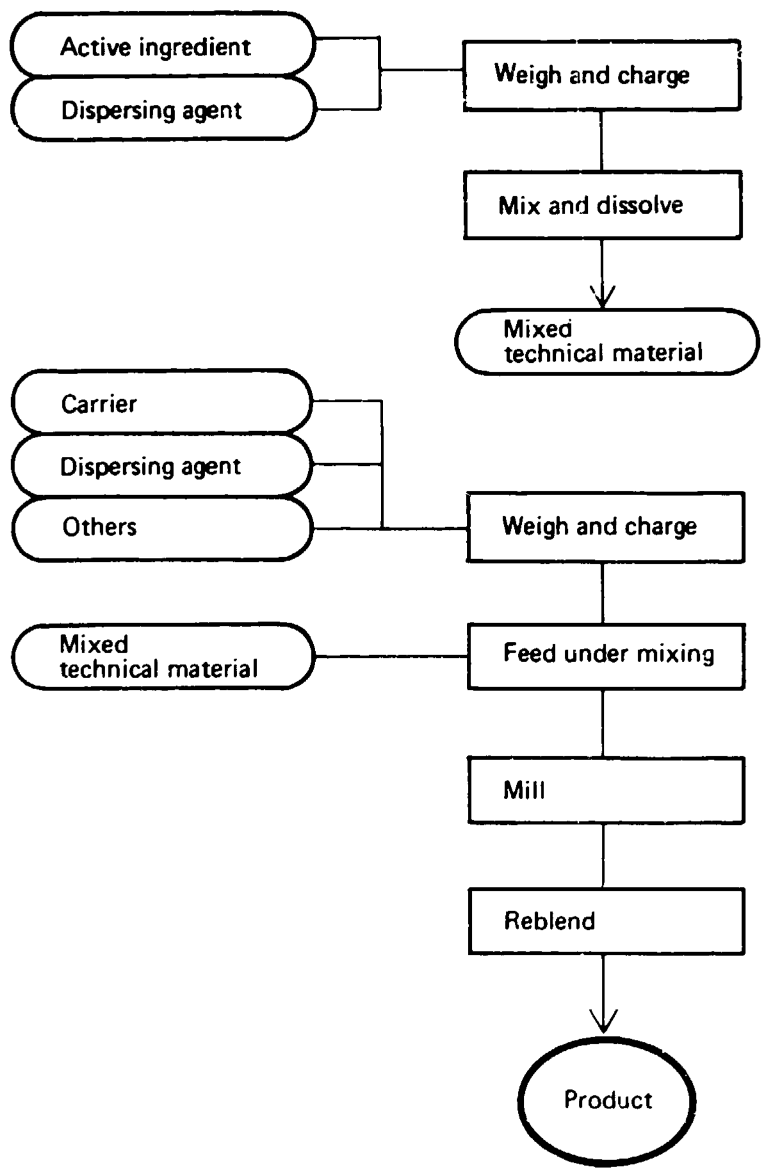


Figure VI. Block-type process flow-sheet for water-dispersible powders (solid active ingredient)

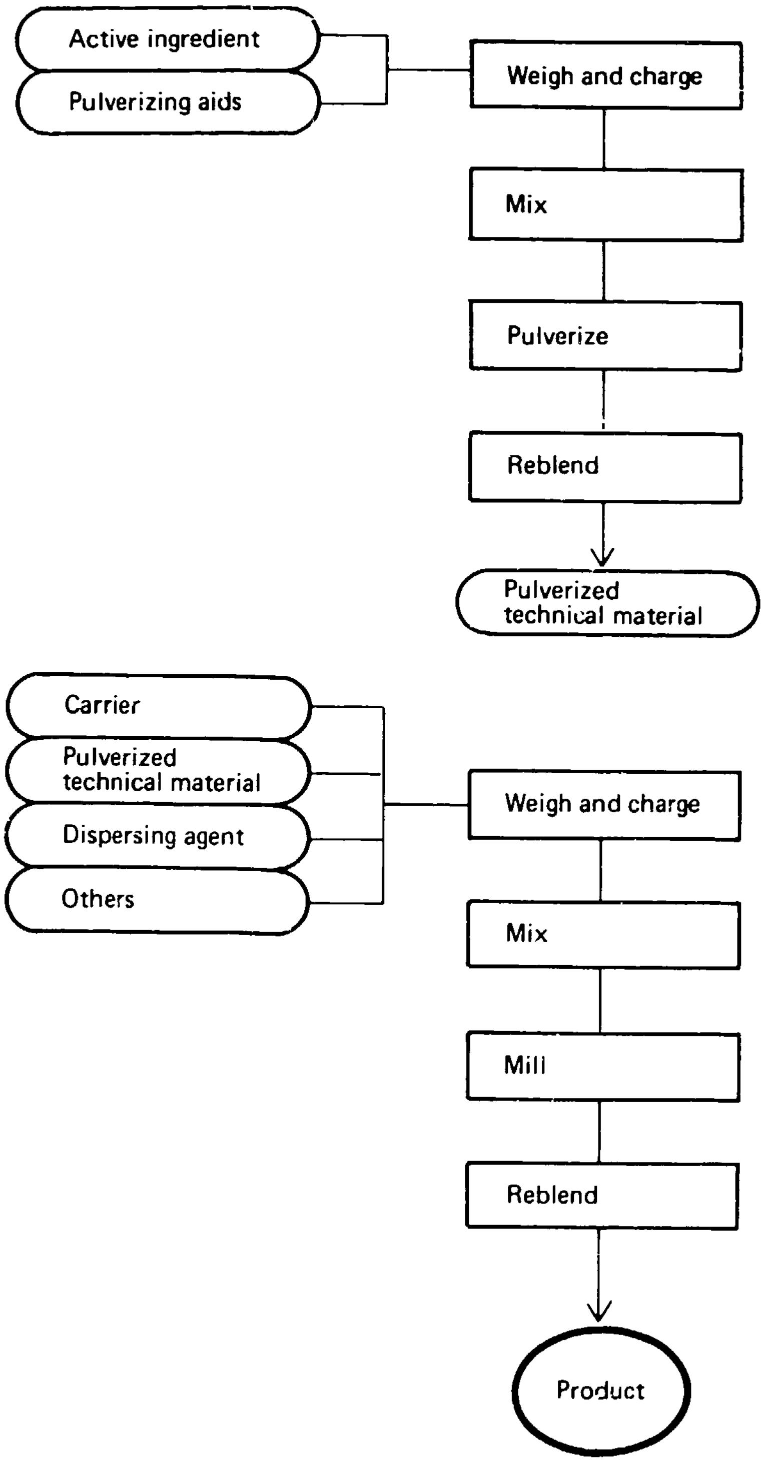


Figure VII. Equipment flow-sheet of milling process

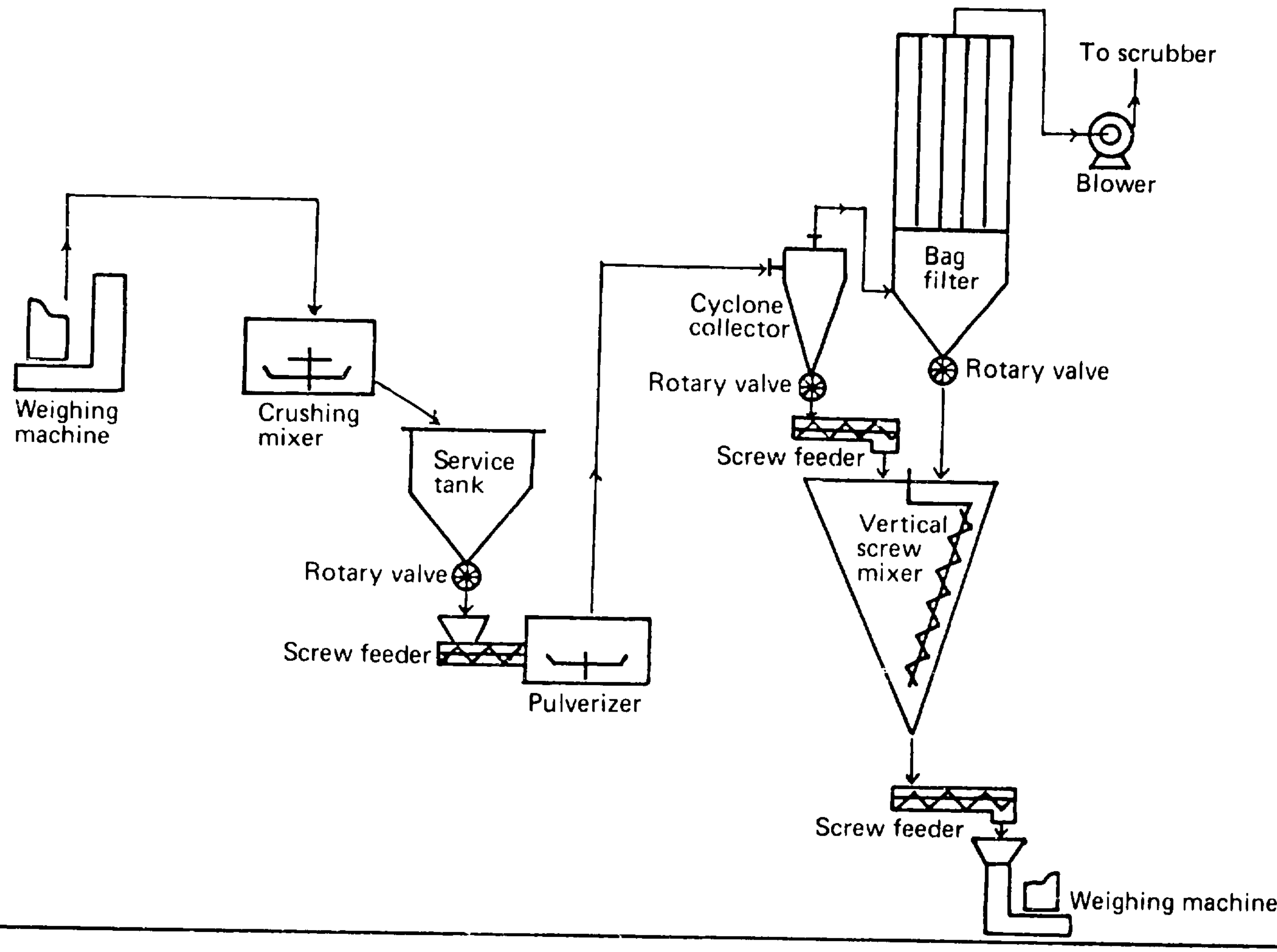


Figure VIII. Equipment flow-sheet for water-dispersible powders and dust concentrates

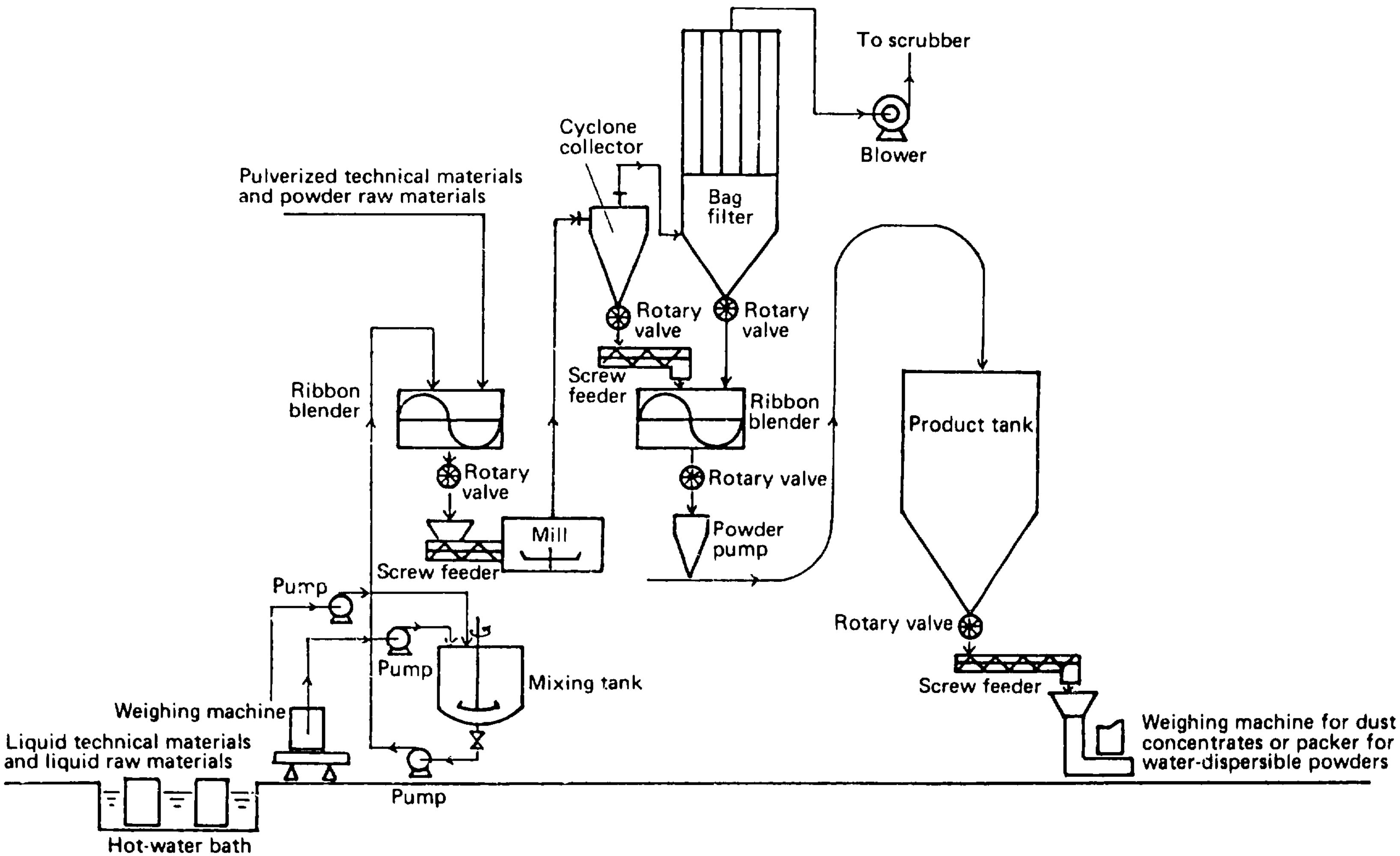


Figure IX. Block-type process flow-sheet for granules (extrusion method)

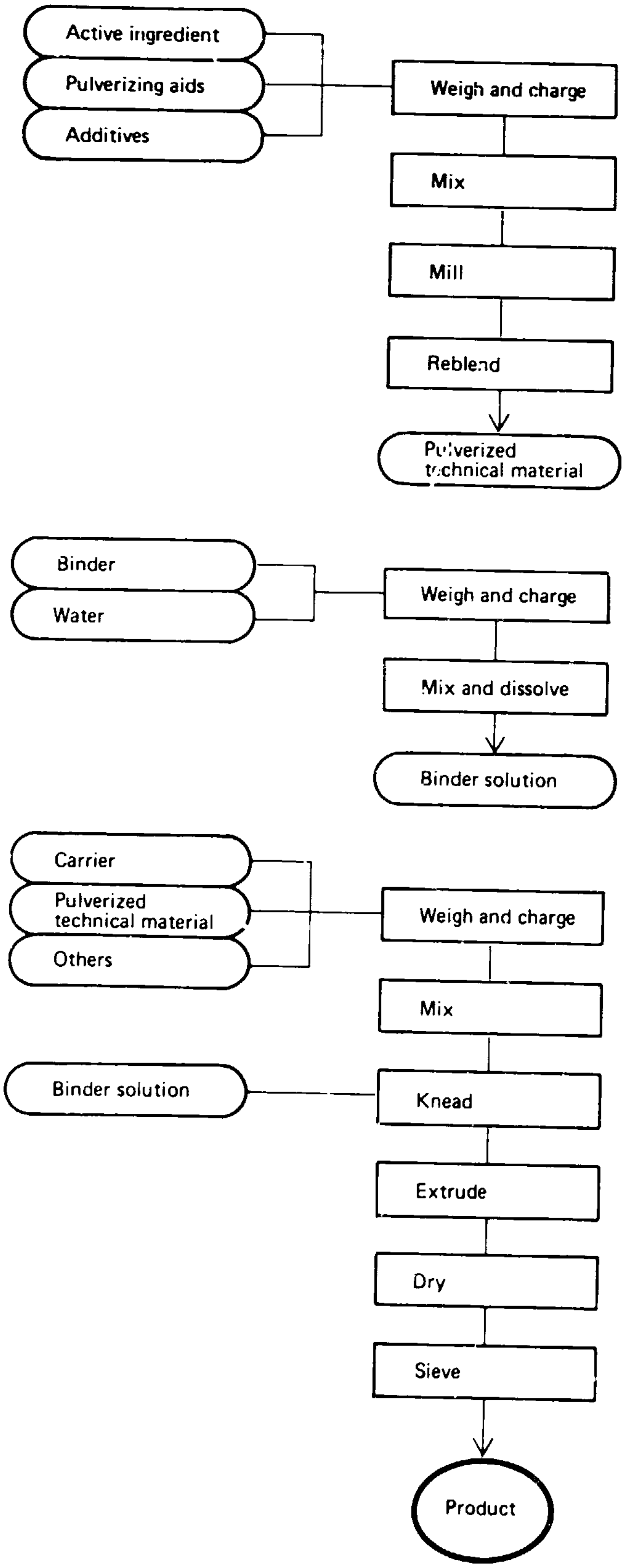
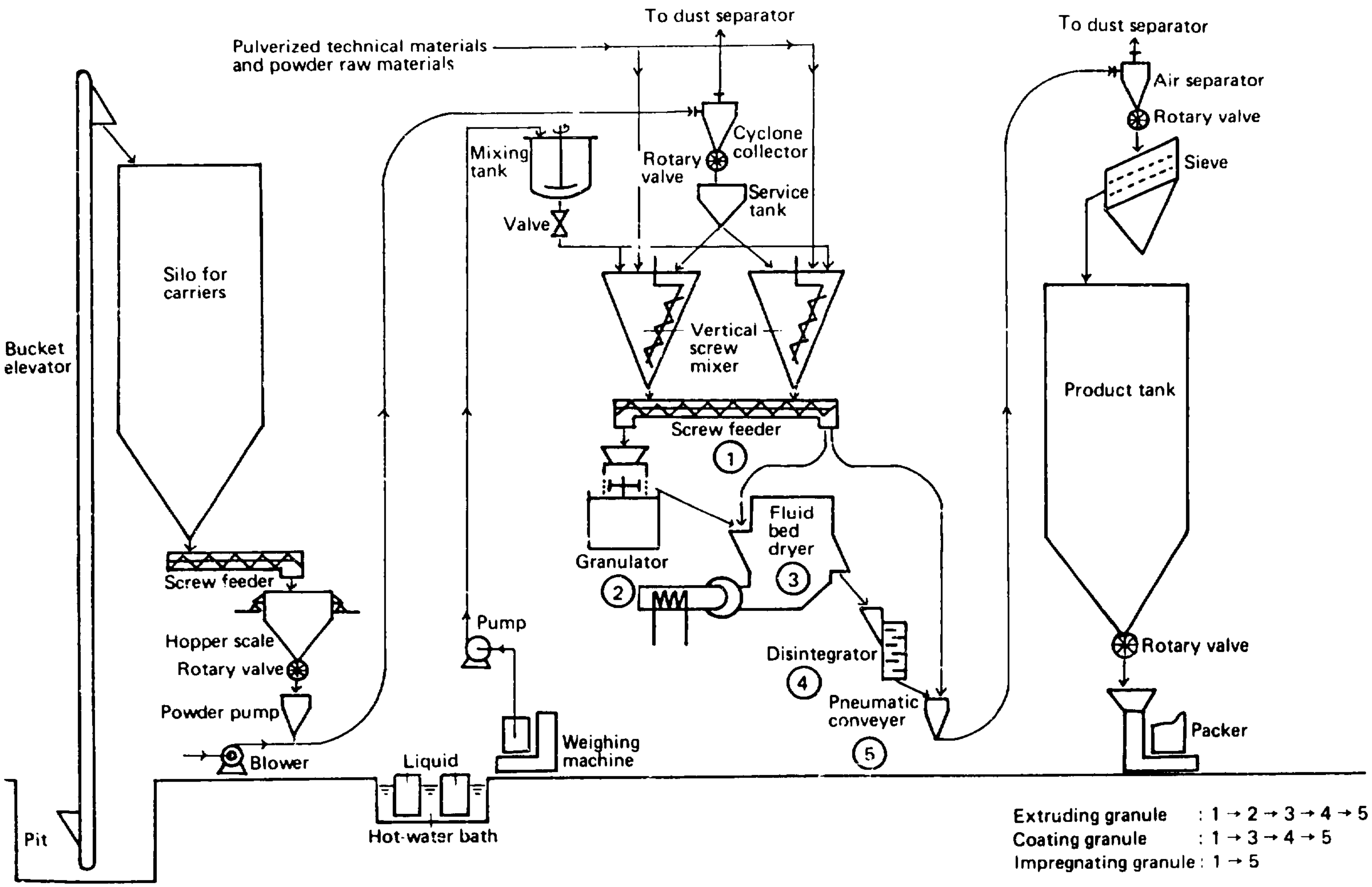


Figure X. Equipment flow-sheet for granules



Spray method (impregnation or coating)

The spray method involves spraying the active ingredient or its solution or suspension on to granular carriers manufactured to the correct particle size. Clay, silica sand, calcium carbonate, vermiculite and pumice are used as granular carriers, after milling the material to the correct size. Some granular carriers are made by an extrusion granulator. Liquid technical materials are sprayed onto the granular carriers in a mixer with suitable stirring facilities. The vertical screw mixer, concrete mixer and V-type mixer are suitable, since the granules are not destroyed in them. When granular carriers such as silica sand and calcium carbonate, which do not have an oil-absorption capacity, are used, the surface of the granules becomes sticky. In this case, synthetic silica hydrate, which has a large oil-absorption capacity, is added to give flowability. When solid technical materials are required to be coated on the carriers, liquid binders such as machine oil and polyethylene glycol are sprayed first, and then the fine technical materials are added. If aqueous or organic solutions of the binders are used, subsequent drying is necessary. A block-type process flow-sheet of the impregnation and coating methods is shown in figure XI.

Selection of the extrusion method or the spray method depends on the kinds of pesticides and availability of the carriers. If granular carriers are readily available, the spray method is easier. Moreover, the extrusion technique requires sophisticated technology and may not be suitable for every developing country.

Plant layout

Once the appropriate individual flow-sheets have been agreed on, the location of each process (master plot plan) and of each machine involved in the process (unit plot plan) can be established. There is no universally applicable plot plan. Each plot plan must be designed to fit the given conditions economically and functionally. The following items should be taken into consideration.

Master plot plan

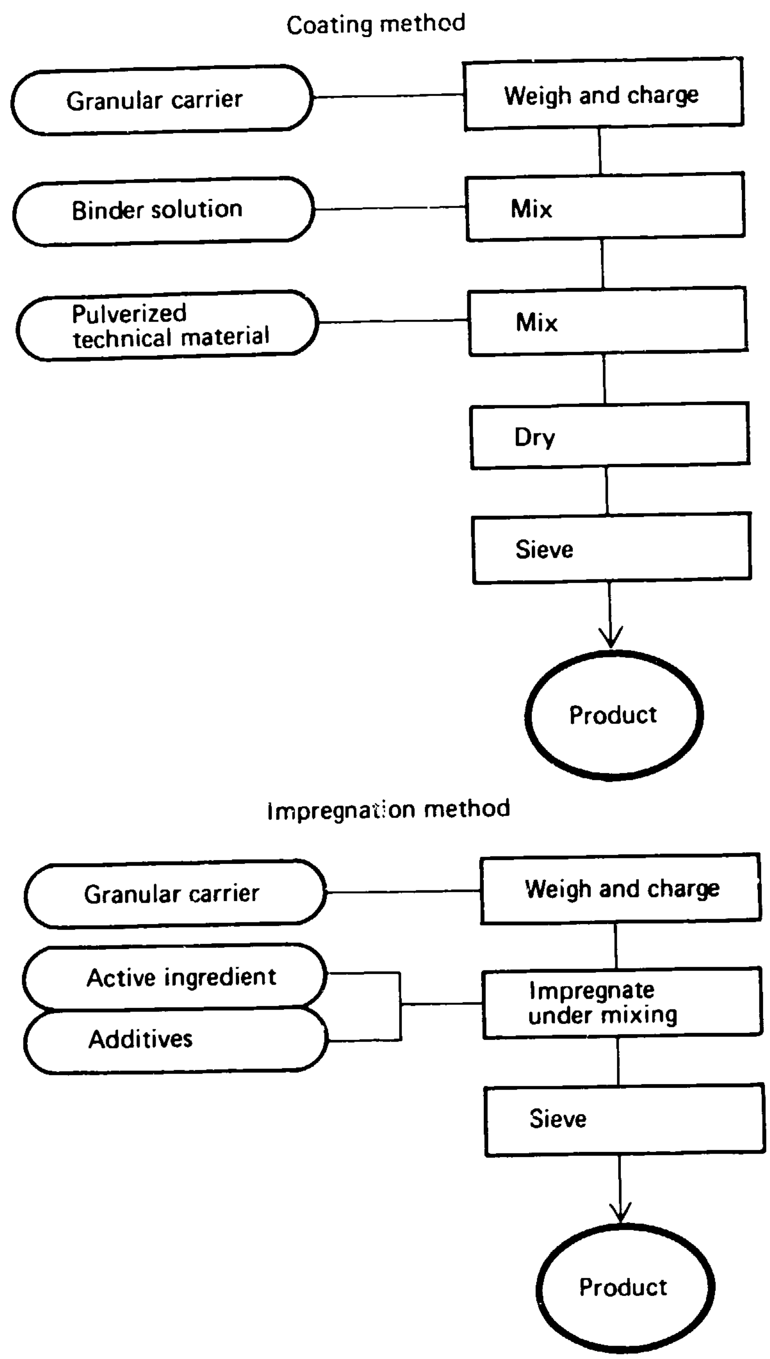
Process plan

Related processes should be located in the same grouping. Liquids and solids should be in separate blocks to facilitate raw material handling and usage and transport of finished products. As production and packing will form a continuous flow, the packing area is best located next to the production area. Solvent tanks should be sited close to liquid formulation plants and carrier silos close to solid formulation plants. Herbicides should be located away from insecticides and fungicides to avoid cross-contamination.

Offices and services

Offices, laboratories, stores, waste disposal facilities and other services should be located outside the process area. Stores and storage tanks should have easy access by road and rail. If raw materials are transported by sea, storage facilities are best located near the harbour.

Figure XI. Block-type process flow-sheet for granules



Safety considerations

The process area should be laid out with due regard to possible fire and explosion hazards (see chapter IX).

Orientation of buildings

The orientation of the building should take account of shade requirements and the prevailing wind. The lee side of the building should not be open to permit odour drift. Similarly, advantage should be taken of an attractive view from the site, which might be further improved with tree-planting and landscaping.

Recreation facilities

Provision should be made for recreation facilities, including a playing field.

Construction requirements

The building should have a steel-frame structure and be fire- and earthquake-proof. The floor should be made of material resistant to oil, water, acid and alkali, and strong enough to resist impact and abrasion. The floor should not be slippery and be easy to keep clean without producing any dust. Walls should be smooth and free from falling dust. In order to prevent dust from piling up, beams and pillars should not have horizontally flat planes. The structure of the roofs should be designed in such a way that lighting, ventilation, temperature and noise abatement are taken into consideration. An example of a master plot plan is shown in figure XII.

Unit plot plan

Experience will help to produce an optimum unit plot plan, which will be influenced largely by space limitation and the kind of equipment used. The following planning procedure is a useful guide:

(a) List all machinery and equipment;

(b) Determine the height of each piece of equipment;

(c) Arrange each piece of equipment according to the process flow and operational method of the plant;

(d) Assemble equipment of the same category;

(e) Having established clearly the method of maintenance and repair of the equipment, arrange the equipment to make maintenance easy;

(f) Arrange equipment to meet safety regulations;

(g) Determine distances between plant items for ease of maintenance, repair and operation;

(h) Arrange plant items for ease of construction;

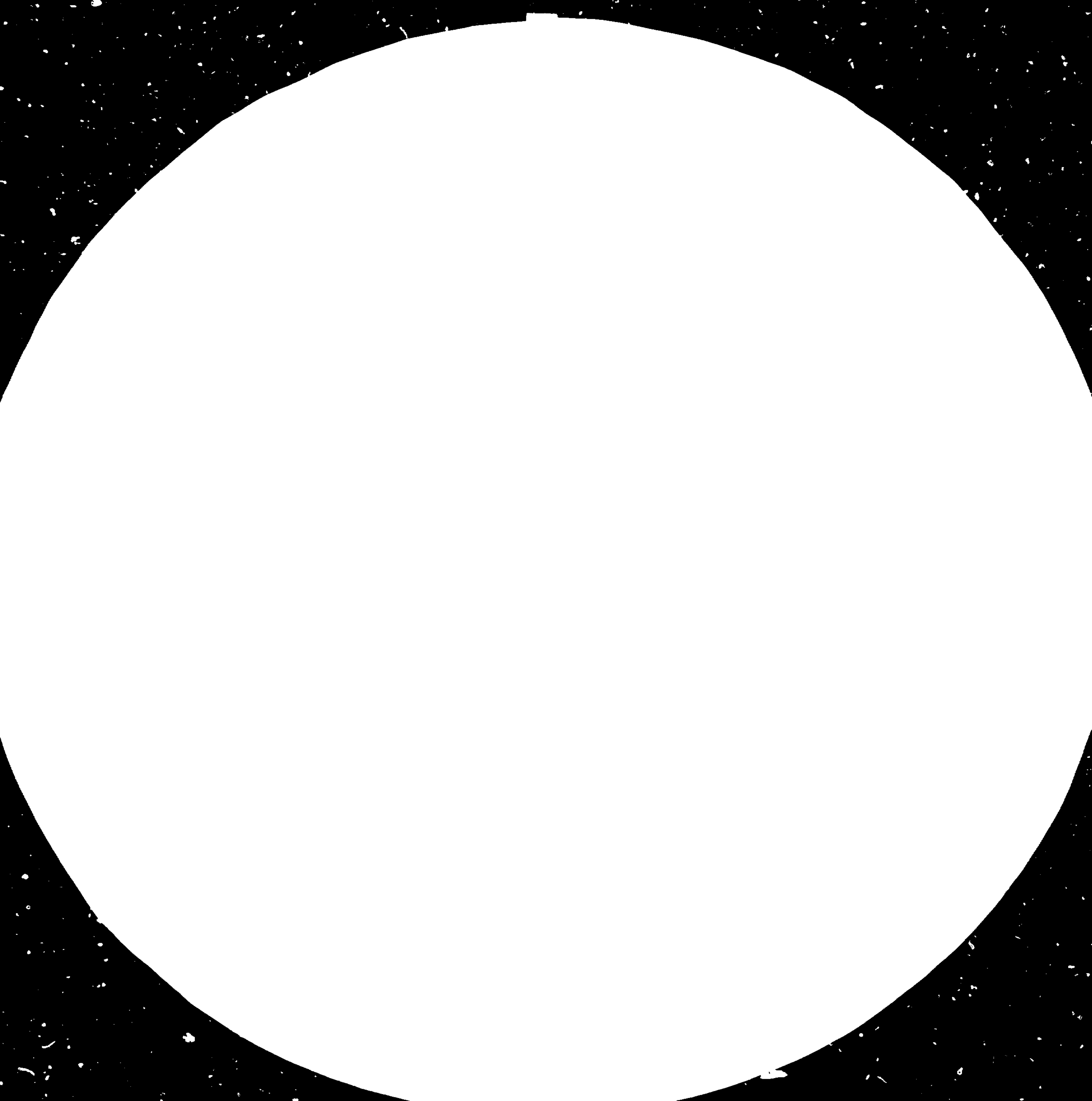
(i) Put plant items which need frequent inspection and supervision near the control room;

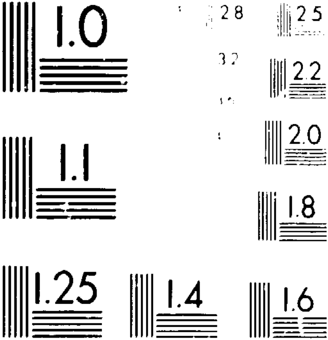
(j) Keep pipe lines as short as possible and reduce to a minimum the number of pipe bends.

Environmental factors[6]

Environmental factors relate directly to waste disposal from the formulation plant. There are solid, liquid and gaseous wastes. Solid wastes cause land pollution and can lead to ground-water pollution by leaching and run-off. Gaseous and liquid wastes cause air and water pollution, respectively, but solid wastes may also cause air pollution as a result of dusts.

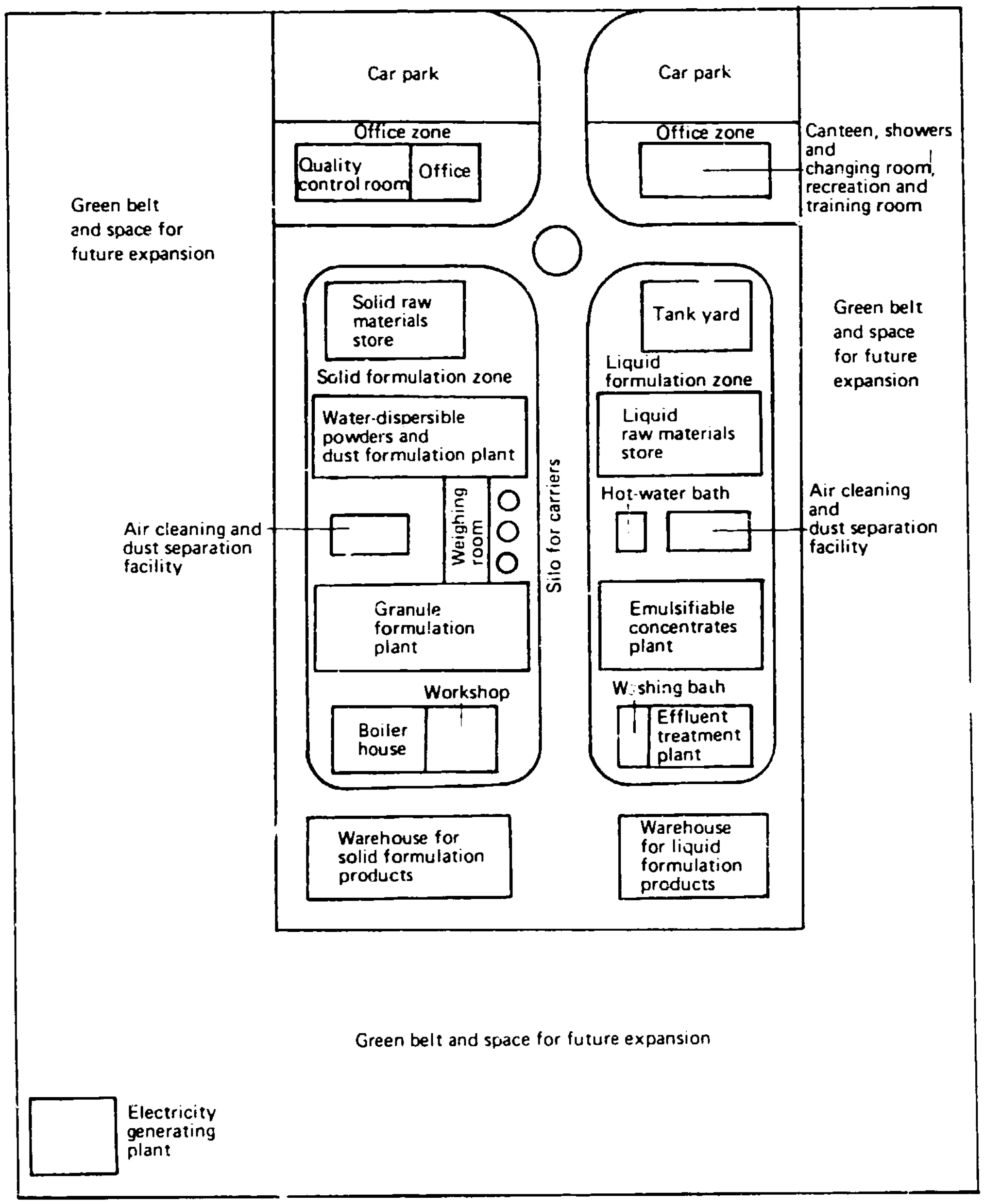
[6] See also earlier section on environmental factors in this chapter.





MICROCOPY RESOLUTION TEST CHART

Figure XII. Example of master plot plan



Air pollution

Air extracted from, for example, dust plants should be passed through bag filters, scrubbers, cyclones and washers to remove dust. Odours should be removed by activated carbon.

Water pollution

Water is considered polluted if it contains sufficient waste matter to make it unsuitable for domestic or industrial supply or for the proper support and growth of marine life. Primary washing water should not be discharged into rivers without treatment. Residues from the primary washing water will contain considerable quantities of pesticides, and these should be disposed of by routing to an evaporation pond (see section on waste disposal presented earlier in this chapter). Disposal of solid waste materials on land may cause underground stream pollution by the leaching action of surface wastes. Dangerous solid waste should be incinerated or encased in concrete blocks, or disposed of by placing in the evaporation pond.

Noise pollution

Some equipment such as jet and hammer mills cause serious noise pollution and should, therefore, be installed in separate closed areas to avoid harm to workers or others in the vicinity. Noise abaters are also useful.

Operation

Operational specifications

The specifications for plant operation should cover the following: promotion of safety and high efficiency; adjustment of operating methods to the production plan; rapid training of workers to maintain and improve the process; and application of methods of quality control. The specifications are important because they provide basic information for controlling operations, the product recipe, safety, hygiene etc. Operation specifications covering the following items should be prepared for each formulation.

Name and purpose of the formulation

The name of the formulation and the particular operations should be the same, for example, fenitrothion 40 per cent water-dispersible powder. In addition, the trade name, common chemical name, abbreviation, code number etc. should be shown together with the plant or equipment used. If necessary, the generic name which may correspond to the official one should also be included.

A brief explanation of the purpose of the formulation and its method of application should be included together with relevant legal restrictions, if any.

Plant location and required qualifications of operators

The plant where the formulation is produced and the qualification requirements of operators should be described.

Recipe and formulation specification

The fundamental recipe and quality specifications together with the appropriate analytical method should be described. The method of quality control to maintain formulation quality based on the specifications should also be stated.

An example for fenitrothion 40 per cent water-dispersible powder is shown in the following recipe and in table 2. It should be noted that the values in table 2 are shown as examples only and do not always agree with the actual case.

Recipe

		Weight per cent
Active ingredient	Fenitrothion (pure)	41.6
Dispersing agent	Sorpol 2495G	2.0
	SanX P-201	2.0
Carrier	Tokusil GU-N	26.5
	Radiolite No. 200	27.9
		100.0

TABLE 2. SPECIFICATIONS AND TEST METHOD

Item[a]	Specification	Control limit
Content of active ingredient[b]	40% (min.)	41.0-43.0
Particle size[c]	98% (min.)	99.5 (min.)
Wettability	60 sec (min.)	20-40 sec.
Suspensibility[c]	70% (min.)	80% (min.)
Dispersibility[c]	90% (min.)	95% (min.)
Apparent density	0.20-0.35	0.25-0.30
Foaming	20 mm (max.)	15 (max.)
pH[c]	5-7	5.5-6.5
Appearance	Pale brown fine powder	
Storage stability		

[a] Sumitomo test method applied to each item.

[b] Content of active ingredient: not less than the nominal content.

[c] Acceleration test should comply with this item of the specifications after accelerated storage at 70°C for two hours.

Raw materials and containers

Specifications for containers and raw materials such as active ingredients and auxiliary materials should be stated and information given on the supplier and the type of packing. Specifications should be established for each material received from each supplier, including standard values, control limits and test method. The amount of raw materials required for one run or batch or a reasonable amount of storage should also be described. Because the quality of the formulation depends largely on the properties of the raw materials, especially on auxiliary materials it is essential to set a reasonable standard for selection of raw materials and to confirm that the materials used in the formulation conform to the specifications. The production plan should also take into account the area of storage. All these specifications are essential for rapid, cheap and safe production of a high-quality formulation.

As an example, the items in the specification of the carriers used in the formulation of the fenitrothion 40 per cent water-dispersible powder are as follows: appearance, apparent density, pH, oil-absorption capacity, particle size, moisture and ignition loss. In the selection of the carrier, formulation specifications, including compatibility with active ingredient, should be determined and stated.

Formulation procedure

The outline of the formulation procedure and the flow of the raw materials to the final product is shown in figure XIII with an indication of the equipment used, operating conditions and operating hours for each unit process. It is also preferable to prepare a time schedule to show one production cycle from the charging of raw materials to the final formulation product.

In figure XIII, an example is shown for the production of 1,000 kg of fenitrothion 40 per cent water-dispersible powder.

Equipment and process operation

A list of equipment, a process flow diagram and a unit plot plan of equipment should be prepared. The maximum production capacity of each item of equipment should be specified and instructions given on the following points:

(a) Arrangements and inspection before operation, using equipment assembly manuals, the pre-operation inspection manual, and the check-manual for cleaning and tidying work space;

(b) Operation, including production methods and check-points before and during operation;

(c) Suspension of operation and inspection, including the stopping of machinery, inspection after operation and the cleaning and tidying of work space.

Instructions for production and hygiene[7]

There are written instructions for product quality, safety, hygiene and environmental problems. Information concerning such matters as personal protective clothing applicable to each unit process should also be stated. These include safety footwear, head covering, face shields, aprons, ear protectors, gloves etc. Instruction that clothing should be changed and laundered every day, and immediately after any obvious contamination, should also be added.

Quality and process control

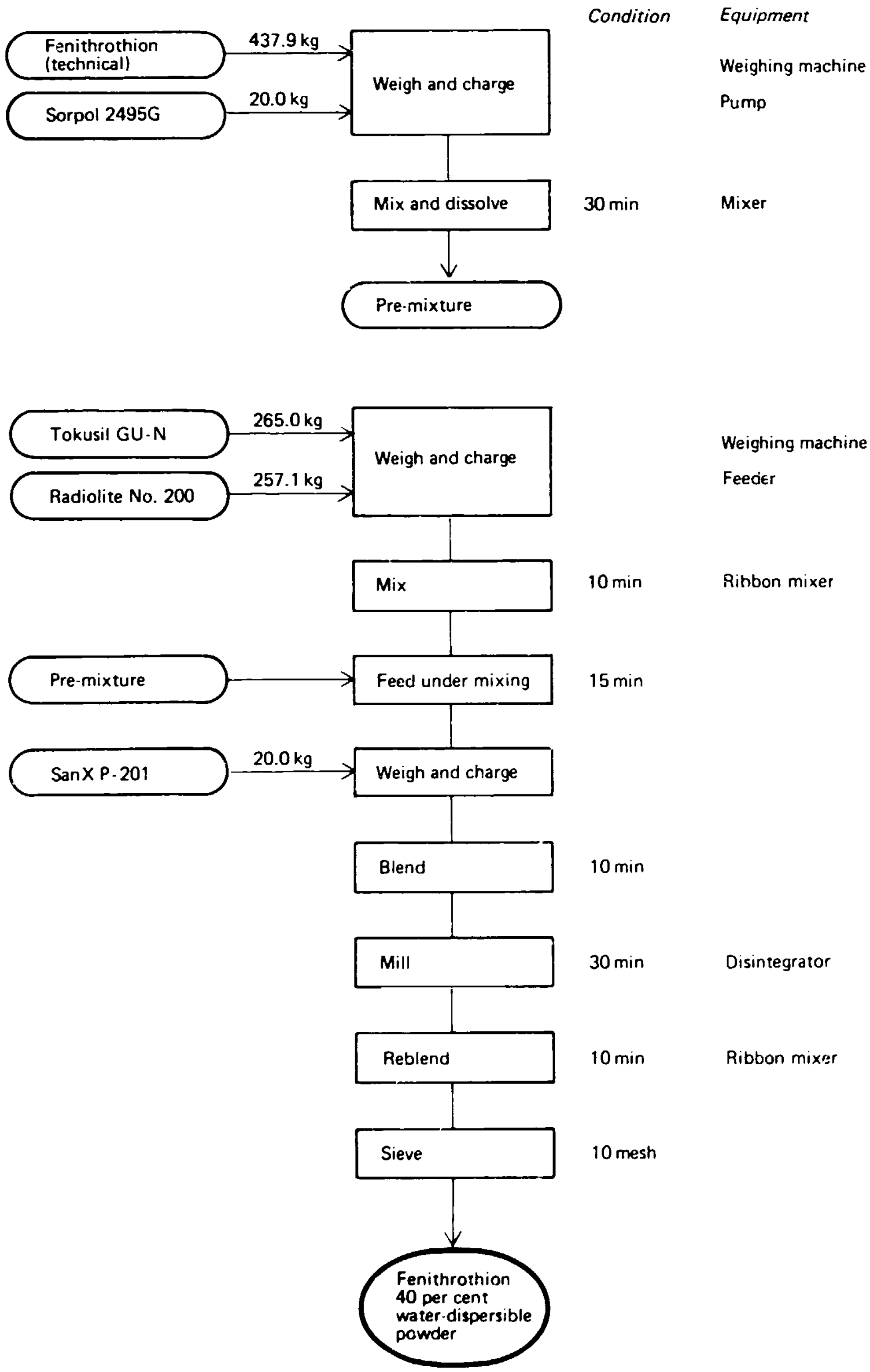
Although special analyses for process control are not necessary in the formulation of pesticides because the process is mainly a mixing operation and not accompanied by chemical reaction, the following items nevertheless should be controlled: particle size, content of active ingredient and its distribution in the pulverizing process and in the mixing process, end-point of drying in drying procedure for granules etc. Suitable methods are developed so that sampling, examination and preventive action can be carried out quickly and correctly.

Emergency measures

Written instructions for emergency measures in case of disaster or accident, power failure and damage to equipment or parts must be readily available.

[7] See also chapter X.

Figure XIII. Flow-sheet for the production of 1 ton of fenitrothion 40 per cent water-dispensible powder



Maintenance

Periodic maintenance of equipment is usually carried out by a special maintenance unit using the appropriate maintenance manuals. However, daily maintenance or visual inspection, which is done by the plant operators, is important and useful for the early detection of damage to the equipment before, during and after operation. The experienced operator will most likely observe any obvious damage, but he must refer to the inspection manual which has been prepared for each item of equipment. It is important to record the results of the inspection on a check-list and to take the necessary action quickly.

The check-list should include the following: unusual noise, vibration, heat, degree of wear and tear, belt tension, lubricant, trouble in the electric system etc. For maintenance materials used on the equipment, such as lubricants and other consumable articles, the name, type, makers or suppliers and prices should be recorded in case an urgent supply becomes necessary.

Results of inspection, maintenance and operating conditions, such as the amount of charged raw materials, mixing time, temperature and electric current, should be recorded on the maintenance and batch sheets. The filing procedure and length of retention of reports should be specified.

Maintenance is of two kinds, breakdown and preventive. Breakdown maintenance is the repair of failed equipment; preventive maintenance consists of daily or periodic adjustment of equipment to prevent breakdown. Quantitative data and know-how obtained from periodic inspection and adjustment or repair of equipment are of great value in subsequent maintenance. This improved maintenance is known as corrective maintenance and is incorporated in future plant design to give high reliability and good equipment performance. Thus, maintenance is not only the inspection and repair of equipment, but also a dynamic element in the design of new equipment and improvement in production efficiency and safety. This is known as productive maintenance. It maintains initial performance of the plant, improves production capacity by modifying design, and prevents secondary accidents due to unexpected breakdowns.

Maintenance includes the following:

(a) *Daily inspection.* This should be done before, during and after plant operation to locate any breakdown. The results of the inspection should be recorded for future reference. Where necessary, lubrication and cleaning are carried out;

(b) *Periodic inspection and adjustment.* Periodic inspections are made in order to inspect and locate breakdown and wear of the equipment. The results should be recorded for reference. Where necessary, adjustments and repairs are carried out.

Based on information obtained from daily and periodic inspection, the following work will be done:

(a) Plant modifications will be carried out as required by the quality of the raw materials and the plant design;

(b) Breakdown repair work will be carried out where necessary;

(c) Structural repairs will be carried out on the site, buildings, structures, components and sanitary facilities;

(d) Safety repairs will be done on safety equipment where necessary;

(e) Improvements will be carried out to improve performance and operational procedures and to increase production yield.

Except for daily maintenance, it is usually desirable to perform maintenance work during the shutdown for periodic inspection.

Training

Training of operators is essential for safe and effective operation of the plant. Training content will vary in detail, but the most important requirement is to make training systematic and to include certain subject matter common to all operators in formulation plants, examples of which are as follows:

- General information about pesticides
  - Kinds of active ingredients and their use
  - Kinds of formulations and their application method
- Basic knowledge about raw materials and formulated products
  - Typical physico-chemical properties in relation to quality control, methods of measurement and specifications
- Formulation procedures
  - General information about formulation equipment
  - Formulation procedures for each formulation
  - Process specifications
  - Process records
- Maintenance
  - Productive maintenance
  - Maintenance records
  - Kinds of equipment and their maintenance
- Safety, hygiene and environmental considerations
  - Proper use of protective equipment such as rubber gloves and shoes, dust respirators, full-face chemical gas masks and protective clothing
  - Personal hygiene and the need for showers[8] at the end of each shift to ensure that no toxic materials are in the hair or on the body
  - Cessation of work in case of spillages in order to remove clothing, shower and change to clean clothing

Trainees need to be tested to confirm that they have understood what they have learned.

Managerial responsibility

Modern concepts of managerial responsibility transcend the rather narrow scope of operating the plant at high cost efficiency to include the broader concept of the welfare of the work-force.

[8] It should be noted that amenity showers in the changing room are quite distinct from emergency shower facilities located at appropriate places in the plant.

Although government regulations in most countries are concerned with safety and hygiene, enlightened management is equally and independently concerned with the health and welfare of the workers in the enterprise. A happy and healthly work-force contributes greatly to the profitability and efficiency of an operation. If the manager of an enterprise must delegate some responsibility to subordinates or to a committee representing both management and workers, this responsibility must be clearly defined because the ultimate responsibility rests with the manager.

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IV. Key decision criteria for establishing a local formulation plant

C. F. J. Kohll and L. S. Dollimore***

In the early 1950s, when the synthetic pesticide industry was expanding rapidly in areas with highly developed systems of agriculture, formulation plants were established in many countries, especially in the United States and Western Europe. Originally, the trend was to build large-scale, fully-integrated formulation plants, often situated at or near the major production centres for technical pesticides. Such plants usually functioned as central supply points for meeting world-wide market requirements.

In the late 1950s and during the 1960s, small formulation plants covering specific local requirements began to be established in a large number of developing countries. Initially, they were simple blending and packaging units for the production of liquid concentrates; facilities for the local production of dusts and wettable powders were established in relatively few areas. Insecticides were the first products to be handled. Later, and on a much smaller scale, local formulation of fungicides and herbicides was undertaken. These developments closely followed local market demand for pesticides, as modern practices of cultivation were gradually introduced and the convenience and benefits of modern methods of pest control were recognized.

The late 1960s and early 1970s saw the emergence of more sophisticated formulations such as suspension concentrates, as a means both of overcoming problems in formulation, handling and application, and of reducing ingredient and transport costs. Later in the 1970s, the introduction of very active, high-cost chemicals such as the synthetic pyrethroids created a need for more precise formulation blending and quality-control equipment and procedures. At the same time, there was a growing world-wide awareness of aspects of industrial hygiene, safety and environmental conservation, factors which have contributed to a substantial increase in both the capital expenditure required for the construction of a modern formulation plant and its operating costs.

While detailed statistics on local formulation in developing countries are not available, it is currently estimated that over 80 per cent of pesticides used in developing countries are formulated locally, except in certain areas, particularly

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in Africa and some parts of Asia, where local requirements of pesticides are purchased by national or international organizations through competitive bidding.

Formulation plant and its infrastructure[1]

The key parts of a formulation plant are obviously the formulation production and filling units. However, these units cannot operate without the necessary support facilities, which, depending on the diversity and complexity of the plant operations, include: warehousing, laboratory, workshop, effluent treatment unit, waste disposal facilities, electrical switch-room, steam or hot water, compressed air, bulk storage, canteen, first-aid room, laundry, washing and changing facilities and administration offices. A schematic plant layout is shown in figure I.

Formulation production and filling units

Agrochemical formulations can be divided into two distinct classes, namely liquids and solids, each of which can then be further subdivided. For example, liquid formulations include emulsifiable concentrates, aqueous solutions, water-miscible concentrates, low and ultra-low volume solutions, fogging solutions, emulsions, and suspension concentrates (flowables). Solid formulations include dusts, wettable powders, water-soluble powders, conventional granules and water-dispersible granules (dry flowables).

Liquid formulations

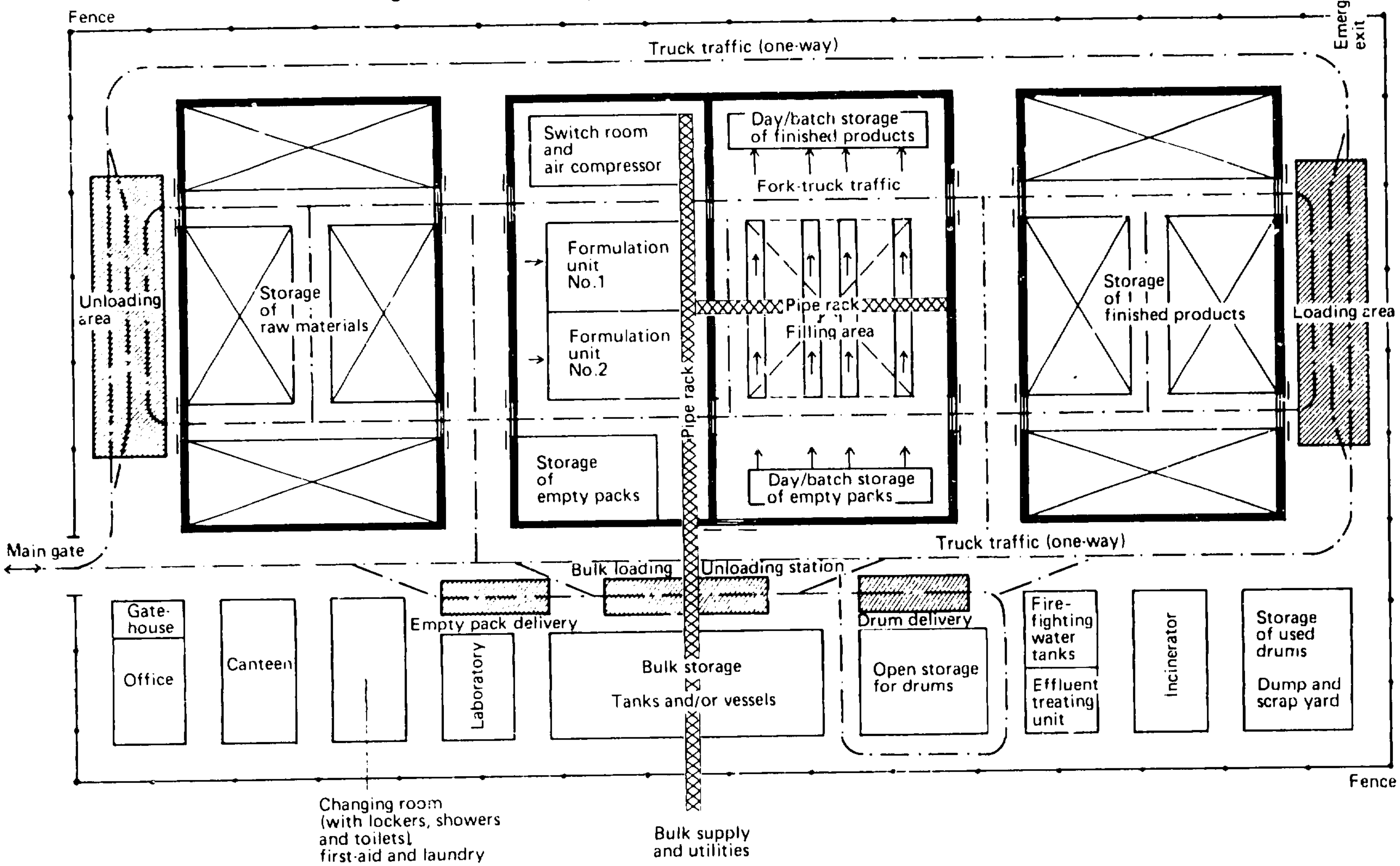
Conventional products

With the exception of suspension concentrates, most of the conventional liquid formulations are produced by either blending different liquids together or by dissolving solids in liquids. These products can therefore be produced and filled in a conventional liquid blending and filling unit. Special attention must be paid to the nature of the products handled. For example, aqueous products require the use of stainless steel or otherwise corrosion-protected equipment, and with flammable materials all the electrical equipment must be approved for fire safety.

With a conventional unit, measured amounts of active ingredients, solvents, emulsifiers etc. are added to a blending vessel equipped with a suitable stirrer. If necessary, heat can be applied to the vessel to aid dissolution. The blended product is then passed through a filter (if required) to a storage vessel, and from there to the filling equipment. In view of the popularity of liquid formulations and the relatively simple nature of the equipment required, and hence the relatively low cost, such a unit is by far the most common type of formulation production unit throughout the world.

[1] See also chapter III.

Figure I. Schematic layout of an agrochemical formulation plant



Suspension concentrates (flowables)

Suspension concentrates are suspensions of a finely divided active ingredient in a liquid medium (usually water). During production, particle size reduction is generally achieved in a two-stage milling process.

In view of the relative sophistication of suspension concentrate units, in particular the mills and associated cooling units, the capital cost is usually significantly higher than that of an emulsifiable concentrate unit. As a rule, suspension concentrates are only produced from products that are insoluble in common aromatic solvents and water. The technical products must have the required physical properties, such as a high melting point, to enable them to be milled. Since suspension concentrates are special products requiring expensive production units, such plants are not very common in developing countries.

Solid formulations

Dusts and powders

Both dusts and water-dispersible powders are dry-milled products. Dusts are low-concentration products for direct application, whereas water-dispersible powders are high-concentration products that are just dispersed in water before application.

Dusts are produced by first making a dust concentrate, which is a concentrated mixture of active ingredient and inert ingredient that has been dry-milled in a coarse-grinding mill such as a hammer mill. Since coarse grinding is sufficient for dusts, the concentrate is then diluted with further inert ingredients to give the final field strength dust, which is then bagged.

Water-dispersible powders have a finer particle size than dusts. The mixed active ingredients and inert ingredients are usually first dry-milled in a coarse grinding mill and then given an additional fine milling using, for example, an airmill, before being bagged.

The capital investment required for a dust and water-dispersible powder unit is generally significantly higher than for a liquid blending unit. The capital cost increases even further if dust-explosive products are milled, since explosion suppression, venting or inert gas blanketing is then required.

Water-dispersible powders have declined in popularity with the advent of suspension concentrates, and show signs of declining still further with the introduction of the safer-to-use water-dispersible granules.

Conventional granules

Conventional granules are products for direct application. They can be produced by various processes, including the spray-on or stick-on techniques, extrusion or agglomeration. Spray-on granulation is the most popular process because it involves the relatively simple spraying on to an absorbent granular core of either a liquid active ingredient or a solution of a solid active ingredient. The capital expenditure can be particularly low for plants already having a dust or water-dispersible powder unit because it often only requires a relatively simple modification to one of the mixers.

Stick-on granulation is somewhat more complicated, and usually requires a special stick-on granulation unit. The process involves the coating of a solid granular core with the active ingredient and a binding agent. Whether or not a drying process is needed depends on the product.

Extrusion and agglomeration techniques are more complicated, and as a result such units are not common, particularly in developing countries.

Water-dispersible granules (dry flowables)

Water-dispersible granules can best be described as granulated water-dispersible powders. Their principal advantage over water-dispersible powders is that they are dust-free and hence safer for the user. As with water-dispersible powders, these products are dispersed in water before application, and hence usually contain relatively high concentrations of active ingredient. The popularity of these relatively new products in the agrochemical market appears to be growing rapidly.

Various processes can be used to produce water-dispersible granules including spray-drying, extrusion, and a variety of other agglomeration techniques. The finished product has to be sufficiently granular to avoid being dusty, it must have sufficient dry strength to avoid dust formation during storage and handling, and it must be free-flowing and disperse readily in water to give a stable suspension.

Production plants are currently found mainly in North America and Europe, but as the products become more popular such plants may also become established in developing countries, replacing to a certain extent existing water-dispersible powder and suspension concentrate plants. In terms of capital cost, such units are comparable to a water-dispersible powder plant.

Support facilities

As with all manufacturing operations, formulation plants require the basic support facilities of administration, canteen, warehousing, workshop and plant utilities such as electrical supply, steam or hot water and compressed air. Moreover, because many agrochemicals can be toxic and present a risk to the environment if not handled properly, and because all agrochemicals are products that are judged by their performance, formulation plants require the special support facilities described below.

Laboratory[2]

A well-staffed and well-equipped laboratory is an essential part of a modern formulation plant. Its key role is to ensure that the quality of products leaving the plant are in accordance with local regulatory requirements and with the claims made on the product label.

A laboratory may require a sizeable investment if special equipment is needed for, *inter alia*, gas chromatography, high-performance liquid chromatography,

[2] See also chapters VI and VII.

infra-red or ultraviolet and visible spectrophotometry, although the investment is small compared with that required for the production units. However, with the increasing cost of active ingredients, laboratory investment is soon paid off because good quality control avoids active ingredient wastage, ensures consistent product standards and facilitates a thorough investigation and speedy handling of potential customer complaints.

Effluent treatment and waste disposal[3]

Modern formulation plant operations should take good care of any effluent or waste produced during formulation. In most plants, good housekeeping can virtually eliminate aqueous effluent (which is usually the most difficult to treat) by using non-aqueous cleaning methods, for example, cleaning up liquid spills with sawdust, and cleaning out vessels with solvent that can be stored until the next batch of the same product is produced. For plants where aqueous effluent is unavoidable, such as a suspension concentrate plant, the sophistication of the effluent treatment unit can vary from an evaporation pond to a sophisticated rotary vacuum and active carbon filter.

The control of air pollutants is usually considered as part of the actual formulation production unit and may require dust filters and scrubbers.

Solid waste is best disposed of in a purpose-built incinerator. However, such facilities usually require a relatively large investment and can only be justified for plants of medium size or larger. Hence they are not commonly found in developing countries, where plants tend to be small since they produce only for the local market. Plants without their own incineration facilities may have to rely on either local contractor facilities or on the services provided for toxic waste disposal by the local authorities. Even this may not be practical in some developing countries, in which case it will be necessary to resort to other procedures such as chemical treatment or detoxification and burial in a well-controlled dump site.

First-aid and medical facilities

Although all plants should have a basic first-aid kit, those handling acutely toxic products also need a room equipped with emergency treatment equipment that can be used, if necessary, until the patient can be transported to a local hospital. The room and equipment require only minor investment, and a safety-conscious plant management will make arrangements for such a facility in consultation with its medical and toxicology advisers.

Washing and changing facilities

In order to minimize exposure to potentially toxic products, workers in formulation plants must wear special protective work-clothes, and in order to prevent contamination of their everyday clothing, special washing and changing

[3] See also chapters III and XI.

facilities are required. Ideally, the formulation plant itself will launder all clothing and provide clean clothes or overalls for employees. Safety aspects also require a special design for social amenities and rest rooms.

Organization and staffing

A typical organization chart for a small formulation plant operating one shift and integrated with a sales organization is presented in figure II. Larger formulation plants would have a larger, more comprehensive on-site organization, including, for example, a personnel manager, a finance manager and a safety and security officer. Multiple shifts require a proportionate increase in the number of direct operators, and, depending on the circumstances, additional maintenance and laboratory personnel.

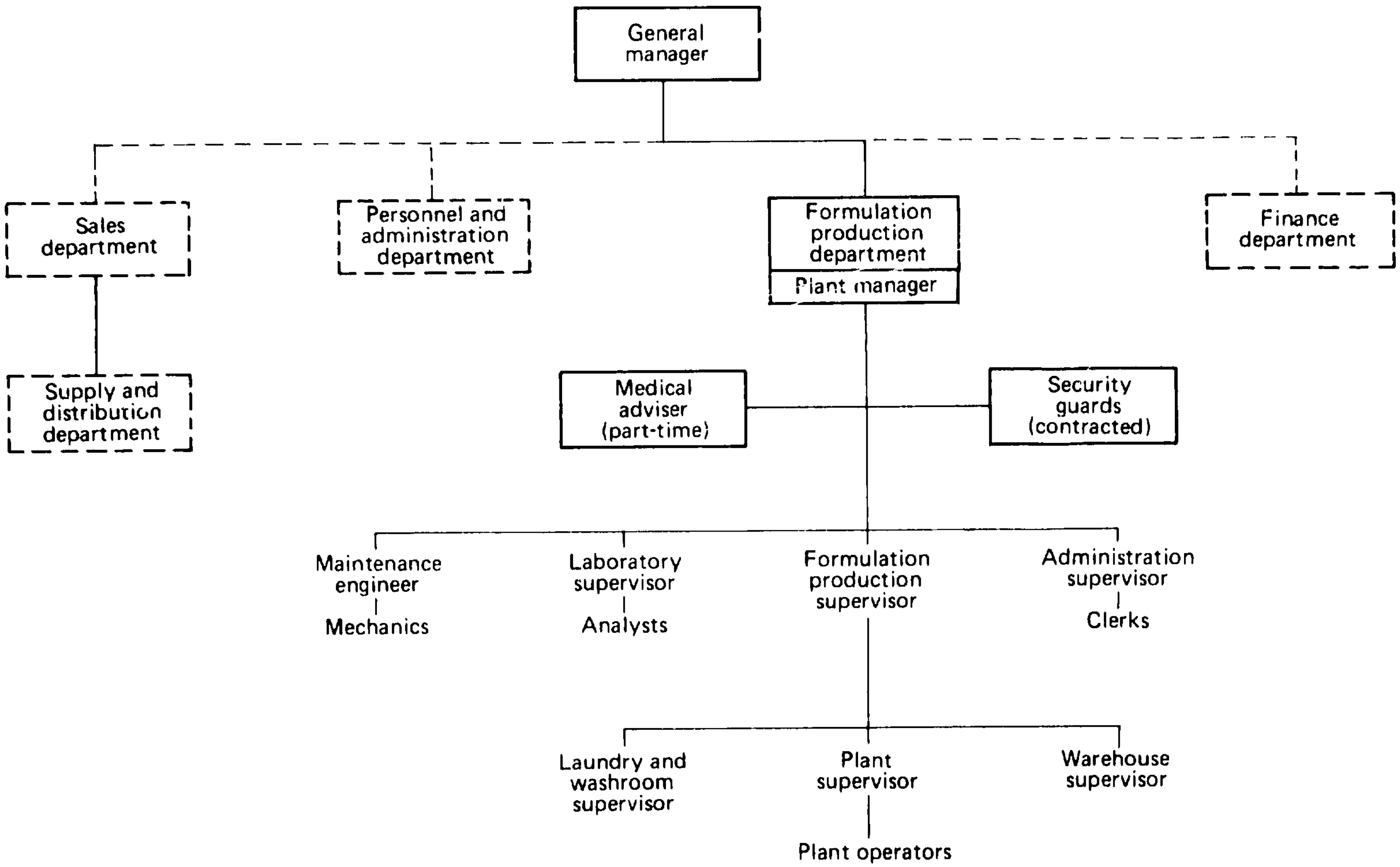
Managing and operating a modern formulation plant safely and efficiently has become a fairly complex task requiring its own special expertise. The plant manager and senior department heads need to be qualified professionals with some experience in formulation operations. Special staff at intermediate levels, such as quality control analysts and shift foremen, must have a reasonable level of education, training and expertise. At lower levels, plant operators and maintenance mechanics in particular must be well trained. It is most important that a low level of staff turnover is maintained, to enable personnel at all levels to gain and preserve a high degree of experience, know-how and safety awareness.

Formulation: a market-oriented operation

Formulation is regarded as primarily a market-oriented operation, and therefore formulation plants, including filling and packaging facilities, are generally located in or near the major markets. Where a market of sufficient volume and potential exists, the need for shortening distribution lines and for prompt response to market demand, together with the local availability of ingredients (fillers and solvents), may provide sound economic justification for establishing formulation plants close to the market. It is clearly preferable from an economic and logistical point of view to transport relatively small tonnages of technical pesticides and special ingredients like wetting agents to the formulation plant for incorporation into less concentrated formulations suitable for field use, rather than to move substantially larger tonnages of finished formulations over considerable distances.

While the use of pesticides in a particular market or market sector may show a fairly consistent pattern when averaged over a three- to five-year period, sales of various agrochemical formulations according to type and volume may fluctuate considerably in a particular season or year because demand is heavily dependent on a number of uncontrollable factors, in particular the following: prevailing climatic conditions; pest incidence; competition and the introduction of new products; and special seasonal factors.

Figure II. Typical organization of a small formulation plant integrated with a sales organization



Production in small local formulation plants is normally geared to meet short-term demand, and production for stock is generally carried out only for a small number of products in limited quantities. On the other hand, depending on import lead times, and in order to cope with sudden demand, stocks of expensive ingredients (wetting agents, emulsifiers etc.) may have to be relatively high. Siting the formulation plant close to the market makes it possible to cope more effectively with such eventualities. This requires, however, an effective communication and co-ordination between the local sales, distribution and production organizations and departments. The local operation must be sufficiently flexible in terms of plant design, capacity of major product lines, stocks of main ingredients, and staffing to be able to cope with and respond rapidly to sudden changes in product demand.

A further advantage of siting a formulation plant close to a particular market is that the design of the various facilities and the production programme can be geared more readily to local needs. This is becoming more important as local markets increasingly require their own specific formulation variant of any standard technical product. Moreover, with the growing importance of mixed pesticide products, many countries require the design of different formulated products in addition to formulation variants around a single product. As an example, the development of a new cotton insecticide, in view of differences in the pest complex in different regions and countries, may involve the design of more than 30 different products, which may in turn require over 200 different formulation variants to be developed and produced. Concentrating the development and production of a limited number of specific formulations in a particular country or region therefore has obvious advantages.

With the proliferation of formulation plants in many developed and developing countries over the past 20 years, a serious problem has become apparent, in that the volume of sales and consequently plant loading in many cases does not allow an economically sound operation. Because of the strongly seasonal demand pattern and the uncertainties in forecasting market requirements, it is common experience that many plants are only operated for a short period of the year prior to and during the actual selling season. Consequently, a significant part of the available production capacity remains unutilized. This can adversely affect the manpower arrangements and the economic operation of a formulation plant, particularly in developing countries with a restricted market volume and potential.

As mentioned earlier, formulation plants are becoming more sophisticated with advances in formulation technology and with the increasing requirements to raise standards of quality, industrial hygiene, safety and environmental protection. Qualified staff must therefore be selected for managing such operations, and plant operators must be thoroughly trained for the safe and efficient operation of the plant. All these factors have added significantly to initial plant investment in hardware, and have substantially increased operating costs when compared with similar operations some 10-15 years ago. In this context, the seasonality of the local business and the inherent problem of plant loading become even more relevant, and the siting and sizing of the formulation plant require careful consideration before an investment decision is made.

Nevertheless, for many of the well-established pesticides, local production of formulations can provide real savings, not least in terms of reduced requirements of foreign exchange to finance imports. Apart from purely marketing considerations, the availability of investment grants and special tax incentives and the imposition of tariff barriers to the import of finished products may be important considerations for establishing a local formulation operation.

Key feasibility criteria for establishing a local formulation plant

The following basic criteria are applied to determine whether a local formulation plant can be operated successfully. They apply equally to developed and developing areas.

Market volume and potential

Since the primary objective of a new formulation venture is to satisfy future market requirements, it is essential that market demand and future potential for specific individual product formulations are well defined through appropriate market research. This involves a detailed analysis of the nature of the market, its size and future potential. It may be necessary, if such information is not already available from other sources, to carry out an in-depth analysis of current agronomic practices, of the use of agrochemicals, and of special characteristics of the local pesticide market. Furthermore, the structure of the market with respect to potential customers, the required distribution network and the need for suitable warehouse facilities and their location must be analysed. In a developing country market environment it is of particular importance to obtain reliable information on agricultural development plans and government policies, since these are highly relevant for estimating the rate of change and the direction agricultural development is likely to take over the lifetime of the new formulation project.

With the basic market information and against projections of likely economic and agronomic developments and future pesticide use patterns, market demand and growth for each product sector and each individual product can be estimated. Many factors may distort the figures for market demand, for example: climatic conditions in a given year may favour a high or low incidence of some particular pest; carry-over of stocks from one season to another may suggest that demand for a product, if measured by imports, is falling off; demand for a particular pesticide may be high simply because it is currently the cheapest product imported, although its performance and the spectrum of control is limited. Well-designed and well-conducted market research will identify such distortions. Realistic cost-performance analysis will then provide a sound basis for selecting the most suitable pesticides and types of formulation for production in a given area.

Finally, sales forecasts and packaging requirements for individual products must be sufficiently detailed to enable a proper sizing and design of the various formulation units and packaging lines. For each active ingredient, the type of formulation, container size and package, volume, and period of sale should be determined. Data on market demand must indicate in which month of the year the product is required and the main areas of distribution. In some developing countries, transport by road may be restricted in the wet season, and the product may therefore be required for distribution several weeks or even months before it is actually applied.

Local availability of raw materials

The ready availablility of cheap formulation ingredients of consistent quality, solvents and fillers in particular, is of primary importance for the economic operation of a local formulation plant. Import of such materials may seriously reduce the economic attractiveness of the local formulation project, as freight costs, insurance and import duties might considerably increase the costs of the materials. Moreover, long shipping lines will create logistical problems, and are impracticable for seasonal production. A quick manufacturing response to unpredictable market demands would hardly be possible unless excessive stocks were maintained at the plant, and as a consequence a major advantage of a local manufacturing operation would be lost. For similar reasons the local availability of small pack containers and packaging materials is highly desirable. It should perhaps be noted that the characteristics of the locally available ingredients may be such that it is difficult if not impossible to match exactly the concentration, properties and specifications of an imported formulation. In all cases it is essential to ascertain through laboratory tests that the physical and chemical properties of local ingredients are suitable for the proposed use. The performance of formulations developed from these ingredients must be tested in the field before decisions are taken to establish local formulation facilities.

An important aspect to be considered before selecting the local material is, therefore, its quality. Specifications for ingredients and packaging materials are defined during the development of the formulation. Once the specifications, covering all the critical characteristics, have been established, it is essential that the quality of future supplies should stay within the defined specification limits. Other criteria also requiring careful consideration include security of supply and cost. It is generally advisable, depending on local circumstances and availability, to invite competitive offers from a number of local suppliers.

Active ingredients

Technical pesticides for local formulation may not be available locally because the small tonnages required may not warrant local manufacture. Supply arrangements with the foreign suppliers need to cover such aspects as price, quality and security of supply. Adequate shipping arrangements have to be agreed on, and the stock position at the supplier's plant must be sufficient to cater for unforeseen demands of formulated products.

Solvents

In many countries, (aromatic) hydrocarbon solvents are available from local refining operations. Other organic solvents used in agrochemical formulations, such as alcohols, esters, ketones, glycols and glycolethers, may have to be imported, except for countries having a petrochemical capability.

Before switching from an imported solvent to its local equivalent, it is essential to confirm that all the key characteristics of the local solvent, such as distillation range, aromatics content, flash-point, solvency, water miscibility, water content etc., are within the defined specification limits. The specifications should be agreed with the local supplier in order to guarantee that future deliveries of the product will be of constant quality. Furthermore, even though physical characteristics may appear satisfactory, with emulsifiable concentrates it may be found that the local equivalent solvent requires an emulsifier balance different from that of the imported solvent. This must also be determined before making any change.

Carriers and diluents

One of the key criteria in deciding whether to build a local wettable powder or dust plant is the availability of a local supply of a suitable carrier or diluent. This is of particular relevance for "field strength" dusts, since there would be no economic sense in having to import large tonnages of inert diluent.

Apart from having all of the required characteristics, including appropriate particle size, sorptivity, flowability and abrasivity, it is essential that the local carriers and diluents are compatible with the active ingredients concerned. The process of carrier and diluent selection is usually done in the first instance by testing a sample provided by the supplier. However, a decision should not be based on the sample alone, because it could be unrepresentative of future supply. One must therefore ascertain that the mineral source is of consistent and uniform quality and that the reserves are adequate. Finally, a representative sample of the carrier is tested against specifications and in the target formulations. It is also important to check whether access to the reserve by road or rail is adequate in all weather conditions, because supplies could be thereby affected. Under potentially unfavourable transport conditions, sufficient stocks should be held at the plant and special delivery conditions must be arranged with the supplier.

Surfactants

Surfactants include emulsifiers, wetting agents and suspending agents. The tonnage of those products consumed by the agrochemical industry in individual countries is relatively small, and hence for this outlet alone local manufacture is not common.

Once again, quality is the prime concern. Where a formulation has been developed using local products, the most effective way of checking their quality is to prepare a small sample of the formulation and to test its surfactant-related characteristics.

Adjuvants

Adjuvants cover a range of special products, including deactivators, anti-caking agents, stickers, structuring and anti-foam agents etc. Such specialities, which, like surfactants, are used in small quantities, are generally not available locally and have to be imported.

Packaging

Local availability of packs such as bottles, pails, cans and drums is a key factor when considering local formulation because the import of empty containers would be an expensive and highly inefficient operation. Packaging material may consist of glass, metal or plastic containers. Glass bottles are universally available and are the simplest type of pack because selection is based principally on straightforward physical aspects such as bottle weight and dimensions, and any compatibility problems are associated only with the insert and the cap. Metal containers such as cans, pails and drums can present more problems because of incompatibility with the product. Where this is a problem, containers may need to be internally lacquered, sometimes with multiple coats. Plastic containers are frequently ideal for water-based products, but for non-aqueous products compatibility is often a major problem.

In view of safety considerations and because of the high value of most agrochemicals, selection of suitable containers and efficient quality control is absolutely essential. Contractual arrangements with the local suppliers should cover these aspects.

Local technical resources

Specialist knowledge is required not only during the design and construction of a formulation plant, but in particular once the plant starts operating, in order to maintain the equipment and to provide specialist general technical services.

The design of a formulation plant requires special know-how that may not be available in some developing countries, but may often be readily obtainable from outside agencies such as engineering companies with agrochemical experience. Depending on the level of technical development of the local supporting industry (industrial substructure), major equipment, utilities and general facilities may be obtained locally. Civil engineering and local plant construction resources are available in most countries. In those countries where technical resources are limited or non-existent, it is possible to have, for example, a liquid blending unit made in a simple-to-install modular form which can be constructed overseas and then imported ready for assembly.

Once plant production has started, the more important type of local technical support needed for a formulation plant is for the repair and maintenance of plant equipment such as mills, compressors, motors and valves, laboratory equipment and general facilities. The limited size of most local formulation operations does not normally justify the establishment of an extensive technical service and maintenance department on the plant site, and hence those services may have to be contracted out. Where such local support is not available, the plant organization should have an engineer trained to carry out those tasks. At the same time, if equipment is not manufactured locally, spares should be kept of all key equipment items.

Availability of qualified staff and labour

A basic reservoir of staff with managerial, technical and scientific qualifications and technically trained labour should be available locally to facilitate the staffing arrangements. Temporary assistance and training by outside specialists may be required. Depending on the size of the operation, staffing arrangements have to be made for the following areas of activity (see also figure II):

Plant management

Administration and finance departments

Plant operation: production supervisors and foremen, team of operators for each formulation and packaging line, team to operate waste disposal (incinerator) and effluent treatment units

Technical service and maintenance team

Quality control and technical support for marketing

Warehousing and dispatch

Medical services

Special attention needs to be given to finding experienced, high-calibre staff for key management positions. This is a major step towards having an efficient, safe and environmentally secure operation. The simplest way of finding a source of experienced people for the key positions is to locate the plant in or near an industrial area compatible with the field of activity involved (chemical industry) and with market and distribution requirements. A competitive salary policy with attractive career prospects should be used to hire competent staff in order to build and retain expertise. As previously mentioned, in some countries staff turnover may be high, and it may be particularly difficult to keep qualified personnel such as maintenance engineers and laboratory analysts.

The complexity of formulation plant operations varies considerably, for example, liquid blending units are not as difficult to operate as suspension concentrate or water-dispersible powder plants. The qualifications required by the plant operators are therefore largely determined by the complexity of the operational unit and the process to be carried out. It must be borne in mind, however, that the handling of many pesticides may be potentially hazardous if correct operating practices are not followed. Operators therefore need to be of a standard enabling them to be easily trained to carry out the defined procedures. A regular, well-designed training programme is the best way of maintaining a formulation plant at peak operating efficiency.

Economic evaluation

From an economic point of view, an investment in a formulation plant is no different from investments in other chemical production facilities. The same decision criteria can therefore be used to evaluate the economic viability of a local formulation plant. For such investment to be worthwhile, the expected future benefits in the form of profits, cost savings and possible social benefits should compare sufficiently favourably with the initial expenditure of capital and other resources. It is the objective of an economic evaluation to quantify the benefits and the resources required, and to ensure that the project under consideration is the best available option for achieving the desired objectives.

In the economic appraisal, the formulation plant is treated as an integrated operation, that is, as an independent cost and profit centre. Starting from the year of the projected first expenditure, annual cash flows are calculated over the lifetime of the project (usually 10 years). The economic attractiveness of the project in isolation and in comparison with other options is analysed and measured by using various profitability indicators such as pay-out time, present value and internal rate of return.

It is recommended, moreover, that a sensitivity analysis should be carried out on the main cash flow items, that is, the volumes of sales, prices (proceeds to plant), capital expenditure, and the main production cost elements, in order to establish the effect of changes in individual estimates on the profitability of the formulation project as a whole. Sensitivity analysis identifies those estimates in which variations, or uncertainty, have significant effects on the financial viability of the project.

In cases of great uncertainty, for example, if the future demand pattern for the main products may vary considerably, a detailed risk analysis may need to be carried out, especially when a relatively large capital investment is at stake. A risk analysis not only takes into account the effects of variations in estimates (sensitivity analysis), but also the chances that they will occur.

The main items of the cash flow calculation, the use of profitability indicators and sensitivity analysis are considered below, with particular reference to formulation plant investment projects.

Main cash flow items

Sales proceeds and formulation fees

Sales proceeds are the major item of cash income in a formulation plant, and, if any contract formulation is done, additional income accrues in the form of formulating fees. The annual sales proceeds or formulating fees are the product of the annual tonnages of each individual formulation and their selling price (ex plant) or formulating fee per ton. Since this is the critical cash income item for evaluating the viability of a formulation plant, it is essential that the estimates of volume, selling price and formulating fee are as accurate as possible.

Capital expenditure

In order to make an accurate estimate of the capital expenditure required for the construction of a formulation plant, the project scope must be well defined. The following elements need to be considered:

(a) *Type of formulation.* The process and equipment required will be determined by the type of product required, for example, emulsifiable concentrates, granules, water-dispersible powders etc.;

(b) *Sales volume estimates.* Market research provides estimates of annual volumes for each individual product over the evaluation period, taking into account seasonal variations. From such data the annual formulation programmes are derived, and after establishing the number of shifts to be operated which may be a factor of local circumstances and labour costs, the capacity of the equipment of all plant units can be defined. The capacity of the warehouse and the required size of general facilities, such as canteens, washrooms and utilities, can then also be determined;

(c) *Formulation recipes.* They provide detailed information for the process and equipment design, including the number of ingredients that need to be dosed, whether they are solids, liquids or both etc.;

(d) *Pack type and size.* Projected data for the packaging of the end-products are required in order to define the type, size and throughput of the filling equipment;

(e) *Safety and environmental considerations.* Such factors determine whether, for example, a process must be explosion-proofed, whether exhaust ventilation filters or scrubbers are needed, and whether an incinerator or effluent treatment unit is needed.

Once plant design has been completed and a site agreed for the plant, specifications can be defined for the various equipment items, quotations can be obtained from equipment suppliers and local engineering and construction companies, and finally precise data on capital expenditure can be determined. If the plant is built on a green site, the capital estimate has to take into account site clearance costs, the construction of access roads and the supply of basic utilities. In practice, a preliminary capital estimate is always made during the early stages of an evaluation to get an indication of whether or not a project will be viable.

Operating costs

Operating costs include expenses such as the cost of labour and management, rental charges, maintenance materials, laboratory reagents, fuel, electricity and raw materials. In a formulation plant these costs can be divided into what are known as variable and fixed costs.

Variable costs

They are referred to as variable because they vary directly with a change in the level of production. They include the following elements: formulation ingredients (active ingredients, emulsifiers, solvents etc.); processing materials (filter aids, nitrogen used for blanketing etc.); packaging materials; and auxiliaries (steam, electricity, compressed air, water etc.). Auxiliaries are occasionally regarded as fixed costs to facilitate budgeting.

Fixed costs

These costs are referred to as fixed because they are considered not to vary significantly with a change in the level of production. They can be subdivided into direct fixed costs and overheads.

Direct fixed costs

Such costs are directly attributable to the formulating, filling, maintenance and warehousing activities, and include: operating labour (wages and overtime, shift allowances, bonus payments, leave pay, sick pay, pension contributions, national health contributions etc.), that is, the gross direct cost to the company of its own labour force; contract and casual labour; plant maintenance (bills from maintenance contractors, labour costs of maintenance staff, materials costs); utilities (electricity, fuel, water, waste disposal, effluent treatment etc.), when not included under variable costs; laboratory costs (labour, reagents, maintenance of analytical equipment etc.).

Overheads

These are the general costs that cannot be charged directly to a specific part of the plant operation, and include the plant general management, warehousing and dispatch, finance departments and general services such as security, gatekeepers, canteen staff, nurses and clerical services etc.

Working capital

Working capital includes funds tied up in stocks of raw materials and finished products, money receivable from debtors, accounts payable and credit received from suppliers. For evaluation purposes, input data have to be standardized according to local circumstances. For example, raw material stocks can be taken at three months of annual requirements, finished product stocks at one month of annual requirements, and the average repayment time for debts fixed at one month. In practice, however, the agrochemical business is seasonal, and stocks are usually built up until just before the application season, when, subject to climatic conditions and pest incidence, the inventory is sold over a short period.

The number of months covered by raw material stocks follows the same pattern, although when materials such as active ingredients have to be imported, it is frequently necessary to hold stocks for long periods. With locally produced ingredients, for which there is a rapid and plentiful supply, stocks need only be held for short periods. Debt repayment periods vary considerably from country to country.

The above assumptions have been used in the cash flow calculations for a typical formulation plant project in tables 1 and 2. For stocks of finished products, the assumption is that the major part of the stockholding (covering 3-6 months) in distribution and marketing channels will be for the account of the trading companies concerned, which may or may not be part of the same enterprise.

TABLE 1. SIMPLIFIED CASH FLOW CALCULATION FOR A FORMULATION PLANT PROJECT

(In thousands of constant pounds as of the first year of project)

	Year of project life								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Capital expenditure	(600)	(1 400)	—	—	—	—	—	—	—
Residual value of plant	—	—	—	—	—	—	—	—	800[a]
Sales proceeds (ex plant)	—	—	600	900	1 350	1 650	1 950	1 950	—
Formulating fees	—	—	50	300	800	800	800	800	—
Gross operating income	—	—	650	1 200	2 150	2 450	2 750	2 750	—
Operating costs									
Fixed	—	—	(200)	(200)	(200)	(200)	(200)	(200)	—
Variable	—	—	(337)	(469)	(687)	(837)	(975)	(975)	—
Total	—	—	(537)	(669)	(887)	(1 037)	(1 175)	(1 175)	—
Net operating income	—	—	113	531	1 263	1 413	1 575	1 575	—
Fiscal depreciation (10% per year)	—	—	(200)	(200)	(200)	(200)	(200)	(200)	—
Finished product stock increase/decrease value	—	—	82	22	4	11	(5)	0	(114)
Tax paid (50%)[b]	—	—	(0)	(174)	(534)	(612)	(685)	(688)	—
Raw material stock increase/decrease value[c]	—	84	33	55	38	34	—	—	(244)
Net annual cash flow	(600)	(1 484)	80	302	691	767	890	887	1 158
Cumulative cash flow	(600)	(2 084)	(2 004)	(1 702)	(1 011)	(244)	646	1 533	2 691

[a] In practice, a cash flow calculation would be carried out in money of the day, and therefore the residual value of the plant and the fiscal depreciation would differ less from the initial value than in this table and in the net present value and internal rate of return derived in table 2.

[b] It is assumed that 50 per cent tax is charged on net operating income and on the increase of stocks of finished products (assumed to cover one month of the requirements of the following year and valued at 10 per cent depreciated production costs) after allowing for fiscal depreciation of the initial plant investment at 10 per cent per year.

[c] To simplify the working capital calculation, debtors and creditors have not been included and raw material stocks have been assumed to cover 3 months of the requirements of the following year.

TABLE 2. PROFITABILITY INDICATORS DERIVED FROM A SIMPLE DISCOUNTED CASH FLOW CALCULATION

(In thousands of constant pounds as of the first year of project)

	Year of project life								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Net annual cash flow	(600)	(1 484)	80	302	691	767	890	887	1 158
Cumulative cash flow	(600)	(2 084)	(2 004)	(1 702)	(1 011)	(244)	646	1 533	2 691
Mid-year discount factor (10%)	0.953	0.867	0.788	0.716	0.651	0.592	0.538	0.489	0.445
Discounted cash flow (10%)	(572)	1 287)	63	216	450	454	479	434	515
Cumulative discounted cash flow (10%)	(572)	(1 859)	(1 796)	(1 580)	(1 130)	(676)	(197)	237	752

Notes:
1. Net annual cash flow figures drawn from table 1.
2. Calculation based on a six-year operational life and a nine-year project life.
3. Net present value of project at a 10 per cent discount rate over a nine-year project life = £752,000.
4. Internal rate of return of project = 17.9 per cent.

Financing arrangements

For financing the project, it may be necessary or advantageous, depending on local circumstances, to use loans from financial institutions, Governments or other sources (development aid organizations), especially if the capital required cannot be provided out of available project funds. In that case, interest payments, loan repayments, and, if appropriate, investment grants have to be included in the cash flow calculation. Since capital expenditure is usually phased over the whole design, engineering and construction period, with a peak being reached in the final stages of plant construction, the cash flow items have to be phased accordingly.

Residual value

The residual value of a project is the disposal value, after a given project lifetime, of the assets or business, including working capital, net of any taxation arising from disposal and other closing-down costs, such as site restoration expenditure. For evaluation purposes, however, the fixed assets (excluding land) are generally calculated as being the book value (acquisition cost less accumulated book depreciation). Land is included at the estimated future market value. Stocks are either sold out in the final operational year or a residual value can be assumed equivalent to the market or replacement cost at the end of the evaluation period (horizon year). In practice, a horizon of 10 years, or less, is chosen for an agrochemical project because it is not usually possible to estimate a cash flow accurately beyond that period.

Tax on income

The amount of tax to be entered into the cash flow calculation depends on the net annual fiscal income and the locally applicable rate of income tax. Certain tax incentives are given in many areas of the world to stimulate local industrial development, and they should be taken into account in the cash flow calculation. In calculating the tax liability, fiscal depreciation of the investment should be taken into account.

Cash flow calculations

A cash flow for a project is derived by relating the annual incoming cash to outgoing cash for a fixed period of years. A typical simple cash flow for a small emulsifiable concentrate formulation plant project on an existing site, not involving outside financing, is shown in table 1. The example is based on the following assumptions:

(a) The capital expenditure would be phased over two years, with the major part of the investment in the second year, when the processing equipment would be installed;

(b) The working capital appears in the pre-operational year, when raw material stock build-up occurs, with a gradual increase in subsequent years as sales increase.

Cash flows should be expressed in terms of the main currency actually invested in and generated by the project. When more than one currency is involved, the local currency should be adopted as the common unit of measurement, and, if possible, estimates of likely exchange rate movements should be taken into account.

High rates of inflation make it necessary to consider the effects of inflation on individual cash flow items. It should not be assumed that all cash flow items move in line with the general inflation index for a given country, because the effects of price controls, wage increases etc. on specific items can be different for different items of the cash flow. The recommended procedure is to estimate cash flow items in "money of the day" starting from prices or unit costs prevailing in the base year and using assumptions about the inflation rates for the various cash flow components. The net cash flow, calculated in "money of the day", is then converted to constant money by deflating the net annual cash flows to the value they would have had in the first year of capital expenditure, by using a general inflation index.

Profitability indicators

The principal profitability indicators are described below.

Pay-out time

The pay-out time is the time it takes for the cumulative net cash flow in constant money to become positive (see figure III). The pay-out time of a project is not a measure of overall profitability, because it says nothing about what happens to the project after the pay-out period has been reached. It is, however, a useful indicator in helping to assess certain kinds of risk. For example, if there is the possibility that a process could become obsolete in a short time because of new technological developments, then a company will want a short pay-out time, such as 2-3 years, or even less.

Present value

The present value is the amount of surplus cash in constant money generated by the project over its operating life at a specified discount rate. For example, if the discount rate (minimum acceptable rate of return on investment) is set at 10 per cent and a given project generates in addition to the 10 per cent a cash surplus of $2 million over a project lifetime of eight years, then its present value (PV 10 over eight years) is equivalent to $2 million. For a present value calculation, the discount rate to be applied to a project is the minimum rate of return in constant money that a company would accept for an investment, taking into account the degree of exposure to specific business risks.

Internal rate of return

The internal rate of return is the rate of return in constant money on the original investment that a project is likely to earn over its lifetime. It can also be regarded as the discount rate that results in a zero figure of net present value.

Figure III. Cumulative cash flow graph showing pay-out time (cash flow figures from table 1)

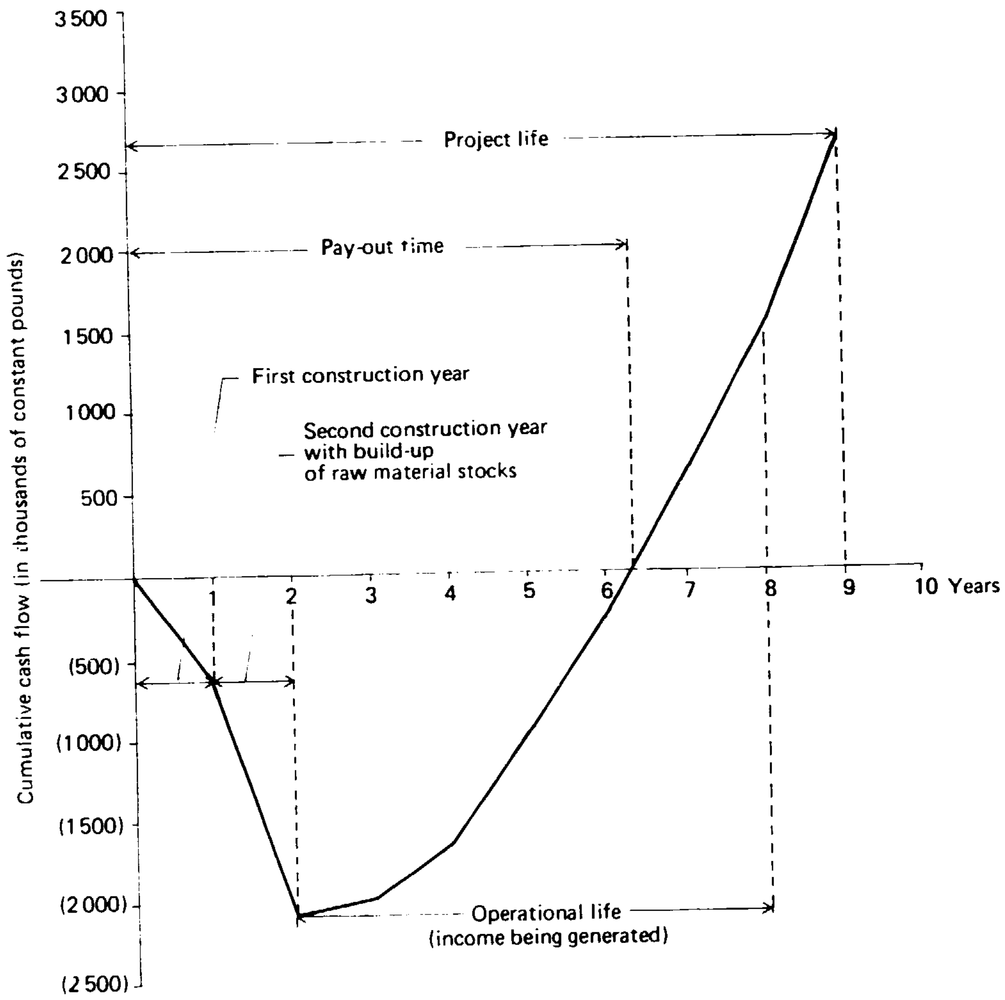


Table 2 shows a discounted cash flow calculation for the data used in table 1, and it gives the derived profitability indicators of present value and internal rate of return.

Sensitivity analysis

Before any decision is made to build a formulation plant, the sensitivity of the profitability indicators to, for example, a 10 per cent change in the main input data must be determined. With local formulation plant projects, this usually means estimates of formulation volume, selling price or proceeds and capital expenditure. As the scope of a project becomes better defined, so the capital expenditure estimate becomes more accurate, leaving volume and selling price as the key items of doubt. If the profitability of a formulation plant project proves very sensitive to a change in volume or selling price, which is often the case, and the estimates appear doubtful, then the wisdom of proceeding with the project should be seriously challenged.

When analysing a project cash flow, it is also important to establish what part of the present value cash surplus at the chosen discount rate is due to the residual value. If it is a significant part, then it is not a sound principle to justify a project largely on the basis of an implied sale of the assets at the end of the horizon year.

Future trends in pesticide formulation

While some pesticide product sectors, in particular herbicides, are highly developed, there is still considerable scope for innovation in all major product sectors because of product obsolescence arising from regulatory and resistance problems and the commercial introduction of superior new products. Moreover, continuing improvements in existing formulations and the development of new types of formulations of already well-established technical products will provide an additional challenge to formulation scientists and commercial formulators for many years to come. The following paragraphs describe various trends in pesticide research and development that will have a profound influence on future formulation activities in both developed and developing countries.

It is expected that in coming decades the emphasis will be on the discovery of new compounds that are more active and selective, and which can be used with minimum risk to the producer, the user and the environment at large. As a result, the familiar large-volume commodity products with a broad application range will tend to be replaced gradually by new selective products with a more limited market potential. This undoubtedly will contribute to the diversity and complexity of local formulation operations. Furthermore, the current trend towards more active products with application rates as low as a few grams per hectare as against kilograms in the past will not only present a challenge to formulation design and production from a technological point of view, but will also inevitably affect the economics and viability of local operations.

New types of formulations are being developed. They are designed primarily to improve the performance of the pesticide for certain applications, to eliminate undesirable side-effects and to decrease the cost of production. Examples are further developments in the area of suspension concentrates and in particular of water-dispersible granules. Conventional pesticide formulation facilities may not be suitable for manufacturing some of the new products, and new investment will certainly be needed.

With the increasing cost of crude oil products a move from conventional aromatic solvents towards cheaper alternatives is foreseen. This could include water-based suspensions and emulsions. A move towards higher-concentration aromatic solvent-based products is also foreseen in order to reduce unit formulation costs. However, because of the low application rates of many modern pesticides, this will mean smaller volumes of formulation being used per hectare, which may necessitate a parallel development in pack sizes and design to facilitate the more precise dosing of formulations to spray tanks.

The rapid advancement of modern cultivation methods in developing countries will require new techniques of pesticide application in crop protection. Already the ultra-low-volume application technique enjoys significant advantages in many areas. Further developments of this technique and new developments in the area of controlled droplet applications and electrostatic spraying techniques are likely to be introduced on a commercial scale in the next decade. Such developments could also have a profound effect upon the viability of formulation units originally designed to handle large quantities of conventional formulations.

The increasing awareness of problems of safety in use, occupational health and environmental conservation and the concomitant advancement of technology in those areas will greatly influence pesticide development and plant operations. In the manufacture of technical pesticides and formulations more attention will be paid to personal protection measures, to pollution-conscious design, engineering and construction, to pollution abatement, waste disposal and effluent treatment facilities. For small formulation plants the cost of such special facilities could exceed the capital investment required for the actual production unit. This aspect must be carefully considered when evaluating new investment opportunities.

The development of more complex technical pesticides and formulations will result in a need for more sophisticated quality control facilities and procedures. This is already apparent with the commercialization of optical isomers as active ingredients. Quality control laboratories will have to be equipped with special high-precision analytical instruments, and qualified staff must be available to operate them. Moreover, quality control laboratories will be increasingly used as a local formulation development resource.

The general trends in pesticide and formulation development and use patterns described above will increasingly call for a high degree of professional expertise, diversification and flexibility in production methods and also in the manufacture of formulations. A local formulation operation is more likely to be successful if it has continuing support from a major research and development effort. Both in the early evaluation of opportunities for economically viable local formulation facilities and in maintaining their viability in future, co-operation is clearly a key factor.

V. Marketing and distribution

*M. N. Hill**

The previous chapter examined the economic criteria on which the decision to establish a formulation plant is based. It correctly emphasized the need for a market-oriented approach. This chapter concentrates on the concept of marketing itself, of which product distribution forms an important part.

Although marketing is considered from the point of view of the formulator, the activity in reality starts with the customer, in the present case the farmer, who may be defined as the final user of the product. There will in fact be a number of intermediate commercial stages in the distribution chain at which money may change hands, but marketing is the continuing process by which the needs of the farmer are identified and met by the resources of the formulator, through the distribution chain between them. In other words, marketing may be regarded as the integration of all operations required for the following purposes:

(a) To define the market;

(b) To meet current and, where possible, anticipate future requirements;

(c) To steer the product through all its stages, before, during and after manufacture, until it reaches its ultimate user;

(d) To maintain and increase the acceptability of both the product and the formulator, especially through the brand name, which is a symbol of the product quality.

The marketing process may be divided into four main steps which partly overlap in time, namely market research, design, execution, and monitoring and feedback.

Market research

When a pesticide is a candidate for market use, the following questions should be asked:

(a) Concerning crops:
- (i) What crops are at risk and how do they fit into the agricultural pattern in terms of land allocation and value?
- (ii) What weed, insect, pest or disease is attacking the crops, and in what seasons does the attack occur?
- (iii) Do climatic conditions have a bearing on the attack?
- (iv) Are non-target species likely to be at risk when using a pesticide treatment?

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(b) Concerning the status of the farmer:

(i) Is a plantation crop, cash crop or subsistence crop under cultivation?

(ii) What return does the farmer earn?

(iii) Is the farmer subsidized?

(c) Will the pesticide reach the farmer through a distributor and then a retail outlet or is the Government the distributor?

(d) What degree of technical help can the farmer expect from the distribution network or the government extension service?

(e) Are there other means of dealing with the crop damage, and if so what features of the candidate product are likely to prove superior to its competitors?

Answers to the above-mentioned questions should be provided in order to enable the marketeer to assess the existing market, forecast future market trends, and proceed to the next step in the marketing process.

Design

The essence of marketing skill lies partly in the ability to take a technically equal product and present it in such a way as to offer clear advantages to the user, even where the price per unit of active ingredient remains the same. The pesticide marketeer has several weapons at his disposal, all of which fall under the general heading of design.

Product

The marketeer sells not so much a product as a problem-solving effect. In other words, instead of just selling a formulation of technical ingredients, the marketeer offers a specific formulation of high and consistent quality which, for example, will attack the pest or adhere to the weed or crop in adverse condition, and the application of which will cause minimum damage to the environment and to non-target species.

Packaging

The package should be designed so that its contents can be poured and measured with minimum hazard, perhaps in quantities which allow a specified acreage to be treated, thus limiting spillage or stock accumulation resulting in possible deterioration and the unnecessary tying-up of cash (see chapter XII). During trans-shipment to the market-place and throughout the distribution process, the package serves as the storage container of the product. It must therefore be robust enough to carry the product for substantial periods, particularly where the contents may be highly concentrated and potentially harmful to life or the environment.

Labelling

The label should be designed not only to convey statutory and other essential information, but also clearly to reveal by colour and design many other points of interest (see chapter XII), and possibly to establish a house style which will characterize other products from the same organization and confirm their high quality standards.

Plant design

The decision as to which formulations to produce has an effect on the design and provision of plant and machinery, a topic which is fully covered in chapters III and IV.

Personnel requirements

Finally, the design of the organization will need to be considered and personnel recruited. The service required from the distribution system is considered below in greater detail.

Execution

The third phase of the marketing process involves execution. It will be assumed that the product to be formulated is based on an active ingredient which is available from a number of different sources, that it is a commodity-type product rather than a proprietary speciality. That assumption is made because the proprietor of a speciality will have strong views on how it should be marketed and will tend to become directly involved in marketing, even if the product is to be formulated by a third party. In the following analysis, the marketeer negotiates for the supply of active ingredient and other raw materials and ingredients.

Raw material and production costs

The quality and price of the finished product will depend on the purchasing skill of the marketeer and the efficiency of the production process and of management (see chapter III). The full manufacturing cost of a pesticide includes plant overheads, depreciation and general charges, plus the cost of financing the very considerable amount of working capital represented by the stock of finished products (inventory), the cost of debtors (receivables) and selling expenses, such as advertising and the sales force.

Selling price

The full manufacturing cost rarely determines the selling price, which is not based on a simple cost formula plus a stated theoretical profit level. Costs are commonly viewed as a constraint on the lower limit of pricing discretion. The emphasis in the pricing decision is placed upon considerations such as what the market will bear, the level of competition and consumer perception of the relationship between product cost and the benefit received. It may also be determined by the choice of specific marketing strategies, for example, whether to aim at low cost and a high volume of sales or the converse. Similarly, prices may be affected by government policy on subsidies and by government-established price levels for farm products. Marketing may thus be seen to start with the consumer, and what is left after all the costs have been covered, including the costs of the links in the distribution chain, is the surplus available for distribution as dividend and further investment.

The realistic forecasting of the selling price is thus a crucial element in assessing the viability of any investment. It should be further noted, without attaching too much importance to the point, that the selling price of a local formulation plant will not necessarily be lower than the landed duty-paid price of a comparable imported product. If the locally manufactured product cannot compete, Governments may be prompted to consider a price subsidy or other protective measures, since they will wish to avoid penalizing farmers, especially poor farmers, by replacing imports with local products at substantially higher prices.

Finally, when there is more than one local formulation plant, Governments may decide to tender for the supply of their requirements. In such cases, there may be a temptation to quote prices based on the marginal cost of production, that is, on variable cost only (see chapter III). If the quantity concerned forms a very substantial part of the total output of the plant, the results can be economically disastrous.

Sales force

Pesticide sales require a technical input from sales staff who, while selling their product, are able to impart technical information to potential customers. At the same time, the pesticide salesman should learn from the customer about his particular needs and relay the information back to management, thereby playing an essential role in the two-way communication process that is the essence of good marketing. The existence of an extended distribution chain in a country would enable major distributors, in co-operation with the sales staff of the formulator, to send their own sales force to the market-place. A training component, frequently involving seminars and training sessions for the sales staff of the distributor, is therefore an essential ingredient of pesticide promotional activity. The leading farmer in an area may prove to be the best of advocates, given the relative ease with which farmers tend to become familiar with the methods employed by their neighbours. Contact can and should be made with government departments to secure their endorsement of properly established technical recommendations.

Finally, while management should remember that no sale is concluded until payment has actually been made, a well-defined and wisely administered credit policy will create a good foundation for continuing business.

Advertising and promotion

Since the distribution chain may contain two or more links between the formulator and the farmer, at least three groups of people must be made aware of the existence, purpose and price of the product. The function of advertising and promotion is to assist in the communication of information in order to create awareness and to stimulate the desire to buy and to continue buying. In fulfilling that function it supports both the sales force of the marketeer, and the sales effort of the main distributor and his retail outlets. In other words, it must support both the "selling in" to the distributor and the dealer, and the "selling out" from one or both to the farmer.

Because advertising is an emotive and complex subject, this chapter will only indicate various options open to the marketeer.

The marketeer can choose from one or all the media available for the conveyance of his message, including newspapers, trade and professional journals, radio and television, cinemas, billboards and posters, exhibitions and trade fairs, direct mailing, public relations activities such as dissemination of information to the press, publications, including point of sale material, and, last but not least, labelling and packaging. Skilful use of the available media should enable the marketeer to reach the full range of his potential customers, from the highest government official to the poorest farmer.

The message conveyed may announce the launching of a new product or simply consist in a reminder of either the product name or the seasonal need for its application. The medium or media chosen should be the most suitable for the target audience. The content of the message must often be subject to statutory regulations designed to ensure that claims for efficacy and safety are correctly presented, together with proper instructions and precautionary measures for handling the product. In the absence of regulations, such matters are left to the discretion of the marketeer. Although the industry as a whole behaves responsibly in this respect, there are nevertheless exceptions which, by the successful marketing of their products, threaten the standards of the whole industry. Irrespective of statutory requirements, the content of the message conveyed by the advertiser should be viewed against the cultural and social environment of the country. Rural communities are characterized by a strong resistance to change and adherence to traditional ways. The promotional message must therefore be clearly stated and supported by readily understood practical examples.

Advertising may stress the unique selling points of a product or convey a simple technical and commercial message illustrating its benefits to the farmer. Where the message is more technically complicated, there is a need for personal contact, the expertise of salesmen and extension services, demonstrations and meetings with farmers. The frequency and timing of the advertising needs to be known in advance by the distribution chain so that it can reinforce the campaign through its own merchandising efforts within the shop or through the efforts of its salesmen. Merchandising, including the use of shop displays and point-of-sale material such as free plastic measuring beakers, hats, T-shirts and other items of clothing bearing the product name or logotype, carries the message into the field. They represent a degree of sophistication in marketing which may go beyond what is required or can be afforded in a given country. But in a rapidly changing world, what may seem out of reach or novel today becomes the commonplace of tomorrow. The aim remains to convey a message of real benefit to the farmer, but the exercise will fail completely if the necessary infrastructure of distribution and credit facilities is not available to him.

Distribution

From the point of view of the farmer, the distributor or dealer has one main function, to provide the right product at the right price and in a package of the right size at the moment he needs it. Not only can the farmer not afford to buy the product in advance and store it for later use, but he may very well be unable to pay until after the sale of the crop. The distributor or dealer therefore needs to finance his stocks and debtors, a function which in many countries may be removed from the private sector and taken over by public sector financing, if not actually managed by the Government. Since the main (regional) distributor may have to transport supplies over long distances, it may be necessary for the Government to own the means of transport, to ensure that roads are built to bring the farmer his supplies, and to store them until required.

Where distribution remains in the private sector, it is often conducted by small commercial firms located close to the sales area. Such distributors would normally carry a wide range of agricultural products in addition to pesticide formulations. Depending upon the level of demand for the pesticide product, considerable effort on the part of the formulator may be needed to ensure that stocks are available when required. The slow rate of transport and the lack of a good storm-proof road network makes communication difficult. Pesticides are invariably required on a seasonal basis, which makes it hazardous to predict levels of pest infestation and, consequently, of pesticide requirements. From the point of view of the distributor, stocks tie up capital which could be used elsewhere in his business. It is therefore usually difficult to persuade the distributor to hold adequate pesticide stocks to meet every requirement. Even where the pesticide is imported under government tenders, the reluctance to commit capital in such an unpredictable area as pest control can mean that too small an amount of pesticides arrives too late.

There is consequently scope for effective dialogue between the formulator and the distribution chain to ensure that adequate pesticide products are available when and where they are needed. Such a process may require strengthening through government forward planning to deal with eventual pest attacks, and through investment or fiscal policies designed to help maintain specific levels of pesticide stocks. The education of users and statutory requirements for pesticide use would lead to a smoother pattern of pesticide supply and demand and improve distribution and availability.

Monitoring and feedback

It may be useful to summarize some of the factors that management needs to review at the end of the season in order to monitor performance against forecasts and prepare for the following year.

Sales volume

The volume sold will be the volume invoiced to the first customer, who is normally the main distributor. Much more important is the assessment of the volume actually used in the market, which will depend on a reasonable evaluation of stocks left at the end of the season in the distribution chain. It may only be possible to obtain an estimate of the stocks of the main distributor. The information obtained will provide a basis for the production programme of the following year, although there will be many other inputs, such as the actual incidence of pest attacks as compared with statistics for an average year.

Sales value

The gross invoice value received less all costs shows the state of health of the business. The unit selling price may require review in the light of feedback from the market-place.

Costs

The following questions must be answered:

(a) Were the costs as forecast;

(b) Is a correct balance maintained between stocks of raw materials, volume of production, sales and stocks of finished products?

Information from the market

The following information from the market, or feedback, is required:

(a) How did the product perform? What strengths and weaknesses did the user or distributor report?

(b) Was the product considered to be good value?

(c) Was the package effective, safe and of the right size?

(d) Was the label clearly understood?

(e) Was the advertising effective? Which medium was the most effective? Did the merchandising attract comment?

(f) Were farmers able to buy when and where they wished?

(g) Did distributors and dealers sell at the anticipated price, or did they give extra discounts?

(h) What was the reaction of competitors?

(i) What was the reaction of government authorities?

An assessment of the above information and other points needs to be made in order to determine what action may be required prior to the sales programme of the following year.

Conclusion

The analysis presented in this chapter reinforces the view that the business of formulating pesticides is a market-oriented operation. By skilful attention to all the steps in the process, the marketeer adds value to the basic active ingredient and satisfies the farmer that the product he is buying gives him an unmistakable benefit in return for his outlay.

VI. Establishment of a pesticide laboratory[1]

*D. P. Nag**

The specific project design and subsequent successful operation of a pesticide laboratory depend upon the precise identification of its functions, which vary according to its aims and objectives and may involve a research unit for the discovery and synthesis of novel active ingredients,[2] a research and development unit for new formulations, a regulatory agency or the routine requirements of a formulating plant. It is, therefore, essential to discuss the functions of a pesticide laboratory for a particular purpose before considering the project design and the basic requirements of the laboratory. In this chapter only the laboratory associated with the routine requirements of a formulating plant will be considered (see the section on formulated products in annex I).

Functions of a laboratory attached to a formulating plant

The prime function of a laboratory attached to a formulating plant is quality control of the products. This function includes: analysis of raw materials and ingredients required for the formulation, analysis of the finished product for specifications, bio-assay for pesticidal activity, and in some cases acute toxicity testing.

A secondary function is associated with monitoring the health of plant workers engaged in toxic processes.

The identification and characterization of a chemical is essential before its commercialization. If the product has not been properly characterized, later batches may differ, thus invalidating any testing that has been conducted on the initial material.

Before products are released for use, stability determinations should be conducted on the technical pesticide and its formulations, and stability of the products must be demonstrated for the required duration of storage. It is

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[1] Parts of this chapter were updated and taken from chapters 5 and 7 of the 1972 edition of this publication, *Industrial Production and Formulation of Pesticides in Developing Countries*, vol. 1, *General Principles and Formulation of Pesticides* (United Nations publication, Sales No. E.72.II.B.5).

[2] A selection of the very wide range of data required for the registration and certification of a new active ingredient is presented in annex I. The section on formulated products is applicable to the laboratory considered in this chapter.

necessary to show that the products do not degrade appreciably due to prolonged storage or storage under adverse conditions, like heat or humidity. This is relevant in the context of storage facilities available and the practices followed by farmers in developing countries. Even a pesticide like malathion with a good safety record caused 2,500 cases of poisoning in Pakistan in 1976 among malaria spraymen, five of which proved fatal.[3] An investigation carried out by the World Health Organization in co-operation with various laboratories showed that the accident was due to a major toxic impurity, isomalathion.

Impurities are sometimes formed during storage as a result of interaction of the active ingredient with inert carriers or diluents. It is, therefore, necessary to study the toxicology of pesticide formulations after subjecting them to accelerated storage and long-term natural storage conditions, especially in tropical countries.

Laboratory requirements

The following sections describe some typical project needs of a laboratory attached to a formulation unit and cover location, physical facilities, laboratory equipment and personnel. The laboratory can range from a simple organization composed of several chemical technicians performing physical tests for particle sizing (screening) and emulsification and chemical analyses for active ingredients to a more sophisticated staff of professional chemists developing analytical methods, analysing all finished formulations, checking the specifications of all raw materials and testing for cross-contamination (see also chapter VIII). Regardless of the size of the laboratory, samples for retention and analysis should be taken of all raw materials and of each lot or batch of the finished product. All analytical work on samples received in the laboratory should be recorded for ready reference in case of complaints and possible government inspection, as required by good laboratory practice.

Location and building

It is always desirable to establish the pesticide laboratory on the same site as the formulation unit but not directly adjacent to the working plant. Indeed, it is recommended to locate the laboratory near management offices, since a clean, well-equipped laboratory can also be a show-piece for a generally well-managed facility. It is also desirable in the context of the developing countries to locate the laboratory in a place where the temperature fluctuations are minimal, so as to minimize the maintenance cost involved in the air-conditioning of the laboratory. The specific design of the building varies, depending upon the local availability of already constructed buildings, building material etc.

Physical facilities

The laboratory should have adequate power supplies, air-conditioning (if needed), and maintenance services. The building or project buildings may be renovated structures or newly constructed.

[3] World Health Organization Technical Report Series, No. 634, 1979.

Some countries may be able to supply a good portion of their own needs. However, usually the machinery, formulation equipment, reagents, glassware, scientific apparatus, instruments, fume hoods, and books and journals for the library must be imported. The journey of the glass apparatus and analytical and electronic equipment over land and sea is expensive, time-consuming and hazardous; it has not been unusual to find evidence of rough handling as well as breakage of equipment. Such damage could be avoided if the project management was able to arrange, through the appropriate government officials, for special supervision and handling of its incoming crates and packages at the docks and during transport to the laboratory.

Laboratory equipment and instruments

Laboratory safety is of paramount importance in the design of a chemical control laboratory. Another important consideration is cleanliness or housekeeping to eliminate cross-contamination during sampling analysis. Thus, a well-ventilated room in a location not directly adjacent to processing and packaging facilities is highly desirable.

A well-ventilated explosion-proof fume hood to carry out operations with toxic or highly inflammable materials in mandatory. Explosion-proof solvent storage and dry, cool storage for finished products are necessary. Other safety features are discussed below in the section on laboratory safety.

A list of basic instruments for a well-equipped chemical control laboratory is given in annex II. Most of these instruments are required to meet WHO Specifications for Pesticides Used in Public Health.

A gas-liquid chromatograph is now one of the most commonly used analytical instruments for formulation analysis (see chapter VII). Among its advantages are rapidity, reproducibility and ease of assay. Due to highly sensitive detectors, such as the flame ionization detector, smaller amounts of the product need to be analysed, thus reducing interferences from impurities and other components of the formulation which would complicate spectrophotometric methods and require clean-up prior to final analyses. The gas-liquid chromatography (GLC) method, therefore, lends itself to the analysis of many samples per day. As an illustration of the acceptance of this technique of formulation analysis, several chemical quality control laboratories of custom formulators of a respectable size possess only a GLC apparatus and a micro-balance for their analytical instrumentation and are able to perform the required services for their particular company.

Thin-layer chromatography (TLC) is another extremely easy analytical procedure that does not require sophisticated electronic repair services. This technique can be employed for chemical identification and cross-contamination tests. GLC and TLC can be performed by technicians after a relatively short period of training. With these two procedures and a modest capital outlay, a large part of the analytical work for quality control of pesticide formulations can be accomplished.

Library and reference books

Since many formulating facilities and associated chemical control laboratories may be located in an isolated area away from any extensive library, it is recommended to build up a core selection of reference books and scientific journals. A selected list of recommended publications is found at the end of this chapter.

Laboratory safety

Very early in the planning stage of a laboratory, serious thought must be given to safety (see also chapter X). In ordering supplies for the project, the usual laboratory safety equipment, such as goggles, rubber gloves, aprons and similar items, should be included. The installation in the laboratory of fire extinguishers and safety sprinklers with quick-opening valves and drenching shower heads must not be overlooked. First-aid equipment and facilities for personal cleanliness must be provided. As mentioned above, a well-ventilated chemical safety hood is mandatory. The same procedures for disposal of laboratory residues and wastes should be followed as indicated in chapter III.

There should be no eating, drinking of beverages or smoking in the laboratory. These are all common-sense rules, and good supervision should be exercised to see that they are kept.

Laboratory management must emphasize the necessity for safety to all personnel connected with the laboratory. The understanding of safety and the attitude toward prevention of accidents may not be as prevalent as in some highly developed industrial countries. Improvement in this situation calls for education and patience. Probably one of the first steps should be the formation of a safety committee by staff members. The committee should establish and implement a practical safety programme including enforcement of a simple fundamental code of essential rules of safety.

Personnel

The laboratory manager or supervisor will normally be responsible for product quality control. Either he or the analytical chemist responsible to him should be of graduate status.

The analytical chemist will carry responsibility in the macro-determination of percentage composition of technical products, raw materials and finished formulation. Many of the tests, however, such as sieve analysis, determination of specific gravity etc. may be performed by technicians after some training, since most of these tests are routine, but interpretation of results must be the responsibility of a professional chemist.

Some formulation laboratories may not be able to perform all the necessary tests at the plant. One of the reasons may be that the only method available for the assay of the active ingredient requires an analytical instrument not available at the plant. In this case, it will be necessary to send the samples to a qualified government or commercial analytical laboratory.

It may be appropriate to have an electronic technician on the staff. Because instrumentation is now an essential part of chemical analytical procedures, the electronic technician should prove invaluable in maintaining the instruments in proper condition. Often, much time and production can be lost when instruments break down, and local expert help as well as parts and tools may not be available for their repair.

An administrative officer is required to expedite procurement of local supplies, to correlate office procedures and building services, and to supervise office and service personnel.

Training of personnel will have to be an integral part of the laboratory plan of operation. In addition to trained scientific personnel, various other levels of training are important. Scientists may receive their formal education and gain their skills in their home countries, or they may have the opportunity to continue their education and develop expertise in pesticide specialities in foreign countries through fellowships or other arrangements. But a working project needs trained technicians who can assist scientists and thus allow more efficient use of scarce scientific personnel. In developing countries, the need for skilled or semi-skilled technicians should not be overlooked; dependable personnel must be able safely and adequately to handle reagents, equipment and simple instruments, and to count, measure, weigh and draw significant samples. Trained technicians can assume greater responsibility as they gain skill, and should therefore enjoy greater incentives and prestige.

Supervisors should make training an integral part of the laboratory because the training of new personnel, especially in the safe handling of chemicals and personal hygiene, is essential. Technical assistance from United Nations agencies and other organizations, such as the United States Agency for International Development, is also available and requests for such assistance should be made through appropriate governmental channels.

ANNEX I

DATA TO BE GENERATED BY A PESTICIDE LABORATORY ENGAGED IN THE DISCOVERY AND SYNTHESIS OF NEW ACTIVE INGREDIENTS

Information required on chemical and physical properties

Active ingredients

- Structural formula
- Chemical name
- Empirical formula and molecular weight
- Manufacturer's code number(s)
- Melting- and boiling-point and decomposition point
- Vapour pressure (preferably at 20° C; only when above 10^{-5} millibar)
- Solubility in water (preferably at 20° C)
- Distribution coefficient between water and non-miscible solvent
- The minimum active ingredient content in weight per cent
- The maximum content of relevant manufacturing impurities and of additives in weight per cent

Formulated products

- Content of active ingredient
- Components included in the formulation of the commercial product, for example, active ingredient, adjuvants and inerts
- Storage stability (both for composition and application properties)
- Density range (for liquids only)
- Flammability: Liquids (flash-point)
  Solids (a statement must be made as to whether the product is flammable)
- Acidity
- Alkalinity
- Moisture content
- Bulk density (powders)
- Wettability (for dispersible powders)
- Persistent foam (for formulation applied in water)
- Suspensibility (for dispersible powders and suspension concentrates)
- Dry sieve test (for granules, dusts)
- Emulsion stability (for emulsifiable concentrates)

Data on efficacy of the product

Effectiveness

Phytotoxicity

Translocation within the plant or animal being treated

Persistence in soil, water etc.

Compatibility with other chemicals

Direction concerning the dosage (concentration)

Time of application, type of application, equipment and the manner in which the insecticide is to be used at the time of application

Experimental data on residues

Methods of sampling and residue analysis in food and feeding stuffs, water and soil and wildlife

Expected residue level in edible crops and soil, that is, amount of residue to be left following good agricultural practices and the residue disappearance curve

Experimental data on safety

Acute toxicity studies in mammals

- Oral
- Dermal
- Inhalation
- Eye and skin irritation
- Skin sensitization

Subacute studies in mammals

- Oral, 90 days
- Dermal, 21 days
- Inhalation, 14 days

Supplementary toxicological studies in mammals

- Chronic toxicity studies
- Neurotoxicity
- Teratogenicity
- Effects on reproduction
- Carcinogenicity
- Synergism and potentiation
- Metabolism
- Toxic effects of metabolites and residues from treated plants

Information on wildlife hazard

Toxicity to: Birds (acute toxicity)
Fish (acute toxicity)
Bees
Livestock
Wild animals

Stability of the proposed formulation

Stability under different agroclimatic conditions

Rate of decomposition

Identity of breakdown products

ANNEX II

SELECTED LIST OF ANALYTICAL INSTRUMENTS FOR PESTICIDE QUALITY CONTROL LABORATORY

Gas-liquid chromatograph

- Glass columns
- High-sensitivity flame ionization detector
- Electrometer: sensitivity, 10 – 11 A; drift, 1 per cent per hour
- Strip chart recorder or electronic digital integrator, 1 mV range, or computer for area measurement

Analytical balance

pH meter

Spectrophotometer or photoelectric colorimeter: IR, UV, visible spectrum

Testing sieve shaker

Melting-point block

Karl Fischer apparatus for the determination of water content

Closed tester for flash-point determination

Parr bomb or Schoniger flask for total chlorine

Thin-layer chromatography apparatus, including automated densitometer (optional)

SELECTED LIST OF PUBLICATIONS ON PESTICIDES

Books

Berg, Gordon L., *ed.* 1982 Farm chemicals handbook. Willoughby, Ohio, Meister, 1982. Annual revision.
"Pesticide dictionary".

Blalock, C., J. Shaughnessy *and* D. Johnson. Acceptable common names and chemical names for the ingredient statement on pesticide labels. 4. ed. Washington, D.C., Environmental Protection Agency, 1979.

CIPAC handbook. Compiled *by* R. de B. Ashworth *and others*. Harpendon, United Kingdom, Collaborative International Pesticide Analytical Council, 1973. v. 1.

Guidelines on analytical methodology for pesticide residue monitoring. Washington, D. C., Federal Working Group on Pest Management, 1975.

Herbicide handbook of the Weed Science Society of America. Champaign, Illinois, Weed Science Society of America, 1974.

Horwitz, W., *ed.* Official methods of analysis. 13. ed. Washington, D. C., Association of Official Analytical Chemists, 1980.

Manual of chemical methods for pesticides and devices. Washington, D. C., Association of Official Analytical Chemists, 1976.

Specifications for pesticides, insecticides, rodenticides, molluscicides, herbicides, auxiliary chemicals, spraying and dusting apparatus. Geneva, World Health Organization, 1967.

Spencer, E. Y. Guide to chemicals used in crop protection. London, Ontario, Research Institute, Canada Department of Agriculture, 1973.

Wiswesser, W. J., *ed.* Pesticide index. College Park, Maryland, Entomological Society of America, 1976.

Worthing, D., *ed.* The pesticide manual. 6. ed. Worcestershire, United Kingdom, British Crop Protection Council, 1979. 655 p.
Formerly edited *by* H. Martin.

Zweig, G. *and* J. Sherma, *eds.* Analytical methods for pesticides, plant growth regulators and food additives. New York, Academic Press, 1963-1982. v. I-XII.

Journals

Journal of agricultural and food chemistry (Washington, D. C).

Journal of pesticide science (Saitama, Japan).

Journal of the Association of Official Analytical Chemists (Washington, D. C.).

Journal of the science of food and agriculture (London).

Pesticide abstracts (Washington, D. C.).

Pesticide monitoring journal (Washington, D. C.).

VII. Principles of pesticide formulation analysis

*W. R. Bontoyan**

Methods of analysis used by regulatory laboratories for the pesticide content of commercial products should be specific, rapid, precise and as simple as possible.

During the 1950s and 1960s instrumental analysis was dominated by infrared spectrophotometry. In the United States it was not until the latter part of the 1960s that gas-liquid chromatography (GLC) became the most commonly used method of instrumental analysis of pesticide formulations. However, GLC analysis of formulated products did not become popular in many European countries until the second half of the 1970s. In the United States, thin-layer chromatography (TLC) analysis of pesticide formulations was extensively used in the 1960s and early 1970s as a means of detecting contaminants and certain impurities associated with the manufacture of pesticide formulations.

At the Second International Congress of Pesticide Chemistry, Bontoyan and Caswell [1] discussed in detail the various aspects of formulation analysis. Although their study still provides significant general information on techniques using different avenues of chemical analysis, the time has come to review and consider a broader scope of formulation analysis which includes both wet chemical analysis and instrumental analysis. The current trend in Western Europe and North America is towards analysis by high performance or high-pressure liquid chromatography (HPLC), which is as rapid as GLC and has the added advantages of little or no chemical decomposition due to high temperatures and of being able to vary flow rates. It can also be used with solvents individually or in combination with other mobile solvents to achieve separation and resolution. At present, HPLC is primarily used with ultraviolet detection systems with the capability of specific wavelength selection for maximum absorbance. There are also fluorescence detection systems and experimental systems using slide-wire thermal decomposition chemical analysis with specific detectors (such as phosphorus and nitrogen), but these systems are of minor importance at the present time.

The use of TLC analysis by regulatory laboratories was probably directly responsible for minimizing cross-contamination to the point where it is no longer generally considered a significant problem in the United States. Although TLC is still a valuable tool for screening, it has lost ground to GLC, which can be used,

* United States Environmental Protection Agency, Washington, D.C., United States. Statements made in this chapter represent the author's personal opinions and do not necessarily reflect the official views of the United States Government.

particularly by manufacturers, to detect contamination at levels far below the sensitivity of TLC. However, TLC is used by some developing countries to estimate pesticide residues in bulk materials and formulated products. Their laboratories use TLC because of the lack of carrier gas for GLC analysis and of quality solvents for HPLC, the adverse effects of high humidity on infrared spectrophotometers and salt cells, and the unavailability of proper maintenance for instruments. TLC in conjunction with wet chemical analysis will therefore probably be an important part of formulation analysis in developing countries for many years.

The Association of Official Analytical Chemists (AOAC) and the United States Environmental Protection Agency (EPA) laboratories in close co-operation with state laboratories have made significant progress in furthering the use of HPLC. In the near future, GLC capillary column analysis may become the dominant method of analysis for pesticide formulations.

Although HPLC and conventional GLC are the primary methods of analysis, all types of analysis should be used in view of the over 30,000 pesticide products registered for sale in the United States alone. With this in mind, different methods published in the AOAC *Official Methods of Analysis* [2] and the EPA *Manual of Chemical Methods for Pesticides and Devices* [3] are described below. If possible, AOAC methods should always be used for regulatory analysis. These methods have been collaboratively studied and subjected to stringent statistical analysis. One other set of methods that have been subjected to such rigorous testing are those of the Collaborative International Pesticides Analytical Council (CIPAC) [4]. The EPA methods have been critically reviewed by experienced United States federal and state analytical chemists and accepted by joint consensus. All EPA methods have at least undergone reliability analysis within the laboratory of origin and are usually uncontested in legal proceedings. Brief summaries of some classical wet methods and tables containing parameters of instrumental analysis used by regulatory laboratories throughout the world are presented below.

General methods (wet chemistry)

A significant number of pesticides lend themselves to classical wet chemistry analysis. Although many of those pesticides may be analysed by sophisticated methods, such as atomic absorption (AA), it may be difficult to justify the cost of the equipment required, taking into account the frequency of use of such methods of analysis by regulatory laboratories. Various wet chemical methods still used in pesticide formulation analysis will now be briefly described.

Arsenic [2]

$$\text{Sample} \xrightarrow[\text{HCl}]{N_2H_4,\ H_2SO_4,\ NaBr} AsCl_3$$

$$AsCl_3 \rightarrow H_2O \rightarrow As_2O_3 + HCl$$

$$As_2O_3 \xrightarrow[\text{with } I_2]{\text{Titration}} As_2O_5$$

Description of methods applicable to inorganic arsenicals

A sample containing approximately 0.4 g of As is boiled in 50 ml of a solution of hydrazine sulphate and sodium bromide for 2-3 min with the subsequent addition of 100 ml of HCl. The distillate is trapped in two receiving flasks containing H_2O connected in tandem.

The contents of the receiving flasks are transferred to 1-l flasks and a 200-ml aliquot is titrated with standard I_2 solution to the starch end-point. The percentage of As is calculated as either As_2O_3 or As_2O_5. A diagram of the apparatus appears in the AOAC *Official Methods of Analysis* [2].

Arsenic (sodium arsenite and arsenate) [3]

$$AsO_3 + I_2 + H_2O \rightleftharpoons AsO_4 + 2I^- + 2H^+$$

Arsenic in aqueous formulations containing no other oxidizable or reducible substances may be titrated directly with iodine for arsenite and, after reduction, for arsenate. Determination of inorganic arsenic compounds in formulations containing organic substances require oxidation of organic material with HNO_3 and H_2SO_4 followed by reduction with KI and titration with standard iodine solution.

Chlorotoluron and chloroxuron [2]

The pesticide formulation is extracted with CH_2Cl_2. The free acid is removed with acid and the extract is hydrolysed by alkali to Me_2NH which is distilled. The distillate is titrated with standard acid. Related by-products which may interfere are determined semiquantitatively by TLC.

Copper [2]

This method, involving electrolyte determination, is applicable to inorganic copper and copper in the presence of, or associated with, organic material. A solution containing copper (oxidized to its highest valence state) is subjected to electrolysis; the copper is plated on to a platinum cathode and weighed.

A sample containing 50-100 mg of Cu is weighed into a Kjeldahl flask of appropriate size and oxidized until solution is clear. The solution is transferred to a 250-ml beaker, the volume is adjusted to 200 ml and electrolysis is carried out using a rotating anode and weighed gauge cathode with a current of 2-3 A. After all copper has deposited (in approximately 30 min), 15-20 ml of H_2O is added to the electrolyte and electrolysis continued a few more minutes. If no further deposition occurs on newly exposed surface of the electrode, it is washed with H_2O without breaking the current. The deposited copper is weighed after washing with alcohol and drying.

Copper naphthenate [2]

A sample containing approximately 0.2 g of Cu is reacted with HNO_3 releasing the organic naphthenate which along with other organic material is removed with petroleum ether. Copper in aqueous solution is deposited electrolytically on platinum cathode and weighed.

Sodium hypochlorite, available chlorine, calcium hypochlorite [2]

Chlorine as available reacts with excess standard solution of As_2O_3. Excess As_2O_3 is back-titrated with standard I_2 solution to starch end-point. The percentage of available chlorine is determined from the difference between the total milliequivalent of As_2O_3 added and the number of milliequivalents of I_2 used to back-titrate.

Captan [3]

The method is applicable to high-concentration captan formulation and is based on measuring the hydrolysable chlorine in captan. The presence of any material containing hydrolysable chlorine would interfere. Chlorine in the sample is measured before and after hydrolysis. The amount of captan present is proportional to the difference between the initial and final amounts of chlorine.

Chloro-triazine herbicide [3]

A potentiometric titration with $AgNO_3$ is used to determine the total ionic chloride. This includes chlorine from the chloro-triazine by treatment with morpholine and any other inorganic chloride present in the sample. The inorganic chlorine is subtracted from the total chlorine and the resulting organic chlorine is calculated as the chloro-triazine herbicide.

Dioncap [3]

Since the nitrogen is present in the nitro (oxidized) form, it must be converted to the amino (reduced) form before being determined by the regular Kjeldahl procedure. This is done by reacting the sample with salicyclic acid and concentrated sulphuric acid to form nitrosalicyclic acid. The addition of a reducing agent such as zinc then reduces the nitro group to an amine group, forming aminosalicyclic acid. This compound is digested with boiling concentrated sulphuric acid in the presence of an oxidizing catalyst to form ammonium sulphate from the amino-nitrogen. The solution is then made strongly alkaline, and the released ammonia is distilled and absorbed in standard acid.

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Ethylene bisdithiocarbamates (EBDC) [2]

The EBDC is digested with H_2SO_4 to release CS_2. The CS_2 is trapped in a methanol-KOH solution to form the corresponding xanthate which is titrated with standard I_2 solution to a starch end-point.

Diuron, Monuron [3]

Dimethylamine is released by alkaline hydrolysis. The dimethylamine is distilled and titrated with standard acid.

Endosulphan [3]

Determination is based on the alkaline hydrolysis of endosulphan to yield sodium sulphate, which is reacted with an excess of acidified standard iodine solution. The excess iodine solution is titrated with standard sodium thiosulfate solution. Endosulphan is calculated from the amount of iodine used by the sodium sulphite.

Endothall [3]

The sample is neutralized with H_2SO_4 due to residual sodium hydroxide from manufacturing. It is then evaporated and ashed to convert the carboxylic acid to carbonate which is determined acidimetrically. Salts of carboxylic acids other than endothall interfere. If ammonium sulphate is present, it must be volatilized.

Ethyl hexanediol [3]

Acetic anhydriade is reacted with hydroxyl groups of ethyl hexanediol and the excess is titrated with sodium hydroxide. Alcohols, glycols, phenols and the amino groups in primary and secondary amines must be removed prior to analysis.

Nitrophenols (for example, DNOC) [3]

A volume of stannous chloride solution in excess of that needed by a weighed portion of sample is titrated with standard $K_2Cr_2O_7$ without reacting it with the sample. A second identical portion is reacted with the sample and the excess titrated. The difference in titrations represents the amount of $K_2Cr_2O_7$ equivalent to the sample. Other oxidizing compounds, reducible by stannous chloride, are titrated with standard $Na_2S_2O_3$ and are subtracted as milliequivalents from the $K_2Cr_2O_7$ milliequivalents of the sample. The new milliequivalents are equal to the nitrophenolic compound in the sample.

Tin in organotin compounds [3]

The organotin compound is digested with H_2SO_4 and HNO_3, reduced with Ni and Fe, and titrated with KIO_3 and starch as elemental tin. This is then calculated for the specific organotin compound.

Pyrethrins I and II [3]

The pyrethrins are hydrolysed with alcoholic sodium hydroxide to release the monocarboxylic and dicarboxylic acids which together are extracted with ether and steam-distilled for separation. The monocarboxylic acid pyrethrin I is extracted from the distillate, while the dicarboxylic acid pyrethrin II is extracted from the residue. Both are titrated with standard alkali.

Zinc phosphide [3]

A weighed portion of sample is initially washed with distilled water to remove any antimony potassium tartrate which would interfere with the quantitative evolution of phosphine from zinc phosphide. The washed sample is treated with H_2SO_4 under an atmosphere of nitrogen to release phosphine which is swept by the nitrogen into several absorption flasks containing standard potassium permanganate solution. The amount of zinc phosphide is calculated from the amount of $KMnO_4$ reaction with the phosphine evolved from the sample. The potassium tartrate in the wash solution may be determined by titration with iodine solution.

Infrared spectrophotometric methods

Infrared methods are simple and rapid to perform and based on the theory that specific chemical bonds absorb specific wavelengths of infrared energy. The amount of absorbance is directly dependent on the concentration of the chemical containing the specific chemical bond. However, only those chemicals whose concentrations exhibit linear absorbance over a workable range of concentration lend themselves to infrared analysis. Table 1 is a guide to the infrared analysis of pesticides. See also the collection of infrared spectra for commonly encountered pesticides in the EPA *Manual* [3] and *Analytical Methods for Pesticides and Plant Growth Regulators*, vol. IX [5].

Chromatographic methods (GLC and HPLC)

At present, GLC and HPLC are probably the most commonly used techniques for the analysis of pesticide formulations. However, it should be recognized that many of these methods have not been collaboratively studied and should not be used when an appropriate AOAC method is available. When using a GLC method that has not been confirmed by such studies, the analyst must be aware of problems associated with GLC analysis, particularly thermal decom-

TABLE 1. GUIDE TO PESTICIDE FORMULATION ANALYSES BY INFRARED SPECTROPHOTOMETRY

Pesticide	*Formulation*	*Method described in*
Aldicarb	Solids	AOAC *Official Methods* [2]
Atrazine	Solids	EPA *Manual* [3]
Azinphosmethyl	Solids	EPA *Manual* [3]
BHC	Powders	EPA *Manual* [3]
Benefin	Emulsifiable concentrates, granules	EPA *Manual* [3]
Benomyl	Solids	EPA *Manual* [3]
Bensulide	Emulsifiable concentrates, dusts, granules	EPA *Manual* [3]
Binapacryl	Powders, emulsifiable concentrates, dispersions	EPA *Manual* [3]
Carbaryl	Solids, liquid suspensions	AOAC *Official Methods* [2]
Carbofuran	Solids	EPA *Manual* [3]
Chlordane	Granules only	AOAC *Official Methods* [2]
Chloroxuron	Technical grade water-dispersible powders	EPA *Manual* [3]
Coumaphos	Powders	EPA *Manual* [3]
Cyanazine	Solids	EPA *Manual* [3]
DDT	Technical grade powders	EPA *Manual* [3]
DDVP	Sand and sugar bait, 0.5 wt % spray solvent, 1.0 wt % cattle spray in hydrocarbon solvents	AOAC *Official Methods* [2]
Diazinon	Liquids	EPA *Manual* [3]
Dibromochloropropane	Emulsifiable concentrates, granules	EPA *Manual* [3]
Dichlobenil		EPA *Manual* [3]
Dieldrin	All types, except those containing petroleum hydrocarbons	AOAC *Official Methods* [2]
Dinocap	Dusts, powders, granules	EPA *Manual* [3]
Dinoseb	Emulsifiable concentrates	EPA *Manual* [3]
Disulphoton		EPA *Manual* [3]
Endosulphan	Emulsifiable concentrates, granules	EPA *Manual* [3]
Endrin	All types, except those containing petroleum hydrocarbons	AOAC *Official Methods* [2]
Ethion		EPA *Manual* [3]
Fluometuron	Powders, dust suspensions	EPA *Manual* [3]
Karbutilate	Solids	EPA *Manual* [3]
Methoxychlor	Dusts, powders	EPA *Manual* [3]
Ovex	Solids	EPA *Manual* [3]
Phorate	Solids	EPA *Manual* [3]
Pyrazon		EPA *Manual* [3]
Resmethrin	Aerosols	EPA *Manual* [3]
Ronnel		EPA *Manual* [3]
Rotenone		AOAC *Official Methods* [2]
Thiram	Dusts, granules, powders	EPA *Manual* [3]
Trifluralin	Emulsifiable concentrates, granules	EPA *Manual* [3]
Vernolate	Emulsifiable concentrates, granules	EPA *Manual* [3]

position. HPLC analysis is not affected by thermal decomposition, but it is possible to cause hydrolysis of some pesticides in the presence of hydrophilic mobile solvents. The use of internal standards should be used whenever possible for both techniques. Tables 2 and 3 are designed for guidance to GLC and HPLC analysis of pesticides. Detailed consideration of these methods may be found in volumes VI and XII of *Analytical Methods for Pesticides and Plant Growth Regulators* [5].

Methods of formulation analysis are described in the WHO *Specifications of Pesticide Use in Public Health* [6]. FAO also produces a useful series of "Specifications for Plant Protection Products". The FAO specifications, however, tend to be less detailed since their purpose is to ensure that pesticides complying with them are satisfactory for the purpose for which they are intended, whereas the WHO specifications are designed also as aids to the purchasing of raw materials.

TABLE 2. GUIDE TO PESTICIDE FORMULATION ANALYSES BY HPLC

Pesticide	*Formulation*	*Method described in*
2,4-D	Salts, esters, 2,4-D	AOAC *Official Methods* [2]
Butylate		EPA *Manual* [3]
Carbaryl	Dusts, powders	EPA *Manual* [3]
Chlorophenoxy herbicides	Esters	EPA *Manual* [3]
Coumaphos	Solids	EPA *Manual* [3]
Diazinon	Liquids	EPA *Manual* [3]
Diuron	Solids	EPA *Manual* [3]
EPTC	Liquids	EPA *Manual* [3]
Ethion	Powders, liquid concentrates, oils	AOAC *Official Methods* [2]
Folpet	Solids	AOAC *Official Methods* [2]
Linuron		EPA *Manual* [3]
Malathion	All	EPA *Manual* [3]
Methyl parathion	Liquids	AOAC *Official Methods* [2]
Methyl parathion	All	EPA *Manual* [3]
Parathion	All	EPA *Manual* [3]
Picloram	Solids	AOAC *Official Methods* [2]
Remethrin	Liquids, aerosols	EPA *Manual* [3]
Warfarin	All	EPA *Manual* [3]

TABLE 3. GUIDE TO PESTICIDE FORMULATION ANALYSES BY GLC

Pesticide	*Formulation*	*Method described in*
Alachlor	All	EPA *Manual* [3]
Bromacil	Oils, salts, liquids	EPA *Manual* [3]
Butylate, EPTC, molinate, tillam, vernolate	Granules, liquids	AOAC *Official Methods* [2]
Chloroxuron	All	EPA *Manual* [3]
Coumaphos	All	EPA *Manual* [3]
Cycloate	All	EPA *Manual* [3]
DBCP	All	EPA *Manual* [3]
Dacthal	Granules	AOAC *Official Methods* [2]
Diazinon	Liquids	EPA *Manual* [3]
Endosulphan	All	EPA *Manual* [3]
Ethoprop	All	EPA *Manual* [3]
Fluometuron	All	AOAC *Official Methods* [2]
Formothion	All	AOAC *Official Methods* [2]
Heptachlor	All	AOAC *Official Methods* [2]

Pesticide	*Formulation*	*Method described in*
Malathion	All	AOAC *Official Methods* [2]
Methoxychlor	All	EPA *Manual* [3]
Methyl parathion	Liquids, powders	AOAC *Official Methods* [2]
Monocrotophos	All	EPA *Manual* [3]
Parathion	Liquids	AOAC *Official Methods* [2]
Propargite	All	EPA *Manual* [3]
Pyrethrins	Liquids, aerosols	EPA *Manual* [3]
Resmethrin	Aerosols, liquids	EPA *Manual* [3]
Ronnel	All	EPA *Manual* [3]
Terbutol	All	EPA *Manual* [3]
Triazines		
Ametryne, atrazine	Powders	AOAC *Official Methods* [2]
Chlorobenzilate, prometon	Liquids	AOAC *Official Methods* [2]
Prometryn, propazine, simazine, terbutyn	Powders	AOAC *Official Methods* [2]
Trifluralin	Solids	AOAC *Official Methods* [2]
Zinc phosphide	Grain baits	EPA *Manual* [3]

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VIII. Pesticide product quality control

*Mason H. Woolford, Jr.**

An ideal system of pesticide quality control will be considered for a manufacturing plant engaged in the formulation of a wide variety of pesticide products. With ordinary plant equipment – grinding mills, filling machines and blending equipment – problems such as cross-contamination, loss of potency, incorrect formulation and faulty packaging are likely to be encountered in the formulation of pesticide products. No matter how small or how large the operation, some systematic control is necessary to ensure that a product of uniform quality is delivered to the consumer. That is the function of product quality control.

Pesticide quality control in technologically developed countries is a well-established concept. There are a few formulators who practise very little quality control, but most larger operators have highly developed quality-control systems. The larger the plant and the greater the production, the greater is the need for quality control. But in every formulation operation, the minimum need is to verify compliance of the final product with specific standards. What would the consequences be if the production foreman leaves out the emulsifier, or if a parathion emulsifiable concentrate is packaged and labelled as a specified malathion insecticide product, or if glass bottles are overfilled with a liquid formulation which expands during warm weather or freezes when cold and bursts the container? Such problems can be prevented by effective quality control. The failure to produce a uniform and high-quality product will be reflected in economic losses. Conversely, the producer with an effective and economical quality control programme will market an effective product.

Objectives and importance of quality control

The ultimate aim of quality control is to ensure consistently high-quality products. It is difficult for production or laboratory personnel to know customer needs because very few of them have direct contact with the customer. Production and laboratory personnel must rely on information from others within their own organization, including salesmen, agriculturalists and technical service representatives, who have more frequent contact with customers and understand their preferences, needs and complaints. Field and in-plant personnel should therefore co-operate closely in order to offer products which satisfy customer needs.

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The customer can expect that the product he buys will perform according to the claims of the manufacturer. The product purchased today should have the same colour, flowability and emulsifiability as the product purchased yesterday or the product to be purchased tomorrow. Those product characteristics are apparent to the customer and help develop confidence that the manufacturer will provide consistently high-quality products. However, product potency, the compatibility of the ingredients of the formulation with each other and with the container and the expected long-term stability of the product are not apparent to the customer. Poor performance in any of these areas will probably result in severe economic losses.

There are many definitions of product quality and of the system for its control. The following examples are representative:

> *Quality:* "The quality of a product is its degree of possession of those characteristics designed and manufactured into it which contribute to the performance of an intended function when the product is used as directed."[1]
>
> *Quality control:* "An effective system for co-ordinating the quality maintenance and quality improvement efforts of the various groups in an organization so as to enable production at the most economical levels which allow full customer satisfaction."[2]

Quality must be built into the product during research, development and production. Awareness of product quality should be a guiding principle from product conception through the various stages of development to final delivery of the product to the customer.

In developing quality products and in perfecting a system which will help to maintain quality, additional costs must be considered. The criterion is to maintain a quality product in an efficient and economical way.

The functional responsibility of quality control should be delegated to one person who should report to a level of management sufficiently high to support a decision of disapproval of substandard product lots, even though such a decision might cause a delay in meeting schedules. Ideally, the manager or director of quality control should be on the same level as the heads of sales and manufacturing departments. Although the ideal situation is seldom realized, the function of quality control should never be subordinated to sales or manufacturing activities.

On the other hand, the quality control function should not be permitted to become so independent as to become an end in itself and demand a degree of perfection which cannot be achieved. The production department is concerned with deadlines, costs and output, and is therefore often impatient with interference from the quality control department. On the other hand, the main task of the quality control department is the maintenance of quality. When each department recognizes the aim of the other, a better balance of production and quality can be maintained.

[1] *General Principles of Total Control of Quality in the Drug Industry* (Pharmaceutical Manufacturers Association, 1967).

[2] A. W. Feigenbaum, *Quality Control: Principles, Practice and Administration* (New York, McGraw-Hill, 1950).

High quality cannot be consistently maintained without the proper controls. The necessity for quality control should therefore be impressed upon every employee, and the responsible managers to whom the quality control expert reports should issue a written statement outlining the quality control policy and programme.[3]

Responsibilities of the quality control section

An effective quality control section should be assigned the following duties:

(a) Develop methods of analysis and specifications for raw materials and finished products;

(b) Develop specifications for packaging materials;

(c) Check equipment design and insist upon changes when equipment has been found to cause poor-quality production;

(d) Run a continuing check on production practices and report any condition found contributing to poor product quality;

(e) Check incoming raw materials for conformity to specifications;

(f) Check all finished batches for conformity to specifications, after which lots meeting all specifications are released for sale and those found defective are rejected with instructions to rework or destroy;

(g) Handle customer complaints;

(h) Inspect finished materials and check the content of containers;

(i) Collect representative samples for analysis.

Inspection

The staff of the quality control department should include inspectors whose functions are clearly understood. Properly trained quality control personnel should be able to spot faults during production, such as improper container content of liquid or powder, poorly affixed labels or any action which, in their opinion, would contribute to a reduction in quality. The action should be brought to the attention of the production supervisor, who should cease production until the observed deficiency is corrected. It is preferable to discover a quality problem at an early stage and not after the entire lot has passed a particular production step. Furthermore, it is unacceptable to have a quality problem discovered by the customer or a regulatory agency.

Quality inspection must be performed in a careful, intelligent, diplomatic manner, otherwise the entire concept might be resented by the production department. Quality inspectors should therefore be carefully screened to avoid the selection of officious persons, who would be unsuitable for such a position.

[3] *Ibid.*

The following sampling guidelines should be observed:

(a) Sampling of raw materials and finished products should be done by trained samplers from the quality control, and not the production, department;

(b) Sampling procedures should be carefully developed with particular attention to products needing special care;

(c) Safety precautions should be observed in handling toxic and hazardous substances;

(d) Samples should be representative;

(e) Since the approval or rejection of products depends on the sample taken, great care should be taken to ensure the use of proper and statistically significant sampling techniques.

Customer complaints

Customer complaints should be forwarded to the quality control department and handled promptly and thoroughly. Recurring complaints might indicate a serious quality defect in the product and require a major evaluation that could lead to reformulation, use of a different packaging material, an emulsifier change or other action.

There are many varieties of complaints and methods of dealing with them. For example, if the problem is poor emulsification, a generous sample of the water used by the customer should be obtained for laboratory tests to be carried out in addition to an examination of the mixing technique and equipment. Periodic field visits are also important to observe how the material is used. The customer may not follow the label instructions or read the directions, or the directions themselves may be ambiguous and need revision. Observation of the application equipment in operation may suggest ideas for an improved formulation.

Whenever possible, samples should be sent to the testing laboratory in a proper container. Polyethylene bottles and caps with soluble plastic linings are unacceptable because chemical reaction between the liquid product and packaging material may obscure the formulation problem. Powder and dust should be forwarded in wide-mouthed bottles or in strong paper bags, which could be fitted with a moisture barrier and made of resilient polyethylene.

Specifications

The quality control department should be responsible for specifications for raw materials, finished formulations and packaging materials, which should be established, if possible, by committce action. Members of the committee should include representatives from the sales, manufacturing and quality control departments, and its chairman should be from the quality control department.

Specifications are the standards against which are measured both incoming raw materials and the lots of finished products shipped to the customer. They define the allowable limits within which the characteristics of a product or compound may vary and remain acceptable in terms of quality and performance. Failure to comply with specifications should mean rejection of the product. When possible, specifications should be tightened for new products as production experience is gained, and the production process should be reviewed if a relaxing of specifications is proposed. Improvement in the production process may lead to an improved product, whereas one of dubious quality could result from the application of broad specifications.

Specifications must be developed for the raw materials used in formulations, the finished products and packaging materials. In most cases, the supplier of raw materials will apply his own specifications, which will be rigid if the supplier is reliable. Although raw materials can usually be accepted on warranty from the supplier, it is advisable to carry out spot checks, especially if the presence of a known contaminant in the raw material can cause a breakdown or even toxicity in the pesticide formulation. Excess acidity, alkalinity or water often cause product breakdown. Occasional checks could be made on raw materials to ensure that the contaminants do not exceed the specified limits. The screen size of clay granules should be periodically checked, especially when a problem of dustiness in the product exists. Dust diluents and granules should also be periodically checked for the presence of foreign matter such as nails, twine from bagging operations, sticks, stones or any material likely to interfere with the product application.

No raw material should be used for manufacturing unless it meets specifications and is released by the quality control department. A system of tagging or marking should distinguish materials released for manufacturing and those not yet tested. Materials received and not yet tested or cleared should be stored separately from accepted or cleared lots. Alternative sources of raw materials must be sought to ensure a constant supply. Occasionally, suppliers deplete their stock, and the lack of material may cause a loss of business to the manufacturer, since he will be unable to fill orders on time.

Materials from new suppliers, especially clay diluents and emulsifiers, should be checked for compatibility with the company formulation. Some insecticides which are stable in technical form and in liquid formulations show marked decomposition on certain of the commercial mineral carriers used in the preparation of dust and water-dispersible powder formulations (see chapter VII). Before a new carrier is used in formulation, it should be tested by preparing a small batch and checking decomposition of the pesticide by chemical analysis (see chapter VII).

The inherent properties of the pesticide, the carrier and the diluent must be known to produce formulations having both a good shelf life expectancy and satisfactory physical characteristics. The surface of some carriers tends to be catalytic because of the presence of metallic ions, metallic oxides or other surface hot spots which contribute to a breakdown of the pesticide under prolonged storage. Such detrimental effects are especially pronounced in diluted formulations of some pesticides prepared directly on highly absorptive clays and when dust concentrates are diluted. The use of deactivators may improve some carriers to the point where they are compatible with the pesticide. However, each deactivator must be tested for each pesticide, because the deactivator for one pesticide may not work for another.

New and old supplies of emulsifiers should be periodically tested by preparing a small batch and checking emulsification properties. It is also sometimes advisable to obtain an advance sample before purchasing.

Specifications for solvents must in many cases include limits for water and acidity or alkalinity. Some organophosphates are particularly sensitive to alkaline conditions and are rapidly degraded at pH values slightly higher then neutral. For some pesticides, traces of metal cannot be tolerated. Such information is usually supplied by manufacturers of technical pesticides. Solvents should be checked periodically for specific gravity and colour.

Specifications for technical pesticides are generally supplied by the manufacturer on a minimum guarantee basis (for example, not less than 95 per cent). For manufacturing purposes, it may be necessary to obtain the assay results for the purchased lot. Botanicals (pyrethrin, rotenone, sabidilla, ryania and red squill) are marketed on an assay basis. Information on formulation compatibilities and uses is generally available in a formulation handbook provided by the supplier.

To develop specifications for the finished formulation, the quality control department must know the end-use of the product. An emulsifiable concentrate should form a stable emulsion under the test conditions; water-dispersible powders should pass realistic suspensibility tests; dusts should have particle size requirements. Acidity, alkalinity, presence of water or metal, compaction, stability at elevated temperatures, and a number of other variables should be considered. It is important that the physical appearance, colour and flowability do not vary from one batch to another. Prime consideration should be given to the active ingredient content.

Specifications for pesticide content are generally based on the precision and reproducibility of the analytical and production procedures and on the rate of loss of active ingredient during storage. Batches of bulk product should be stored in a quarantine area until released for filling by the quality control department after they have passed all specifications.

Specifications for packaging materials should be developed. Since moisture content is important for dusts and water-dispersible powders, there should be a layer of material in the bag wall as a moisture barrier. Some carriers may take up water which can be deleterious to product stability. Moisture uptake can dilute the product and result in a lower percentage of active ingredient. Some pesticides have an obnoxious odour and a tight seal is required, especially if the product is to be stored in an enclosed warehouse.

Polyethylene bottles may be affected by the solvent or another component of the formulation. The result is collapsed or misshaped bottles after several months in storage. The lining of caps should be unaffected by the formulation; polyethylene inserts are preferable to either rubber seals or plastic-coated cardboard.

Glass and polyethylene bottles should be inspected for chips, cracks or breaks, and their volume should be inspected. Batches from one supplier may differ in capacity from those of another supplier. Care must be exercised not to fill bottles beyond the allowable head space to avoid trouble due to expansion during storage in hot weather.

Many liquid technical pesticides and liquid formulations are unstable when packaged in metal containers because of interaction between the active ingredient and metal. To maintain the integrity of the containers, it may be necessary to coat the inside with two layers of a non-reactive resin properly applied and cured in accordance with the recommendations of the manufacturer. Continuity of lining is essential and all fittings must be properly coated. It is advisable to conduct storage stability tests on individual products before adopting a specific lining for commercial use. Metal containers should be inspected for adherence to volume and especially leakage specifications.

If the writing and printing of labels is a quality control function, the text for labels should conform to all government and international regulations. Instructions for use of the products should be clearly written and not subject to misunderstanding. Statements of composition must be accurate.

If label-writing is not a quality control function, the quality control department should at least be responsible for ensuring that the labels are correct in all details, and are worded and printed in accordance with current regulations. Labels should also be placed neatly on bottles and packages, so as to contribute to the over-all attractive appearance of the packaged product (see chapter XII).

Method of analysis or testing[4]

Methods of analysis of the active ingredient should be available for all formulations. The methods generally supplied by the basic pesticide manufacturer are provided on request. The methods of analysis for standard formulations of widely distributed pesticides are readily available, for example in the specifications of WHO, the Collaborative International Pesticide Analytical Council (CIPAC) and similar compendiums. Those methods are generally recognized as official, and their results are reproducible and representative of the active ingredient content of the product, even after some degradation as a result of ageing, improper storage conditions or other factors contributing to decomposition.

Standard methods of analysis for other tests to be performed can usually be obtained from various recognized collections of methods, which may involve specific gravity, specific rotation, index of refraction, emulsification, apparent density (for dusts and granulars), colour, pH, particle size, dispersibility, acidity or alkalinity. The quality control department may perform other tests developed in its own laboratory. The tests should be reproducible under a variety of conditions to be encountered in different laboratories. For example, such a test might involve a method designed to measure frothing (an undesirable characteristic) for water-dispersible powder mixed in and dispensed from a field spray tank.

In a plant producing a number of liquid formulations, identity tests are indispensable. Relying on odour, colour or other physical properties is unacceptable. At present, chromatographic methods are often used. Most emulsifiable concentrates appear similar but may vary widely in utility and toxicity. The same

[4] See also chapter VII.

is true for dusts, water-dispersible powders and granulars, if a variety of them are produced in the same plant.

For each inventoried raw material, technical pesticide, finished formulation and packaged product, a file should be kept containing specifications, methods of analysis and records of analytical results. Specifications should be reviewed periodically and changed whenever necessary, and methods of analysis changed when improvements are made. A specification change does not necessarily mean a method change. Sometimes a change in method may require a change in specification if the new method is more accurate. Specifications should be as tight as allowed by production, the analytical method and the stability of the product. The goal should always be the production of a product consistent in appearance, performance, and customer appeal. Realistic and soundly conceived specifications are important in the achievement of that goal.

Stability

Pesticide formulations should be stable during the time they are expected to be used and stored by the customer. Products intended for agricultural use are prepared well in advance of the growing season for delivery to the customer when needed. Stocks must sometimes be carried over into the following year. Formulations should therefore contain the active ingredient at label strength for at least 1.5 years after manufacture. Certain technical pesticides are fairly stable by themselves, but when formulated may degrade rapidly. Some organophosphates, for instance, readily hydrolyse even under mildly alkaline conditions, yet they are relatively stable in acid media. Emulsifiers can degrade or react with a formulation ingredient and become ineffective as time passes. In the formulation of pesticides, knowledge of the properties of the active ingredient is essential. The original supplier of the technical material generally provides the necessary data, including data on compatibilities, storage conditions, proper packaging materials, solubilities, and the general, chemical, and physical properties of interest to the formulator.

In most cases, the original supplier does not know all the conditions under which a product may be used, and probably does not determine the stability of the product with all the available emulsifiers, conditioners, stickers, spreading agents and carriers. A formulator may develop combinations never envisaged by the manufacturer of the product. In such cases, the formulator must conduct the appropriate stability studies.

New formulations should be tested periodically for a minimum of 18 months at room temperature (25° C), for 12 months at 37° C, and three months at 45° C. They should be tested for active ingredient content, emulsification, appearance (formation of sludge, separation, change in colour, and formation of odour), suspensibility, wetting time and caking. From the stability study the amount of excess active ingredient required to maintain label strength for a specified period can be calculated.

Solvents are generally well standardized. A grade of a specific solvent from one supplier is much the same as from another. Specifications vary little. If one solvent is substituted for another, such as cyclohexanone for xylene, differences will be found in solubility, compatibility and emulsification. A stability study must be run on a sample prepared with the new solvent.

In order to follow the quality of the products in the field, representative samples of complete packages should be taken from the sample line during the filling operation. Samples should be taken from several lots during the year, stored at ambient temperature and inspected periodically over a period of not less than two years. Information can be obtained which could forestall customer complaints. Product quality problems may at least be recognized and solved before they become serious.

Cross-contamination

In recent years the very serious problem of cross-contamination or the presence of one pesticide in the formulation of another has occurred. It has resulted in such incidents as the discovery of illegal residues of chlorinated hydrocarbons in eggs. An investigation showed that the cause was contamination of the approved pesticide by one that was not approved. The presence of a herbicide in an insecticide formulated for use on an agricultural crop can cause the loss of some or all of the crop.

The extent of cross-contamination was not discovered until the advent of new, highly sensitive analytical techniques and instruments. Up to that time, many formulators were entirely unaware of the problem.

Now that the problem is recognized, means of prevention are being devised. The principal method of prevention is the thorough cleaning of equipment just after preparation of a pesticide formulation, and keeping plant and operating lines clean and orderly. Production scheduling is important, and adequate testing must be carried out to show that the previous formulation has been completely removed from the equipment.

It is generally agreed that the design of most grinding, blending and mixing equipment makes it difficult to do an effective job of cleaning quickly at a reasonable cost. Many formulating plants were custom-built and need considerable redesigning to introduce an adequate quality control programme.

The development and promulgation of a code of good manufacturing practices could be undertaken, as has been done by the United States Food and Drug Administration for the drug industry and for medicated premixes intended as animal feeds.

The United States National Agricultural Chemicals Association (NACA) has studied cross-contamination and suggested allowable limits of cross-contamination of one pesticide in another based on the specific pesticides involved and the end-use of the product. The following guidelines are drawn from a NACA report on cross-contamination:

> "In the preparation of liquid pesticide formulations, great care must be taken to eliminate traces of the preceding formulation from all mixing equipment and filling apparatus. This will be done by the use of solvent

rinses. The amount of solvent required for each rinse will vary with the size of the equipment, the type of product and the solvent used.

"From 80 to 200 litres of solvent are generally sufficient to allow continuous recirculation of the rinse in most types of equipment. Each rinse should be recirculated for 3 to 5 minutes throughout the entire manufacturing and drumming system for the solvent to wash and dissolve all possible contaminants. All strainers in the system should be removed and cleaned. Filters should be cleaned and the residues from the filters destroyed or deposited in suitable disposal locations.

"The number of rinses required to free the system of any contaminants may vary from one to five but can only be determined accurately by chemical analysis. If the solvent used for rinsing is the same material that is used to manufacture the product, the rinsings may be carefully saved, labelled and stored for use as a solvent the next time the same product is produced.

"It is most important to be certain that the sample obtained for contamination analysis is representative of the finished material. Therefore, samples must be taken from the packaging point and not the mixing tank.

"For the granular formulations, particular emphasis should be placed on the importance of proper cleaning of the interior of tumbler-type mixers due to the affinity of the impregnated particles for the interior of the tumbler. Cleaning with mechanical equipment may be required. In other cases, steam cleaning or hot-water washing may be recommended. Visual inspection should determine the effectiveness of cleaning procedures.

"It is necessary to study each blending unit to determine the amount of material that is retained in the equipment after a batch has been emptied prior to cleaning. Cleaning procedures can be established as adequate only after a thorough investigation of existing equipment and practices."[5]

An analysis to determine the presence of one pesticide in amounts measured in parts per million in the formulation of another pesticide often requires an analytical development chemist (see chapter VI). For example, a 50 per cent emulsifiable concentrate contains 50 parts by weight of the technical pesticide. The product itself may be guaranteed as only 90 per cent pure. The resultant emulsifiable concentrate is composed of 45 per cent by weight of the pesticide, an additional 5 per cent for the emulsifier and the balance as solvent. The 5 per cent of the formulation from the technical product itself is probably of completely unknown composition, and contains one or more components which may behave analytically in a similar manner as the contaminant sought.

To compensate for the unknown quantity, a sample of the formulation is prepared in the laboratory from the same ingredients contained in the finished batch. Care is taken to ensure that the mixture contains the identical lot of technical pesticides. The contaminant may thereby be identified with relative ease, or another analytical method must be developed.

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[5] National Agricultural Chemicals Association, *Manual for Prevention of Cross-Contamination of Pesticide Chemicals* (Washington, D.C., Subcommittee on Cross-Contamination of the Grady Committee, 1965).

IX. Acceptable international standards for industrial safety in the operation of pesticide formulation plants

*M. G. Srivastava**

Safety needs in pesticide formulation plants are at least as important as in other types of chemical processing. Risks arise at several stages and in different ways. Besides the normal risk from machinery and moving parts, plant operators may be exposed to pesticides in the form of liquids, vapours and dusts. Other hazards arise from working with formulation machinery, and fire or explosion hazards may arise from dust or a fume-charged environment.

This chapter essentially covers the hazards posed by the contact of workers with machinery and equipment in pesticide formulation plants, while aspects of industrial hygiene relating to exposure to toxic chemicals are discussed in greater detail in the following chapter.

A principal task of management is to create in operators an awareness of possible risks involved in their work and to educate them on how to deal with operational hazards. This chapter seeks to identify areas of risk and their causes, and the ways and means of minimizing them. Management should concentrate on carefully planning layout, purchasing equipment and building plants.

Plant layout is considered in detail in chapter III. From the point of view of operational safety, the equipment purchased should comply with national or international specifications such as those laid down by the American Society for Testing and Materials, the British Standards Institution, the Indian National Standards Institution, the International Labour Organisation and the International Organization for Standardization.

Climatic conditions affect standards. For example, in hot climates it is much better to concentrate on ensuring the best possible plant design and construction so as to avoid excessive reliance on individual protection of workers through the use of uncomfortable safety clothing.

Safety regulations must be established for each plant. Where government regulations for industry in general exist, the standards laid down will take precedence over plant regulations. Despite statutory regulations and plant rules covering certain areas of concern, such as boiler maintenance, gas and flammable raw-material storage, dust-exhaustion facilities and effluent disposal systems, accidents will still occur. The inherent toxicity of pesticides thus demands a firm

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commitment to the achievement of high safety standards at all levels of employment. Highly skilled and well-trained operators are therefore essential. The following sections cover the various aspects of a pesticide formulating operation which require the observance of safety precautions.

Operational hazards

The machinery used in formulation units to produce liquid blends, water-dispersible formulations, granules, flowable powders etc. is not complicated. Nevertheless, all processes should be fully and properly documented and certain precautions followed to ensure the safety of the operators in both normal and emergency operations.

Flammable liquids

The equipment consists mainly of stainless steel or glass-lined vessels and agitators. The operation may be carried out at room temperature or higher depending on the solubility of the pesticide in the carrier. Solubilization is achieved through the use of heating coils. The necessary precautions should be observed.

Charging of vessels

Safety precautions are essential in charging the vessel with ingredients and during the mixing process. For example, solids should be charged slowly to prevent ignition from the build-up of static electricity. Indeed, the whole system, including containers, must be earthed. Solvents and liquid technical and raw materials should be charged separately into the mixing vessel through their respective pump and valve systems.

Ventilation

Because most solvents and some raw materials represent a fire or explosion risk and sometimes a risk from the inhalation of toxic vapours (see below), special precautions must be taken. A proper ventilation system including exhaust fans should be provided. The exhaust should lead to a secondary filter or scrubber and from there be harmlessly vented without violating environmental regulations.

Other explosion and fire hazards

To prevent fire hazards, the following are minimum requirements:

(a) Electrical motors and switches must be flame proof; moreover, there should be no risk of a major explosion should any material creep into the system,

(b) Open flames and smoking must be prohibited in all circumstances;

(c) Spark-producing tools and accessories should be kept away from work areas.

Pumps and valves

Seals on pumps may be a source of trouble. If excessively tightened, they may become a heat source and hence a fire hazard. Pumps and valves may also become leaky, thus requiring the installation and maintenance of catch pots for the safe disposal of their contents.

Heat exchangers

Faulty operation or malfunction of heat exchangers may lead to a build-up of heat and a consequent fire risk.

Blending vessel

The agitator in the mixing vessel is a fast-moving piece of equipment carefully adjusted so as not to interfere with the walls of the vessel. To avoid overflow through frothing and splashing by the agitator, sufficient ullage space should be allowed and the lid must be securely closed before operating the equipment. Accidents may also occur if the agitator is not stopped or is accidentally switched on while the walls of the vessel are being scrubbed. Caution is therefore necessary in locating the start-up switch and preventing its being turned on accidentally.

A safety system for isolation of circuits and switches is referred to below.

Toxic liquids

Additional precautions covering the formulation of toxic (or toxic and flammable) products are discussed below. Personal precautions for operators are covered in chapter X.

Management permission must be obtained before entering a mixing vessel which has contained toxic material. The conditions of entry must be specified and the vessel marked with an "out-tag". The process should not be restarted until authority is given for the removal of the tag. A useful system is to classify raw materials according to handling procedure and the type of personal protection required (see chapter X). Containers, equipment and operating areas may be marked with an alphabetical code to indicate a particular hazard, such as toxicity or flammability. One company handling rubber chemicals has developed an alphabetical system of labelling (A, AB, ABC) for handling procedures and level of personal protective equipment required. Under such a system, the following designations might apply to protective equipment:

(a) "A" requires thin leather or cotton gloves;

(b) "AB" (= +B) requires, in addition, single-use gloves and the use of respiratory protection or goggles as appropriate;

(c) "ABC" (= +C) requires, in addition, protective shoes, disposable overalls or plastic aprons.

Corresponding handling procedures are given under the same alphabetical system. Care should be taken to ensure that such a system, once initiated, is properly managed.

Solids

To achieve correct particle size for the formulation, different types of grinding and milling equipment are used. Each presents different types of hazard.

Jaw crushers

Jaw crushers operate with heavy hammers or beaters and are used to reduce diluent minerals into coarse powders. Hammers and beaters need daily checking, since they may seriously damage the machine itself and expose operators to hazards from metal projectiles if parts become detached while the machine is running. Such accidents occur where fastenings are loose and parts have worn unevenly.

Pulverizers

Roller mills are used to grind the pre-mix comprising technical grade pesticides, diluents and other additives to the desired fineness. Since they involve fast-moving parts, probing to remove blockage should be done only after stopping the operation and locating the blockage.

Chemicals that are liable to melt at high temperatures resulting from friction cause blockages through caking. The operators must frequently open the observation ports to clear up jammed rollers using probes. The machine must be fully stopped before the windows are opened. Similarly, air vents must be opened to increase air flow and adjust internal temperatures. In such cases also, adjustments must be made only after the machine has been brought to a stop.

Equally important is a safe system for start-up without the risk of trapping anyone in machinery switched on unexpectedly. Only one person should have the key for the start-up switch, and that person's name should be on the out-tag. There are several devices with multiple locks or keys for shutting down the system and preventing it from being switched back on until every key is turned or lock removed and the final key used to unlock the switch. For added safety, the technicians working on the shut-down system could be provided with the keys required for the locking devices.

Blenders

Pulverized material is homogenized by blenders. Depending upon the nature of the blender used, appropriate precautions must be observed. The risk is generally greater in hopper and worm types of blenders because of the continuing thrust as well as the structure of the machine itself. It is essential that the lids of blenders are properly shut when the equipment is operating. If any attention is required, the equipment should first be switched off. Moreover, no attempt should be made to disturb any pockets of unagitated material by hand or small probes.

Granulators

Where granulators of the extrusion type are used, plain or pesticide-containing dough is fed through the extruder. The precautions earlier listed for worm blenders should be observed. Special care is necessary to prevent accidents while charging the dough at the feeder end of the extruder.

The drying stage of this operation is mostly effected using a hot-air blast. The air temperature at the exit point could be as high as 85° C. Direct exposure of individuals to the blast must be avoided.

Ventilation and dust collection

Work sites engaged in producing free-flowing powders may cause atmospheric contamination due to dust. Fires or explosions may occur because of static charge, dust clouds or dust particles of organic matter. In addition to exhaust fans, plants producing solid formulations must therefore be provided with dust-catching and, where appropriate, explosion protection equipment. All equipment handling flammable powders must be effectively earthed. It is essential not to disperse dust on the plant, since in addition to the hazards referred to above, dust can cause serious maintenance problems.

Filling equipment

Operational flows for both liquids and solids end at the filling point. Automatic or semi-automatic filling machines are commonly used, especially in the packing of liquid formulations. Depending on the nature of the machine used and the chemical filled (frothing or non-frothing), precautions are necessary against splashing, overflow and contamination of the operators. Machines therefore need to be adjusted for individual formulations to ensure the correct quantity and speed of delivery. Operators must wear goggles, gloves and overalls when operating such machines (see chapter X). Filling machines should be provided with protective guards. Liquid-filling machines should also be provided with automatic closure devices so that product delivery ceases at the moment when the container has been filled to the desired level. Receptacles for spillage and washings of filled containers must be provided and the contents disposed of appropriately. Sufficient ventilation must be provided at the filling point and, where powders are being filled, dust-exhaustion systems must be installed. A safeguard is provided by the earthing of metal containers when these are being filled. This can be accomplished either by using a crocodile clip attached to an earthed lead or by standing the drums on an earthed metal plate.

Services

Hoisting equipment

For transferring pesticide concentrates, solvents, premixes etc. from bulk packs into mixers or pulverizers, hoists are often used. The use of hoists is a safe operation, but the periodical checking of chains and locking devices is extremely important, and generally a statutory requirement. Drums should be properly hooked and secured for lifting to ensure against accidental spillage and slipping which might cause health hazards to workers.

Boilers and pressure-resistant equipment

Larger formulation units have steam generation boilers for warming up reaction and formulation vessels. Where such pressure-resistant vessels or equipment are used, prevention of pipe bursting must be provided for in the design. The delivery lines and equipment must be provided with relief vents and valves to prevent any unusual build-up of pressure. Relief vents should be short and straight and directed away from people. Regular inspection and testing of all pressure equipment is essential and should follow factory safety rules or statutory regulations and guidelines.

General maintenance

An appropriate level of maintenance should be established and monitored. Regular maintenance of equipment, especially if it involves moving parts, against excessive wear and tear is an essential operation. This involves downtime which may be undesirable during the peak season of pesticide demand. Checks and maintenance work should therefore be completed out of season. In formulation units using several types of equipment, the maintenance schedule should be planned in advance.

In this context, it is important to draw attention again to the importance of properly authorized entry systems for areas where there may be a toxic hazard. Entry should be restricted to, and controlled by, authorized personnel. Stand-by staff should be present in case of emergency.

The chance of accidents during maintenance is further lessened if the lock-out devices referred to above are incorporated into mechanical, electrical and chemical systems. Valves must be clearly marked so that no one turns on, for example, the nitrogen system when the air line is required.

Raw material and finished product storage[1]

Storage in plant warehouses and on the shop floor requires adequate space for movement of men and material. Obstructions, careless handling and random depositing of full or empty containers in operating areas may represent a serious safety hazard. Discipline in observing the established safety rules must therefore be rigorously enforced.

Fumes are often a cause of hazard in stores used for solvents or volatile pesticides. Such stores should therefore be designed to provide good natural ventilation. Air exhaust fans designed to be switched on from the outside for a minimum period before the doors are opened for entry would also be desirable. Precautions against fire and explosion similar to those taken at the plant itself, as described earlier, are required. Fork-lifts, autotrolleys and related equipment are used for bringing in technical grade pesticides and other raw materials from stores and removing finished packages. In these operations proper training of the drivers in handling various types of packages is important. Pallets may be used to minimize the risk of slipping. Maximum stacking heights must be prescribed and observed (for details see chapter XI). Fork-lift trucks must be checked for spark-producing hazards.

Housekeeping

Cleanliness of floor area

Deposition of fine dust particles or spillage of solvents, oils or other fluids can lead to accidents during movement of workers or stores. Maintaining clean work floors is therefore an essential safety practice. Floor mops and dust-removal equipment should be readily available. Before the start-up of a shift, work floors should be cleaned of spillage and deposits, and any spillage during the shift must be immediately removed as a good-housekeeping measure. Removal will also prevent the tracing of offensive spills elsewhere in the plant.

Effluent disposal[2]

Besides contamination of the environment through haphazard disposal of effluent, washings etc., the risk of exposure to workers has to be considered (see also chapters X and XI). Methods of collecting effluents, residues, off-specification materials, washings and other wastes such as dust contained in filter bags should be established as a routine practice. Well-designed systems and equipment for treatment (including detoxification) of such wastes, described in chapter III, must be installed in every formulating unit. Where detoxified fluids are discharged into running or static waters, a periodical check is made to ensure

[1] See also chapter XI.

[2] See also chapter III.

that detoxification has been effective and the level of residue is within acceptable limits. Similarly, systems should be instituted for safe disposal of empty containers of pesticide concentrations and other solid toxic material (see chapter XI).

Warning signs

In order to reduce risks, it is essential to install the following warning signs in workshops and warehouses:

(a) For volatile chemicals and solvents: No smoking; No open flames;

(b) For toxic chemicals: Danger! Skull and cross-bones (or other readily understood symbol);

(c) For power-line switch-boxes: Danger! High tension! and "Lightning" symbol;

(d) Emergency exit signs.

The design and message should take account of language differences and cultural attitudes.

First-aid facilities

A manual on the first aid and antidotes for dealing with accidents and exposure to, or ingestion of, pesticides etc. should be available for specially trained personnel at an easily accessible place. In addition, supervisors and foremen must be given training in first aid. First-aid boxes must be put up at prominent points in the workshop and emergency showers and eye-wash facilities should be installed in the plant. To deal with serious injury or exposure, quick accessibility to a medical practitioner should be ensured.

Safety manuals and inspection

Factory managers must ensure that a detailed manual on safety systems, written in simple language, is made available to the workers. It is important that workers should attend a training course on safety before being allowed to work in a formulation plant. Refresher training programmes are desirable. Periodic inspection should be made by management to ensure that the prescribed safety rules are being properly observed.

In recent years a new technique has been developed to pin-point areas of hazard and minimize risks. The technique is called hazard and operability study. It involves a formalized study either before commissioning a plant, or prior to modifications at a working plant. The study is carried out by a team of three persons, including a worker involved in processing and an engineer, both associated with the plant. The third member of the team, also a technician, is not, however, connected with the plant or its operation.

The team undertakes a critical study of the plant design, equipment, reaction flow-sheets and the actual plant on site (whether operating or to be commissioned). It identifies all possible locations involving risk from raw material or equipment failure or process reactions or any other cause. It then recommends such modifications as are essential to eliminate the hazard to operators and other plant personnel. The study also helps to sharpen operator training programmes and improve safety standards. To create a sense of commitment among the workers and reward them for accident-free work hours, a system of group reward may be effective. Many industrial plants that have introduced such reward systems have succeeded in improving worker awareness and safety performance.

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X. Occupational hygiene and industrial health in pesticide formulation plants[1]

*Karl M. Naef**

Many insecticides may be harmful to humans, domestic animals or wild life, since few are absolutely specific to the target pest. Herbicides may destroy or damage cultivated crops and many fungicides may be toxic to desirable fungi.

In normal applications the quantity of pesticides at any one place is relatively small and the risks of unforeseen exposure to man or the environment are limited. However, during formulation, packaging and storage, considerable quantities may be involved or relatively high concentration levels encountered. Experience has shown that if the proper precautionary measures are observed, even very toxic substances can be handled safely. If in case of accidents, effective emergency procedures are also foreseen, the risks of exposure are greatly reduced. The main purpose of this chapter is to indicate various ways of eliminating unnecessary exposure and to suggest methods of ensuring the health of workers in formulation plants.

A high degree of safety can be achieved either by using very sophisticated – and often expensive – equipment or with more conventional equipment and the proper education and training of the people operating it. The latter course is the more common in pesticide formulation plants.

Education of employees

Only well-informed personnel will readily take the proper precautions to protect both themselves as well as their co-workers and the environment. All personnel working in formulation and packing plants must therefore be well trained, and persons undergoing training must be closely supervised. Thereafter, regular training programmes are essential in order to prevent the development of bad work habits. It is advisable to keep a permanent record of the instruction supplied, so as to know when retraining should be carried out.

Education and training should include: knowledge of the potential hazards of the chemicals employed; instructions for the safe and correct use of the

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[1] This chapter is partly a revision of chapter 8 of the previous (1972) edition of this publication: H. R. Wolfe, "Safety problems related to exposure of workers in pesticide and formulation plants", in *Industrial Production and Formulation of Pesticides in Developing Countries*, vol. II (United Nations publication, Sales No. E.72.II.B.5).

equipment; hygiene and safety instructions and procedures; and emergency instructions and procedures in case of spillage, fire, injury, contamination or poisoning etc.

Chemical hazards

Apart from the hazards of fire (see chapter XI), especially with liquid formulations, and environmental contamination from some chemicals, many pesticides are also toxic.

Intoxication

Intoxication can be caused by absorption through the skin, inhalation of pesticide fumes or dust, or, less commonly, actual ingestion of pesticides. Skin contact is the most common cause of poisoning. It is more common than it need be, partly because people are often not aware that they have been in contact with pesticides (perhaps through damaged or internally soiled clothing), and therefore do not take remedial action; and partly because, even when people are aware of contact, they think they are at risk only if their skin is broken. In fact, many pesticides in either liquid or powder form will pass readily through healthy, unbroken skin into the bloodstream (the eyes and the area around the genitals are particularly vulnerable).

Inhalation is potentially one of the quickest ways of being poisoned. This is because the fumes and vapours pass directly into the bloodstream from the lungs.

Ingestion is the least common cause of accidental poisoning. When it does happen, it is usually because people have taken food and drink into the working area, or have been smoking when their hands are contaminated.

Fire

Many liquid pesticides contain organic solvents that are flammable or occasionally highly flammable, such as in aerosol spray cans. Since in operation it is very difficult to ensure that mixtures of air and flammable vapours never occur, every precaution should be taken to ensure the absence of a source of ignition. Electrical equipment should be explosion-proof or at least spark-proof. Naked flames or spark-producing tools must be avoided. People, containers and equipment should also be sufficiently earthed to prevent the build-up of static electricity and their subsequent discharge.

Many powdered organic pesticides, when finely divided in air, can explode violently if ignited with sufficient energy. Sources of ignition must be avoided. These are caused mostly from foreign bodies entering fast-moving mills or from a fire or explosion of a solvent-air mixture. Powders and dust lying on ledges can often be shaken loose through a first explosion and contribute to an even larger secondary explosion. Good housekeeping is essential to avoid any accumulation of dusts.

Environmental contamination[2]

In a well-run plant the most likely risk to the environment is associated with the accidental discharge of product either through equipment malfunctioning or operator error. Training and education aims at eliminating operator errors, while preventive maintenance should keep the equipment in top condition. In case those measures fail, safeguards should include: diking of key areas of the plant or drainage to an impermeable impoundment area; monitoring systems for air filters or scrubbers; meticulous cleanliness to avoid tracking product into the neighborhood.

Another possible source of environmental contamination is associated with the discharge of toxic decomposition products into the air following a fire, or the flooding of drains, watercourses or ground water with contaminated fire-fighting water. The effects can be reduced by careful diking or by leading drainage to collection pits for reuse in fighting the fire itself.

Safe and correct use of equipment

No formulation should be started without a written formulation procedure in which dangers and precautions to be taken are incorporated. It is good practice to have product data sheets on all chemicals involved. Written instructions on working procedures should be available for all equipment. Training on the equipment should be designed to forestall the development of bad or dangerous work habits.

All formulation equipment should be designed to reduce as far as possible all direct or indirect exposure to the worker. This can best be achieved with closed systems. During charging and discharging of the system when an enclosure may not be practical, local exhaust ventilation is the only effective method by which harmful dusts and fumes can be prevented from being released from a clearly defined source into the workplace. Without care in preventing the generation of dusts, even this measure is useless.

Ventilation

To be efficient, it is essential that exhaust ventilation be located as close as physically possible to the point at which dusts, fumes or other contaminations originate. It is recommended that the ventilation provide an air current with a face velocity of 0.5-1.0 m/sec across the openings and discharging points.

The air collected by the source ventilation should be filtered before discharge into the atmosphere if dusts are present. If only vapours are sucked off, the properties of the products determine whether a scrubber is necessary or whether simple dilution may be satisfactory. Consideration must be given to the discharge point (height over roof, predominant wind direction etc.).

[2] See also chapter III.

Although good general ventilation of the work area is always required for more agreeable conditions of temperature and humidity, it is generally not sufficient to rely solely on this means to keep the workplace free of contaminants. General ventilation can often be cheaply achieved by having buildings with open sides. Otherwise, the use of vents close to the floor plus vents in the roof or just below the eaves is often useful.

In cases where source ventilation is not practical due to size, shape or function of the equipment, the latter should be installed in a cubicle ventilated by a separate fan. The source of contaminant in the cubicle should be located between the worker and the point of air extraction. The cubicle does not guarantee protection for those working within.

If the degree of enclosure and the amount of active ventilation does not guarantee complete protection of the worker, personal protective clothing and devices must be worn. These have to be gauged to the risk involved.

Medical supervision

Regardless of the size or type of the plant operation, it is wise to arrange some type of medical supervision. Where toxic chemicals such as chlorinated hydrocarbons, organo-mercury compounds, organophosphates or carbamates are formulated, this becomes essential. Pre-employment medical examinations are strongly recommended for both permanent and contract employees.

Where organophosphates or carbamates are handled, pre-exposure baseline blood cholinesterase activity levels should be determined. This is best done during the pre-employment examinations. All personnel involved in the formulation and packing of such compounds, including maintenance staff working on the equipment, must have their cholinesterase activity checked at regular intervals. A hospital or suitably equipped and qualified laboratory should be used for the determinations. Detailed records should be kept of the results and these interpreted by a medical doctor. Various methods of analysis are given in [1-8].

The following guide may be helpful in interpreting the results (see also [5]):

(a) A fall of more than 20 per cent in blood cholinesterase activity from the pre-exposure value should call for an investigation into the possible cause of the probable exposure and the adoption of corrective measures;

(b) A fall of more than 40 per cent indicates that the worker should be removed from the work situation which might be the source of exposure, until the blood cholinesterase activity is within 20 per cent of the pre-exposure value.

Advice from a medical doctor should be sought as to when it is safe to resume regular duties.

In the case of suspected or acute intoxication, immediate assistance of the doctor or hospital with which an arrangement for medical supervision has been agreed should be sought. The doctor or hospital must be fully informed in advance of the nature of the chemicals handled and should keep the necessary antidotes such as atropine and PAM (Pralidoxim) available. A pesticide first-aid manual, such as that published by the United States Environmental Protection Agency in 1977, should also be made available.

Ideally a plant should have its own first-aid centre and resident trained nurse. The minimum first-aid materials and facilities should permit the treatment of cuts, scratches, burns and fractures and have the means to transport seriously injured or intoxicated persons out of the danger zone for special treatment.

Where there is no resident trained nurse, several of the employees should be nominated as first-aiders and trained in basic first-aid procedures and if necessary in administration of atropine.

Hygiene and safety

Protective clothing

To reduce the risk of accidental exposure, long-sleeved overalls should always be worn. No street clothing should be permitted under the work clothing. Workers must not be allowed to go home wearing the overalls used at work. Rubberized or leather safety boots with a steel toe cap are highly recommended. The legs of the overalls should fit snugly over the boots to prevent dry pesticide from sifting into the footwear.

Hands should be protected by the use of unlined gauntlet-type rubber or plastic gloves. The elastomeric material of such gloves has to be adjusted to the compounds handled. The gauntlet protects the wrist area not normally covered by the sleeves. Without cloth lining they are easier to clean on the inside. A medium-weight glove is recommended, since a heavy glove does not give enough finger flexibility and a light-weight glove is torn or wears out too rapidly. For comfort in hot climates a disposable thin cotton glove may be worn inside the rubber glove.

Where liquids may splash, non-breakable eyeglasses, goggles or even a face shield must be worn. In this case a waterproof apron is especially needed. Aprons are also advisable at bagging or mixing stations, where there is often considerable contamination on the front of the clothing.

Head protection with hard hats or cloth caps should be foreseen if there is a risk of bumping the head or in situations where dust is to be kept from settling in the hair.

To protect the respiratory tract, dust masks or a respirator capable of filtering out the compound in question may be required. Filter cartridges should be changed after seven hours of appreciable exposure and more often if pesticide odour is detected through the mask. Filter pads should be changed if clogging causes difficulty in breathing. Gas masks with cannister-type filters should be used when high concentrations of highly toxic vapours are present. Use of a self-contained air supply respirator is advisable when working inside blender tanks or dust hoppers during cleaning and repair operations.

To be effective, the respirator should fit tightly against the face to prevent leakage. After use, the cartridges and filters should be removed and the face piece washed with soap and water. When dry, the mask should be reassembled with the gaskets properly positioned. The respirator should be stored in a container in a dry place to ensure that it is not contaminated on the inside before being put on.

The use of protective clothing should be commensurate with the risk of exposure involved. Often signs on the equipment or labels on the chemical containers are useful in indicating which types of protection are to be worn by the worker for each specific job (see also chapter IX).

Personal hygiene

Even through the employer may provide a relatively safe working environment, the formulation plant worker should make an effort to protect himself from excess absorption of pesticides through good personal hygiene practices.

Depending on the nature of the chemicals involved, some or even all of the protective clothing mentioned above will be prescribed for various operations. The worker should make sure these are visibly clean before putting them on.

The worker should wash gloves before taking them off at the end of work. Soiled overalls should be collected for laundering and not stored in the locker. The worker should then shower, using plenty of soap to cleanse thoroughly any pesticide from hair and skin before changing back to street clothing. The employer must provide suitable facilities for changing and washing with separate lockers for personal and work clothes.

If a worker should become excessively contaminated at any time with either a dry or liquid pesticide, he should immediately strip, shower (an emergency dousing shower must be provided) and thoroughly cleanse himself before changing into fresh work clothes to resume his duties. If more toxic organophosphate compounds were involved, the worker should be observed by a trained medical person for poisoning symptoms.

It is the employer's responsibility to supply sufficient freshly laundered overalls to the employee, who should be made aware of the potential hazard involved with pesticide-contaminated clothing.

The worker should also take care of the daily cleaning of waterproof protective clothing such as aprons, boots and gloves. It is especially important that rubber gloves be thoroughly cleaned on the inside as well the outside. Gloves should be regularly inspected for small holes or tears and those found defective replaced.

Workers should never smoke, chew tobacco or gum, drink or eat while working with pesticides. A separate clean area should be supplied for this purpose. The hands and face should be washed before eating, drinking or smoking. The hands should also be washed before urinating.

Safety and security

The site in general should be enclosed and adequately protected from trespassers. Visitors should be firmly directed out of potentially dangerous areas.

Safety rules, such as the wearing of protective clothing, prohibition of smoking or use of spark-producing tools must be strictly adhered to. Easily understood symbols and signs indicating the restrictions and showing escape routes and the location of emergency equipment such as fire extinguishers or telephones are highly recommended.

A significant aspect of safety is associated with good housekeeping. Goods, containers or equipment not needed for the operation should be properly stowed. Access to the equipment in use must be unimpeded and the escape route kept free of obstruction.

Good housekeeping is essential if environmental exposure is to be kept at a minimum. All spillages should be picked up immediately. Liquid spills should be dealt with by absorbing onto a suitable dustless solid such as sawdust, granular clays or other absorbtive materials. They must not be washed down a sewer. If necessary, after sweeping up the absorptive materials the area may have to be decontaminated according to the properties of the pesticide.

Dry solid pesticides can be swept up with broom and dustpan or preferably using an industrial vacuum cleaner. The wastes should be collected in a closed container and safely disposed of. Smooth and impermeable floors are much easier to keep clean than rough ones. It is worthwhile to expend the extra effort to produce a smooth floor when setting up the plant.

Drains should be avoided, but if present must not connect directly to waterways or public sewers. A catch pit or holding tank from which the drained liquid must be pumped is therefore recommended. Liquid wastes should be left to evaporate in a disposal pond, after which the smaller volume can be disposed of more easily (see chapter III).

Emergency procedures

If the precautionary measures should not prove sufficient to prevent a mishap or accident, emergency measures must be foreseen to limit the consequences of the incident. These can only be implemented quickly and effectively if they are practised regularly and the equipment periodically checked and maintained.

An alarm and evacuation procedure should be established, which permits a quick head count. Based on the situation, action can then be initiated to fetch missing persons out of the danger zone using the appropriate protective devices. The plan should include a system of notification of supervisors, authorities, neighbours etc. Regular evacuation training should be practised with all plant personnel.

It is wise to have an arrangement with the local fire brigade to provide immediate assistance in case of fire. The brigade should be fully informed of the nature of the chemicals handled and of any specific high-risk area in the plant. If their response time is more than 10 minutes, a fire-fighting squad should be recruited from the plant personnel and trained if possible by the local fire brigade into an effective unit.

In case of large spills or flooding, it is necessary first of all to interrupt the cause of the spill and to prevent the contaminants from reaching water courses, sewers or ground water and from spreading to neighbouring property by damming with absorptive material or sand.

In practice it is often expedient to nominate a security and safety advisor with the following responsibilities:

(a) Analysing past accidents and incidents in order to avoid repetitions;

(b) Reviewing the effectiveness of work practices and procedures from the point of view of safety and hygiene;

(c) Interpreting occupational health and safety legislation applicable to the company operations;

(d) Promoting safety, hygiene and environmental awareness among the personnel;

(e) Proposing training programmes and courses;

(f) Contributing to site emergency plans etc.

In this context, it is recommended that a safety committee chosen from supervisors and workers should be appointed.

Measurement of exposure levels

Only with the full knowledge of the amount of contaminant that the worker may be exposed to in the plant can appropriate precautions for his protection be initiated. Both direct and indirect methods of measurement are used [9].

Direct methods include self-contained air samplers worn for a whole shift by the operator with an air intake close to the face. Desorption of the possible contaminants and microanalysis permits an accurate estimate of the airborne contaminants the worker in his specific job may have been exposed to. Accordingly, corrective practices can be instigated or protective equipment worn. However, for dermal exposure the method is not applicable, and it is necessary to revert to swabbing skin areas and determining the quantity of contaminant collected to make an estimate of the actual exposure.

In many cases it is, therefore, more accurate to employ indirect methods that rely on metabolic derivates or biochemical reactivity in body fluids. A typical example is the measurement of blood cholinesterase activity to gauge exposure to organophosphate compounds or blood coagulation rates after exposure to coumarins.

The level of *p*-nitrophenol and of 4,4′-dichlorodiphenylacetic acid excreted in the urine is a good indicator of occupational exposure to parathion and DDT, respectively.

Summary

Workers in pesticide formulation and production plants are often exposed to relatively high levels of pesticide compounds. Therefore, it is important that all workers, as well as management, be aware of any potential hazard that may

accompany exposure to such compounds. Personnel should know the precautionary measures that must be taken with the different compounds, the possible routes of entry into the body and how to protect oneself. Regardless of the size of the plant operation, some type of medical supervision of employees is desirable. Risk of injury or illness can be minimized only by using properly trained and educated employees. Instruction in correct and careful operation of equipment can prevent unnecessary contamination of the working environment. Protective clothing and devices should be used where indicated or determined by direct or indirect measurement of the level of contaminant. Proper maintenance of all equipment will minimize the chance of mishaps. Good personal hygiene practices must be encouraged as well as general good housekeeping.

The disposal of wastes should be in conformity with local regulations.

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XI. Safety in storage and transport, and disposal of pesticides and containers

Malcolm Harmer and Homer R. Wolfe***

The satisfactory control and safe handling of potentially hazardous materials in storage and in transit must be based on both the normal demands of day-to-day operations and the special problems created by accidents such as spillage and fires. In any assessment of safety problems, the inevitable occurrence of such accidents from time to time must be accepted, and a sense of proportion maintained with regard to the nature and extent of the risks involved.

Under normal conditions, the vast majority of pesticides present little risk during storage. Exposure to the chemicals can occur only as a result of accidental spillage, but in such cases established procedures can deal safely with any problems which may arise. Moreover, since pesticides are rarely stored in bulk vessels, the amount of spillage from a single container, if handled properly, will be limited and unlikely to cause more than a nuisance.

The capacity for causing more serious risk will usually be associated with the influence of an external agency, the most significant of which is fire. While some pesticides are formulated with flammable solvents and will burn readily, other non-flammable products in powder or granular form can cause significant or even serious problems when subjected to the heat of a fire. In such situations the risks will be those associated with the production of toxic decomposition products and the possible discharge of contaminated water from fire-fighting to drains and watercourses. To the authors' knowledge, such incidents are seldom the cause of serious casualities, but they can lead to widespread environmental damage due to contamination of lakes and rivers.

For products in transit, the level of control which can be exerted by the consignor is clearly limited, and it is in this area that some of the most significant incidents involving people and animals have occurred. The use of sound packages and clear and explicit labels represents the best initial defence against accidental spillage of pesticides during transport, but if potentially harmful cross-contamination is to be avoided, it is essential that such products be stored well

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away from foodstuffs and other materials destined for human or animal consumption or use, such as animal feedstuffs, clothing, consumable oils, tobacco and cosmetics.

A degree of risk must always exist, but experience has shown that much can be done to reduce the hazard and deal with any incident that may occur. To this end, the careful selection, maintenance and operation of new and existing storage and distribution premises are essential. The size of the unit has no bearing on whether or not the recommended standards should apply. The essential elements of good basic practice should be applied in all cases.

Safety of pesticides in storage

Location of the store

Although many existing storage premises with a less than ideal location may continue to be used as pesticide stores, the establishment of a new store provides an opportunity to be selective in the choice of its location and, possibly, the type of construction.

The proximity, nature and use of surrounding property should be carefully considered, avoiding, if possible, locations close to domestic property, schools, hospitals, shopping premises and other congested areas. The effect that a fire in a store could have on neighbouring property is an important consideration; conversely, the risks which such property could present to the store itself should not be overlooked. Locations adjacent to timber mills, petrol stations and other relatively high-risk areas should be avoided where possible, or additional precautions taken in the construction of the store. Complete separation from nearby premises is advisable, leaving a clear space of at least 10 m around the building to serve as a fire-break. Such a space would provide access for emergency vehicles in the event of fire, a factor which should be considered together with the access required for vehicles under normal operating conditions.

The location of rivers, irrigation ditches, other water courses and drainage systems should be known and precautions taken to prevent their contamination. This is particularly important in the event of fire, when the drainage of heavily contaminated water from fire-fighting could cause serious pollution problems, having repercussions at least equal to those of the fire itself. In areas known to be threatened by floods, stores should be sited away from or above the highest known flood levels.

Construction of the store

All construction materials used in new premises intended for the storage of agricultural chemicals should be essentially non-flammable. This condition may not be fully met in existing premises, in which case the part which existing construction materials, such as timber roof frames, could play in the spread of fire within the building must be carefully considered. Depending on the size of the building, the nature of materials held on the premises and the availability of internal fire separation, the store may be regarded as suitable for its purpose. In certain conditions, however, an unsuitable standard of construction, coupled with an equally unfavourable location, could make the premises undesirable for the storage of pesticides.

Many new buildings may be constructed around a reinforced concrete frame with inherent fire-resisting properties. Where steel is used for this purpose, consideration should be given to protecting the exposed metal against the effects of fire, using a non-flammable insulation covering such as vermiculite.

Walls should be constructed in brick or a similar non-flammable material which also offers a high degree of security against forced entry. Asbestos cement or other relatively flimsy sheeting is not suitable in the latter respect, though in the interests of economy it may be used for the upper reaches of the walls, provided the lower and more vulnerable areas are solidly constructed. Fragile sheeting is also liable to damage from the handling of materials when used to form the lower walls of warehouses.

Roof construction should be designed to relieve smoke and heat in the event of fire. This can be achieved by the use of automatic ventilators that open at a predetermined temperature or, more simply, by using fragile material such as asbestos cement sheeting. But the latter, instead of providing controlled relief for heat and smoke, would shatter from the effects of heat and flame. The use of plastic roof lights, which, for internal illumination, are preferable to conventional windows in the walls, would lead to similar results. Windows also represent a security weakness.

In larger buildings, or even in smaller stores containing large quantities of flammable liquids, the use of internal walls should be considered. When properly constructed, they reduce the inventory of materials at risk in any one part of the building and serve to segregate materials which have a higher fire risk.

To be effective, internal separation walls should be constructed of non-flammable material, preferably brick, and must be built right up into the roof space. In new buildings, it is recommended that internal fire separation walls should extend beyond the roof on the outside of the building for a distance of about 1 m, but this could prove expensive in existing premises.

Doors in internal separation walls should be fire-resistant. If such doors are not self-closing, care must be taken to ensure that they are closed when workers leave the premises. A simple and inexpensive arrangement using a counterweight and fusible link can be used to ensure that internal doors will close automatically in the event of fire.

Warehouse floors should be in concrete and maintained free of cracks with a good surface finish for ease of cleaning.

Despite the precautions taken to minimize the risk of fire, it must be assumed that such an incident may occur, and consideration must be given to its containment and to the control of effluent, principally contaminated fire-fighting water. This can be achieved most cheaply by the construction of sills across all outside doors, thus creating a well within the floor area of the building. It will usually be necessary to ramp sills in order to allow the passage of fork-lift trucks and other vehicles. The gradients on the ramps should not exceed 1 in 10. It is suggested that sills should be at least 15 cm in height. As an alternative arrangement in new premises, the floor could be sunk to a depth of 15 cm during construction, with a ramped approach to doors used for vehicle access. With such an arrangement however, the possible ingress of storm water should be considered and appropriate steps taken to prevent such an occurrence.

Internal drains in stores must be avoided or, where they already exist, sealed at floor level. Warehouses used to store fammable liquids, such as solvent-based products, should have lightning protection.

Facilities and equipment

Electrical equipment used in stores must be maintained in a safe condition. In particular, battery-charging equipment must be located in a well-ventilated area to allow for the safe dispersal of hydrogen gas generated during charging, and must be kept well clear of stored products and other combustible materials. All electrical fittings, including lights, should be suitably positioned to avoid damage during the handling of materials.

Where heating is necessary in order to maintain the condition of the materials in store, indirect heating by a safe means, such as warm air, is recommended. Heating equipment should be permanently installed rather than portable, and the flow of hot air should not be directed on products, which must be stored well clear of heat sources.

Forced ventilation should not be necessary in storage premises provided adequate provision is made to permit good natural ventilation, using ventilators in the roof or in the wall just below roof level and near the floor.

Fire-fighting equipment must be provided and strategically located near doors and adjacent to higher risk areas such as battery-charging bays. This should include fire extinguishers of a suitable type, hose reels and some means of raising a fire alarm.

Consideration must also be given to the location and adequacy of external water sources which may be used for fire-fighting. In this connection, the use of water sprays for fighting are recommended in preference to single, powerful jets whenever possible. The latter waste water, are inefficient in fire-fighting, and will produce a greater discharge of surplus contaminated water that may create an environmental problem. To this end, an opportunity should be sought to discuss with local fire brigades the problems inherent in fighting fires involving pesticides, and to consider in detail the measures required to protect both fire-fighters and the environment.

Operational procedures[1]

Within the store it is essential that operations be closely supervised and that store personnel have a working knowledge of the materials being handled and the precautions to be taken. The selection, appointment and training of the

[1] See also chapter X.

supervisors will clearly be important in this connection, since it will be largely their responsibility to train the store personnel.

Good housekeeping is of paramount importance, and the orderly arrangement of stock, which should be used on a "first-in, first-out" basis, will do much to reduce package deterioration and damage. Under no circumstances should pesticides be stored where it is possible that they may come into contact with and contaminate foodstuffs and other materials intended for human or animal consumption or use.

The supervisor must ensure that store personnel use the necessary personal protective equipment, which must be properly maintained at all times. Overalls should be used as a matter of routine by persons working in stores. In the event of a spillage, the following items may also be required: impervious boots, gloves and aprons, eye protection, and a dust or light-fume respirator. A means of washing hands and eyes should be provided and emergency showers should be sited in strategic locations (see also the section below on first-aid treatment and the protection of store personnel).

Eating, drinking and smoking in the working area must not be allowed, and store personnel should be encouraged to wash their hands thoroughly after work and before taking meals.

Unauthorized persons should not be allowed to enter the store, and notices warning of this restriction, and of the restriction on smoking, should be displayed at all entrances.

Segregation of products within the store

According to the type and quantity of materials involved, it may be desirable to achieve a degree of segregation in order to reduce the potential fire risk or avoid problems of non-compatibility.

Flammable liquids and aerosols would, in the event of fire, greatly increase the rate at which the fire could spread throughout the buildings. Where substantial quantities of such materials are involved, segregation by means of separation walls of a fire-resistant standard is recommended. They may be practical only in large stores, but even in smaller units some segregation can be achieved by using a barrier of essentially non-flammable products, preferably water-based. Dry powders and granular products may also be used for this purpose, but depending on the active ingredients involved, such materials may produce hazardous decomposition products in the event of fire. Their presence would nevertheless serve to reduce the speed at which fire could spread within a building.

Oxidizing and potentially unstable materials present a special risk, and it is strongly recommended that they be effectively segregated in a well-ventilated area away from all flammable products. In the case of baits, the choice of storage will depend on other materials stored in the near vicinity, but products possessing a strong odour should be kept well clear of baits.

The importance of keeping herbicides separate from other pesticides will depend to a large extent on the nature of the materials and the type of package used. Herbicidal powders packed in multi-layer paper sacks, for example, are particularly vulnerable to damage and the spread of spilled powder is difficult to control. Such packages should be kept apart from non-herbicidal pesticides. Conversely, where the packages used are less liable to damage, for example steel drums, the need to segregate is less important.

The problems involved in ensuring segregation, particularly of a fire-resistant standard, are those of cost and, in small stores, the physical restrictions imposed by breaking up the working area into even smaller units. In such circumstances, the earlier reference to the use of non-flammable products, especially water-based products, to form safety barriers around or between stocks of flammable liquids may be most useful.

The importance of keeping pesticides in transit away from foodstuffs and other materials destined for personal use or consumption has already been mentioned. Such materials must be kept out of pesticide stores. It is also important not to store materials possessing a high fire risk with pesticides. While mixed unsegregated stores containing only minimal quantities of flammable materials are acceptable, those in which significant quantities of such materials are held without segregation from the pesticide products are not suitable and should be avoided.

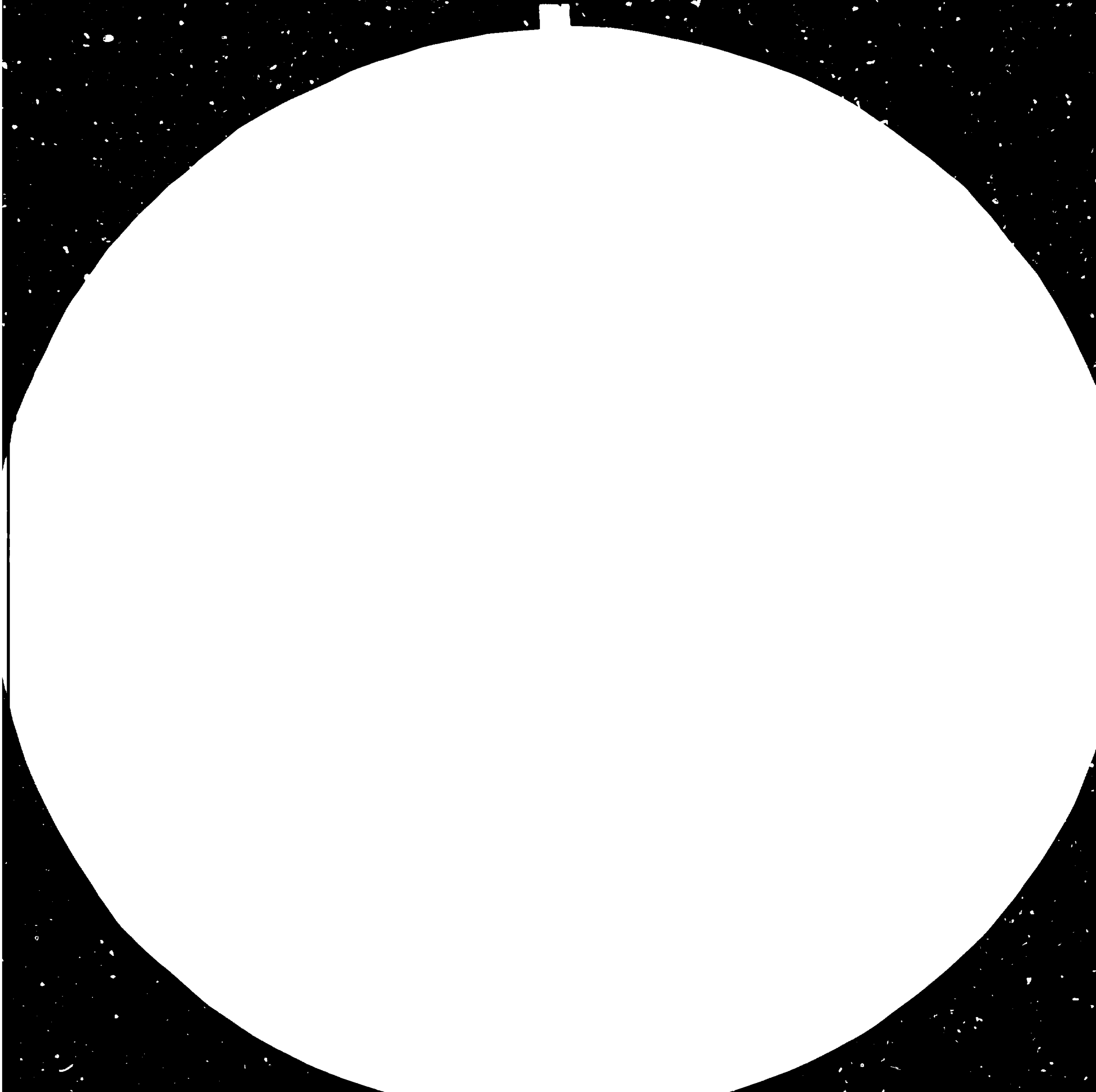
Stacking heights

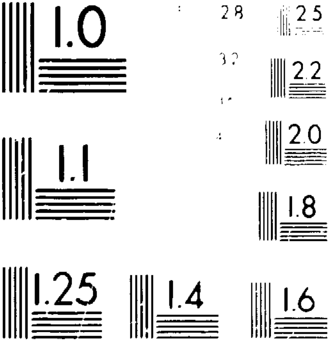
Recommended stacking heights vary with the type of package used, but in every case the height must be limited to the maximum that may be allowed without causing damage to the lower packages. The following table indicates the maximum safe stacking heights for various types of package.

MAXIMUM SAFE STACKING HEIGHTS

Type of package	*Number of packages per pallet*	*Maximum number of pallets per stack*
Steel drum	1-2	4
Fibre drum	2	3
Plastic drum	2	2
Paper sack	4-5	3
Polyethylene sack	4-5	3
Fibre case containing tins	4-6	4
Fibre case containing soft packages, such as plastic bottles or sachets	4-6	2
Wooden cases	2-4	4

To exceed the recommended safe heights without the use of some form of pallet racks or shelving may cause excessive and unnecessary damage to packages. Pallets should also be stacked clear of overhead light fittings, and the effects of package and product deterioration due to solar radiation and wetting by wind-blown rain must be considered when stacking near windows, including those in the roof.





MICROCOPY RESOLUTION TEST CHART

First-aid treatment and the protection of store personnel

The possibility that store personnel could themselves become contaminated by the product is clearly greatest when dealing with spillages, and a supply of absorbent and adsorbent materials such as sand, vermiculite, pumice or bentonite should be available in the store. Toxic waste should be sent to a licensed disposal unit or buried away from watercourses. The use of personal protective equipment, described earlier, is essential when cleaning up a spilled product, but despite this precaution, accidential contamination of the skin or eyes may still occur, in which case prompt action is necessary. Contaminated areas of the skin must be washed thoroughly with soap and water after removing any contaminated clothing, and contamination of the eyes must be treated immediately by irrigation with clean water. In all cases involving contamination of the eyes or severe contamination of the skin, the affected person should be referred to a physician or sent to hospital for further examination. A first-aid kit and a trained first-aid worker should be available.

It is strongly advised that the local medical service be informed of the nature of the materials held in the store. If necessary, advice on specific toxicity of products must be obtained from the manufacturer, and a supply of antidotes should be made available to the local hospital or clinic.

Store personnel must be made fully aware of the nature of pesticides and of the fact that some products can enter the body system through intact skin as well as through the better-understood processes of ingestion and inhalation of dust and fumes. Ingestion, probably the least common process, is usually the result of eating, drinking or smoking by workers with contaminated hands.

Safety of pesticides in transit

Anyone involved in the industrial production of pesticides should have some knowledge about potential hazards during the transport of toxic chemicals. Increasing concern has been felt about health problems arising from spillage of toxic pesticides on loading docks and in storage warehouses, ships, lorries, railway wagons and other conveyances. Every effort should therefore be made to ensure the safe transport of compounds until their delivery to the consumer.

The seriousness of the problem has been borne out by several incidents. In 1967, two separate leakages of endrin on sacks of flour in the holds of ships in the Middle East resulted in a total of 26 deaths and more than 800 cases of illness in persons who ate bread made from the contaminated flour.[2] In Mexico, during the same year, sugar and flour contaminated with parathion caused 16 deaths and many cases of illness,[3] and in Colombia, 63 persons died and 165 became ill from eating food made with flour similarly contaminated during transport by lorry.[4] In

[2] D. E. Weeks, *Bulletin of the World Health Organization*, vol. 37, (1967), p. 449.

[3] E. Márquez Mayaudon and others, *Salud Pública de Mexico*, vol. 10, No. 3 (1968), p. 293.

[4] M. Gomez Ulloa and others, "Epidemiological investigation of the food poisoning which occurred in the municipality of Chiquinquira, Colombia, a preliminary report" (Bogotá, Ministry of Public Health, 1968). Translated and printed by the Bureau of Occupational Health, State of California, Department of Health.

Canada, two children were seriously poisoned by sleeping in flannelette sheets that had become contaminated with parathion in the hold of a transatlantic ship.[5]

In the United States, a number of spillage incidents have occurred. One of the more serious spillages resulted in contamination of a bundle of cotton trousers with the highly toxic organophosphate compound mevinphos. The trousers had been shipped in the same lorry as the pesticides.[6] Six children became poisoned through wearing the trousers before investigators located the entire consignment and withdrew it from the market. In 1968, six members of a family in Texas became seriously poisoned when they ate tortillas made from flour contaminated with the organophosphate compound carbophenothion.[7] The flour had been purchased in an unlabelled 45 kg paper bag from a railway salvage store. Flour samples from the family bin contained 3,220 ppm of the pesticide. In another incident, oxygen respirators became contaminated with the chlorinated hydrocarbon pesticide endosulphan.[8] The pesticide and the respirators were transported on the same lorry. Containers of the pesticide broke and the pesticide dust entered the uncovered ends of the respirator tubes. The companies involved voluntarily corrected the problem. Another incident resulted in the contamination of biscuits by the organophosphate compound azinphos-methyl.[9] Contamination occurred when bags of the pesticide were loaded on a lorry beside the biscuits. Pesticide dust migrated to the food packages. A shipment of 150 cases of biscuits had to be destroyed.

The provision of information on the toxicity and hazards of pesticides, including safety rules for their transport, is important for minimizing accidents. Guidelines should also be provided for persons involved in clean-up operations after an accident has occurred. The recommendations of the United Nations Committee of Experts on the Transport of Dangerous Goods[10] are the standard reference for regulations designed to prevent accidents in transit. The regulations forbid the transport of EPA Class B poisonous liquids or solids in the same vehicle as any foodstuffs, feeds or other material intended for consumption by humans or animals.

Any vehicle used to transport such poisons must be inspected for contamination before reuse. In instances where leakage or spillage has occurred, the shipper of the material must be immediately notified for instructions concerning the best method of decontamination. Any vehicle found to be contaminated, excluding vehicles used solely for transporting poisonous materials, must not be returned to service until it has been decontaminated.

Even though the above-mentioned regulations are in force, spillage accidents continue to occur. The importance of reporting such incidents cannot be overstressed.

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[5] L. S. Anderson and others, *Canadian Medical Association Journal*, vol. 92, 1965, p. 809.

[6] M. C. Warren and others, *Journal of the American Medical Association*, vol. 184, 1963, p. 266.

[7] R. Hatcher, M. S. Dickerson and J. E. Peavy, *Morbidity and Mortality* Weekly Report, 5 October 1968, p. 376.

[8] *United States Food and Drug Administration Papers*, vol. 2, No. 4 (1968), p. 31.

[9] J. G. Stringer, *United States Food and Drug Administration Papers*, vol. 2, No. 4 (1968), p. 4.

[10] *Transport of Dangerous Goods* (United Nations publication, Sales No. E.77.VIII.1).

Suggestions for improving safety in the transport of pesticides

Pesticides must not be loaded on the same vehicle with foodstuffs, animal feedstuffs and other materials intended for human or animal consumption and use. The condition of the vehicle must be examined before loading begins, and unsound floors and protrusions likely to damage packages must be avoided. Similarly, any packages which show signs of damage or leakage must not be loaded, since they will almost certainly cause difficulties in transit. Similar precautions apply to the holds of ships and to small boats.

Loads must be properly sheeted and roped where necessary, and containerized loads must be firmly packed and secured to avoid movement and possible package damage in transit.

Vehicles without a clear separation between the load and the driver should not be used, because in the event of spillage, fumes or dust produced by the spilled product could adversely affect the driver.

Vehicles must carry adequate documentation to ensure that in the event of an accident, the nature and origin of the load can be identified.

Ideally, drivers should have a basic knowledge of the materials being carried, and the vehicles used should be provided with simple protective equipment, such as impervious gloves, eye protection, a rubber or plastic apron, together with a brush, shovel and a small supply of sand or other absorbent material. In special cases, an antidote should be carried and instructions for its emergency use provided. In practice, however, company-owned or regular contract vehicles may be able to meet such a standard, which would be difficult to maintain by drivers and vehicles used only occasionally to transport pesticides.

Handling of pesticide spillage

When an accident occurs, the primary requirement is an evaluation of the toxic hazard of the pesticides involved. Some pesticide chemicals have a relatively low degree of toxicity, and it would be difficult to envisage any circumstances in which workers or bystanders could absorb sufficiently large quantities to produce systemic poisoning. However, other pesticides, in particular certain organophosphate compounds, are extremely toxic, and even very small quantities, which could be easily absorbed by transport workers, police, clean-up crews or bystanders, can result in poisoning. A careful evaluation of the toxic potential of pesticides involved in a spillage accident plays an important role in preventing possible poisoning from more toxic materials and in avoiding unnecessary precautions and concern if the chemicals involved are of low toxicity.

Evidence from a variety of sources seems to reveal a tendency to try to clean up spillages without consulting the shipper or pesticide company or obtaining other expert advice. The result is inefficient decontamination, lorries or trailers are dispatched on the next assignment, and the spillage area may lose its identity as a potential hazard. Personnel involved in the transport and storage of such materials must therefore know the proper precautions to be taken in handling and shipping toxic chemicals.

The clean-up of spillage and safe disposal of toxic materials require personnel with specialized knowledge of pesticides and chemical safety and with proper equipment and sources of technical information available to them when an emergency arises. When contamination occurs, personnel from the pesticide manufacturing plant with a specialized knowledge of the toxicity and safety aspects of the specific chemicals involved may be called for assistance. In the United States, some major pesticide companies can provide a clean-up and decontamination team in certain areas, a service which has proved to be very helpful.

Spillage incidents should be reported to the proper authorities, especially local health officials. Situations may occur requiring official action to prevent movement of a contaminated vehicle or cargo until it has been properly investigated or decontaminated. If cargo other than pesticides has been removed from a vehicle in which a pesticide spillage has occurred, the items should be located and checked for contamination. Careful consideration should be given to whether items intended for human or animal consumption should be destroyed, especially if they are in containers that can be permeated by the pesticide. The location of cargo that has been reshipped following a spillage incident must be traced in order to prevent any hazard to the receiver.

When pesticide spillage occurs, the incident should be assessed and precautions immediately taken to prevent additional contamination. The contaminated clothing of an individual exposed to toxic material should be removed as soon as possible and contaminated skin areas thoroughly cleaned with generous amounts of soap and water to reduce dermal absorption. Exposed persons should be placed under medical observation to ensure that any symptoms of poisoning will be noted as early as possible so that prompt and proper treatment can be administered. This is especially important where there has been contact with one of the more highly toxic organophosphate pesticides.

Spillage at the plant and in the warehouse

Pesticide contamination through spillage can present a serious clean-up problem. It may be difficult and almost impossible to decontaminate certain surfaces to the extent that all of the toxic pesticide is removed. For example, if liquid concentrate parathion has been allowed to remain on wood flooring for any appreciable length of time, it is practically impossible to accomplish an adequate decontamination. The solvent used in the formulation apparently helps to carry the toxic material into the wood and between the flooring strips, with the result that, in most cases, the only reasonable safety measure would be the removal and replacement of the contaminated wood.

When pesticide has been spilled on flooring, the first inclination may be to hose down the floor with water to wash away as much of the pesticide as possible. This is not good practice because flushing with water often spreads contamination over a wider area and causes the seepage of toxic material through the floor. In attempting to remove the pesticide from a surface, the first step should be carefully to remove as much of the pesticide without enlarging the contaminated area. For dusts or water-dispersible powders, the first step might be simply to sweep up the bulk of the material and dispose of it. The broom and other items used in the clean-up operation should be destroyed to prevent future use. The worker sweeping up the powder must be adequately protected from exposure to pesticides.

Large quantities of dust or water-dispersible powders should never be picked up with a conventional vacuum cleaner with an exposed collection bag. The fine inert material may penetrate the collection bag and engulf the operator in a cloud of toxic dust. Commercial vacuum cleaners designed for use in pesticide manufacturing plants are better suited for picking up dry pesticides. They are usually designed to ensure a minimum of leakage into the air during operation. After the first collection of loose material, such vacuum cleaners do a reasonably good job of recovering dry particulate material from seams and cracks in the surface, but it should not be assumed that adequate decontamination has been accomplished without considerable additional cleaning.

The first pick-up of liquid spills should be carried out by means of an absorbent material such as attaclay, fine sawdust, soda ash or even dry soil, and safely disposed of. The worker again must be adequately protected. Final decontamination should be done with a chemical capable of degrading the pesticide. Some of the more readily available materials that have been used are sodium carbonate, household chlorine bleach (sodium hypochlorite), caustic soda, hydrated lime, water and detergent. Of these, caustic soda may be the most generally useful, especially in the case of spillage of carbamates and organophosphates. Furthermore, ethyl alcohol, isopropyl alcohol and trisodium phosphate have been used as solvents to clean surfaces. Contaminated absorbents should be treated as waste pesticides and disposed of accordingly (see the following section on the disposal of waste pesticides and empty containers).

Decontamination of metal lorry beds is possible if the flooring is continuous, that is, without seams or many bolt heads. However, most metal lorry floors have seams and are badly gouged and scratched, making decontamination very difficult.

Cleaning procedures for spillage during transit

It should be remembered that most pesticides are products used every day by farmers in the normal course of their work. The typical pesticide spillage accident will not normally fall into the category of an emergency, and must be kept in sensible perspective. However, the extremely toxic nature of some chemicals such as parathion makes it necessary to regard every accident as representing an acute hazard. The following paragraphs therefore deal specifically with a road accident involving injury to persons or damage to property while transporting pesticides of possibly extreme toxicity, and requiring the intervention of a rescue team.

Such a road accident may present a serious hazard not only to persons directly involved in the accident, but also to those assisting the injured and to workers who clean up the wreckage and road surface. It is important to remember that any persons injured in the accident should be checked by a member of the rescue team to determine whether their skin has become contaminated with a pesticide. The removal of a highly toxic organophosphate pesticide from the skin may be just as important and urgent as other first-aid measures for an injury. In such an emergency, water in almost any form, for example, soft drinks, may be useful for cleansing contaminated skin. If injured persons have been taken to hospital without being checked for skin contamination, the hospital should immediately be advised of the possible hazard. The rescue team called to the scene of the accident as experts on toxic chemicals may be required both to advise on life-saving measures and to deal with the following problems associated with the accident. The pesticides involved must first be determined in order to assess the potential hazard. If the shipping papers are not available, or if they show that several different pesticides are in the shipment, it may be necessary to enter the wrecked vehicle to identify the compounds that are leaking on to the road surface. At this time the foresight of having protective equipment available for such an emergency will be appreciated. The wearing of waterproof protective clothing and a cartridge-type respirator are the minimum requirements for entering wreckage contaminated with toxic materials. Where highly volatile materials are involved, the use of a self-contained air-supply respirator system is advisable. A battery-operated light for checking pesticide container labels in the dark and a shovel for covering spillage with soil are useful items. Until the nature of the spillage is known, police should allow no unauthorized persons or vehicles near the contaminated area. In cases where it has not been possible to prevent this, a check should be made to determine if shoes or vehicle tyres have become contaminated. If the spillage is of extreme toxicity, police may need to divert traffic.

If the pesticide spilled on the road surface is a dust or wettable powder formulation, such dry material might be drawn into the ventilation system of a passing vehicle and create a potential hazard to vehicle occupants, especially infants. In windy weather, dry pesticide material may be blown some distance and cause contamination of nearby areas. Covering dry pesticide with a tarpaulin or moist soil may prevent some movement by the wind, although strong winds make this procedure ineffective. Wetting down should be carried out only if it can be done without danger of contaminating nearby streams or bodies of water. If not, sand or earth should be used to cover the spillage and the whole lot then safely disposed of.

Safe removal of the contaminated wreckage and clean-up at the site require careful management. If a pesticide company sends lorries and crews to collect undamaged cargo or to dispose of waste pesticides and damaged containers, the workers should wear protective gear and take proper safety precautions. Undamaged cargo should be inspected to determine if it is contaminated. Care must be taken to avoid contaminating additional lorries or towing equipment. As much cleaning of the wreckage as possible should be carried out before it is moved, otherwise further spillage or drainage may occur as the wreck is lifted or towed. A thorough cleaning with absorbent material should be accomplished before any washing with water. Contaminated wreckage should not be moved to any location where it might be a hazard. Thorough additional cleaning should be carried out in a safe location under the supervision of a responsible person. This is especially important if the damaged vehicle will be repaired by mechanics.

In cleaning pesticides from road surfaces, it is advisable to follow somewhat the same procedure as noted above for other surfaces. The procedure should end with a thorough cleaning with water, although run-off into water supplies again must be avoided. Contaminated soil, crushed rock or gravel areas should be dug up, and the waste materials buried in a safe location. The site should be visited the following day by a responsible official from the formulating plant. By this time the road surface may be dried out, making it much easier to identify any remaining contaminated areas. After final clean-up, samples should be taken at various locations to check the effectiveness of clean-up procedures if a pesticide analytical service is available.

Disposal of waste pesticides and empty containers

A problem that may present a serious hazard to the public is the improper disposal of waste pesticides that have accumulated in the formulation plants from spillages, floor sweepings etc. Pesticides should never be washed into a drain or flushed into a sewage system. A method of disposal that may be used in certain areas is burial at least 45 cm deep in soil at a location approved for such purposes by local health authorities or other persons having jurisdiction over pesticide disposal. The site must be carefully selected to ensure that no surface or subsurface water will become contaminated. Neutralizing the poisonous effects of most pesticides is not easy, and adding lime or caustic soda is sometimes recommended to hasten the degradation of certain compounds. However, this method is not a completely reliable way to make the buried material completely non-toxic, especially where large quantities of toxic material generated in formulation plants are involved. In such cases the preferred method of disposal is to deal with the material in the manner described in chapter III. Burning large quantities of pesticide wastes is not advisable because of possible air pollution. Even the use of specially built incinerators where very high temperatures produce relatively complete combustion fails to ensure that no toxic smoke or vapour will be emitted.

The disposal of empty pesticide containers at the formulation plant should be carried out in such a way that they do not create a hazard for humans or animals. Combustible containers, such as paper bags and cartons, can be destroyed by burning, although in many areas this may not be allowed because of the creation of air pollution. If such containers are burned, extreme caution should be exercised and smoke avoided. Although formulation plants in the United States have used incinerators for burning combustible containers, there have been increased restrictions on and concern about incinerators that do not completely destroy toxic pesticides. If incinerators are allowed at any place, they should be enclosed by a high safety fence with a padlocked gate to keep out unauthorized persons. If combustible containers are not burned, they should be buried in an approved drum disposal site as described above for waste pesticides.

Disposal of metal drums presents a greater problem. The drums should be returned to the manufacturing plant, but if this is not possible they should be thoroughly drained and rinsed with a decontamination solution that is considered to be most effective in detoxifying the particular pesticide chemical involved. Information on decontamination of drums may be obtained from the pesticide manufacturer. Although the decontamination rinse procedure may not completely detoxify or remove absolutely all pesticide traces from the drums, it should make them much safer than if no rinse were used. Decontamination liquor should be run off to the evaporation pond described in detail in chapter III.

After decontamination rinsing, the bottoms of the drums should be punctured to render them unusable, and the drums should be buried in a safe location approved as a drum disposal site. Empty pesticide containers should not be allowed to accumulate in an area accessible to unauthorized persons who may be tempted to use them for livestock water troughs, storage cans, rubbish-burning containers or other purposes. Provided drums have been rinsed and punctured, they may however be used for roadworks. In this case, they must be stencilled "Not to be used for food or drink".

Conclusion

In conclusion, it may be said that safety can seldom, if ever, be measured in absolute terms, and in almost every respect there will be practical limits to the degree of safety which can be achieved. The problem inherent in seeking to ensure safe storage and transport of pesticides is no exception to this rule, but by careful management, the risks involved can be reduced to the minimum levels tolerable within the industry and, it is to be hoped, acceptable within the community. Events have shown that existing standards can be improved, and the preceding paragraphs have attempted to incorporate the lessons of experience with good current practice.

XII. Labelling and packaging: the formulator's responsibility to the user[1]

*Richard Reynolds**

Preceding chapters on safety procedures in the handiing of pesticides dealt mostly with the work-force within the pesticide formulation plant. In this chapter, the emphasis will be on the formulator's responsibility to the user, that is, the pesticide applicator and the farm worker. Effective labelling and good design of pesticide containers are two major factors in ensuring the safety of the pesticide user and minimizing health hazards.

Knowledge of product hazards

The first basic rule for the safe handling of pesticides is to know the product being handled. The easiest way to do this is to read the label. Every pesticide container is labelled, and every label contains pertinent safety information. Additional descriptive information may be obtained from the manufacturer. Many companies have published manuals containing recommended manufacturing methods, toxicity data, industrial hygiene precautions, ventilation recommendations and medical information.

One company has placed on all of its pesticide packages a STOP sign which warns all users of the material to read the label. For example, on drums of 200 l, the sign is on the seal over the drum bung, and on pails of 5 l and 22.5 l of technical materials or formulations, it is on the flex-spout cap seal. The STOP design shown in figure I is similar to road signs in the United States. Use of this or a similar system by all manufacturers and formulators of pesticides may prove very helpful. The clear intention is that the user should read the label before the package is opened and any attempt made to apply the product. This objective presupposes a degree of literacy which may not exist, and for such circumstances special labels need to be devised (see section below on innovative label designs).

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[1] This chapter is based partly on material generated from a study commissioned jointly by FAO and the United States Agency for International Development and carried out by the author, partly on the chapter entitled "Safety in the handling of organophosphate pesticides", prepared by W. V. Andresen for the previous version of this manual, and partly on material provided by J. C. Caporossi, Director, Industrial Hygiene Department, American Cyanamid Company, Wayne, New Jersey, United States of America.

Figure I. Warning sign for pesticide containers

The label as a means of information and instruction

The label has two main functions: to describe where, when and how to use the product; and to convey warnings and instructions on action which may arise from such warnings. The label therefore needs to be designed to be able to convey such information and permanently to remain, for example by lithographic means, an integral part of the pesticide container. Moreover, it must be in the local language of use. The format of a typical pesticides label is illustrated in figure II.

Content of label

Name of product

The label will usually show the approved name of the product and the brand name chosen to identify it in the market-place and to provide a symbol of quality consistency.

Description of the formulation

The percentage of active and inert ingredients in the formulation must be indicated.

Purpose of the product

The label should state the purpose of the product, for example, a fungicide to combat coffee-berry disease or an insecticide to destroy cocoa capsid. Pictorial material may be helpful in this respect.

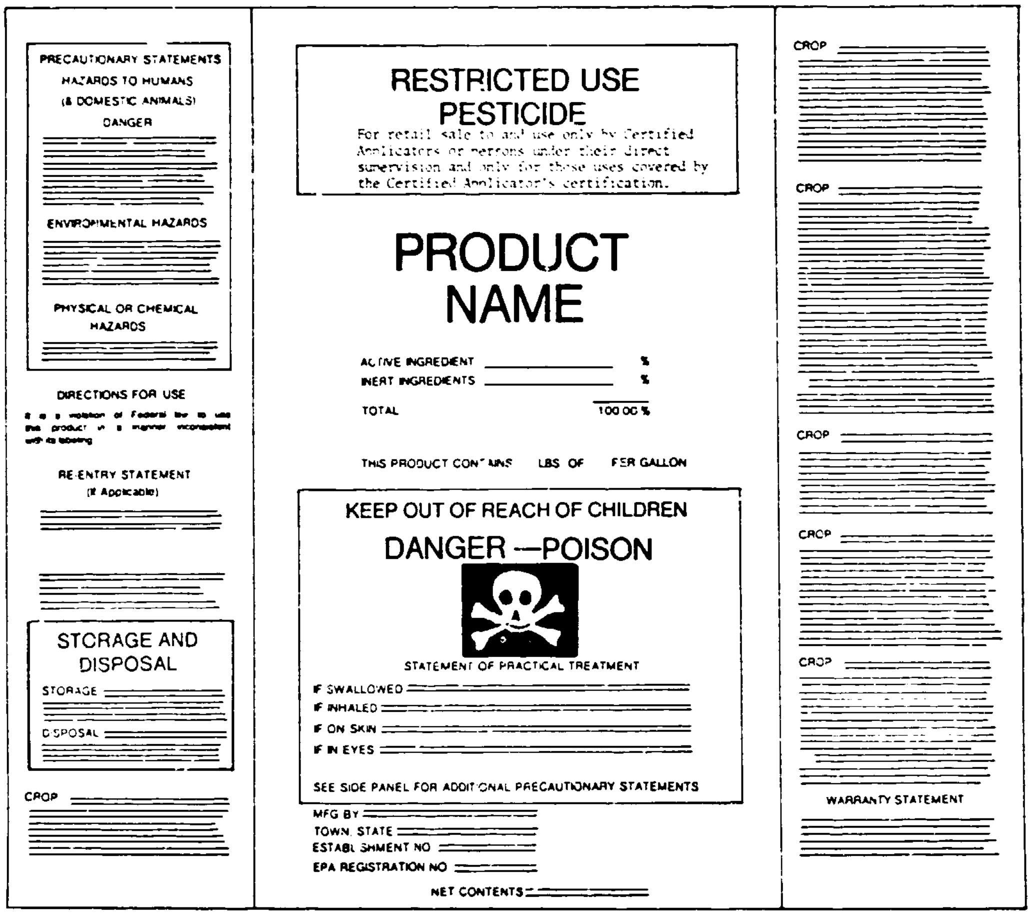
Directions for use

Crop information, method of application, dosage rates etc. must be included.

Warnings

Both general and specific warnings are needed.

Figure II. Format of a typical pesticides label



Toxicity

Table 1 below shows the categories of toxicity in the classification of pesticides by hazard. The hazard referred to is the acute risk to health, that is, the risk of single or multiple exposures over a relatively short period of time, that might be encountered accidentally by any person handling the product in accordance with the directions for handling given by the manufacturer or with the rules laid down for storage and transport by competent international bodies. The document[2] from which the information is drawn also includes lists of technical products classified by hazard. Figure III[3] shows the information in histogram form.

[2] World Health Organization, "Guidelines to the use of the WHO recommended classification of pesticides by hazard", unpublished document (VBC/78.1 Rev. 2). Available from Pesticides Development and Safe Use Unit, WHO CH 1211, Geneva 27.

[3] J. F. Copplestone, "Education and safe handling in pesticide application", Studies in Environmental Science 18 (Amsterdam, Elsevier Scientific Publishing, 1982).

TABLE 1. WHO CLASSIFICATION OF PESTICIDES BY HAZARD
(mg per kg of body weight)

	LD50[a] for the rat			
	Oral		Dermal	
Category	*Solids*[b]	*Liquids*[b]	*Solids*	*Liquids*
Ia – Extremely hazardous	5 or less	20 or less	10 or less	40 or less
Ib – Highly hazardous	5-50	20-200	10-100	40-400
II – Moderately hazardous	50-500	200-2 000	100-1 000	400-4 000
III – Slightly hazardous	> 500	> 2 000	> 1 000	> 4 000

[a]The LD 50 value is a statistical estimate of the number of mg of toxicant per kg of body weight required to kill 50 per cent of a large population of test animals.

[b]The terms solids and liquids refer to the physical state of the product or formulation being classified.

The classification, which is based on the toxicity of the technical compound and on its formulations, distinguishes between the more and the less hazardous forms of each pesticide. In particular, allowance is made for the lesser hazards from solids as compared with liquids. The classification is based primarily on the acute oral and dermal toxicity to the rat, in accordance with standard toxicological procedures.

To understand better the degree of toxicity associated with each category, the approximate amount of material needed to kill an average person weighing 70 kg is estimated as follows:

Category		*Approximate amount required to kill a 70-kg person*
Ia-Ib	Extremely to highly hazardous	A taste to 1 teaspoon (0.5 ml)
II	Moderately hazardous	0.5-30 ml
III	Slightly hazardous	30-500 ml

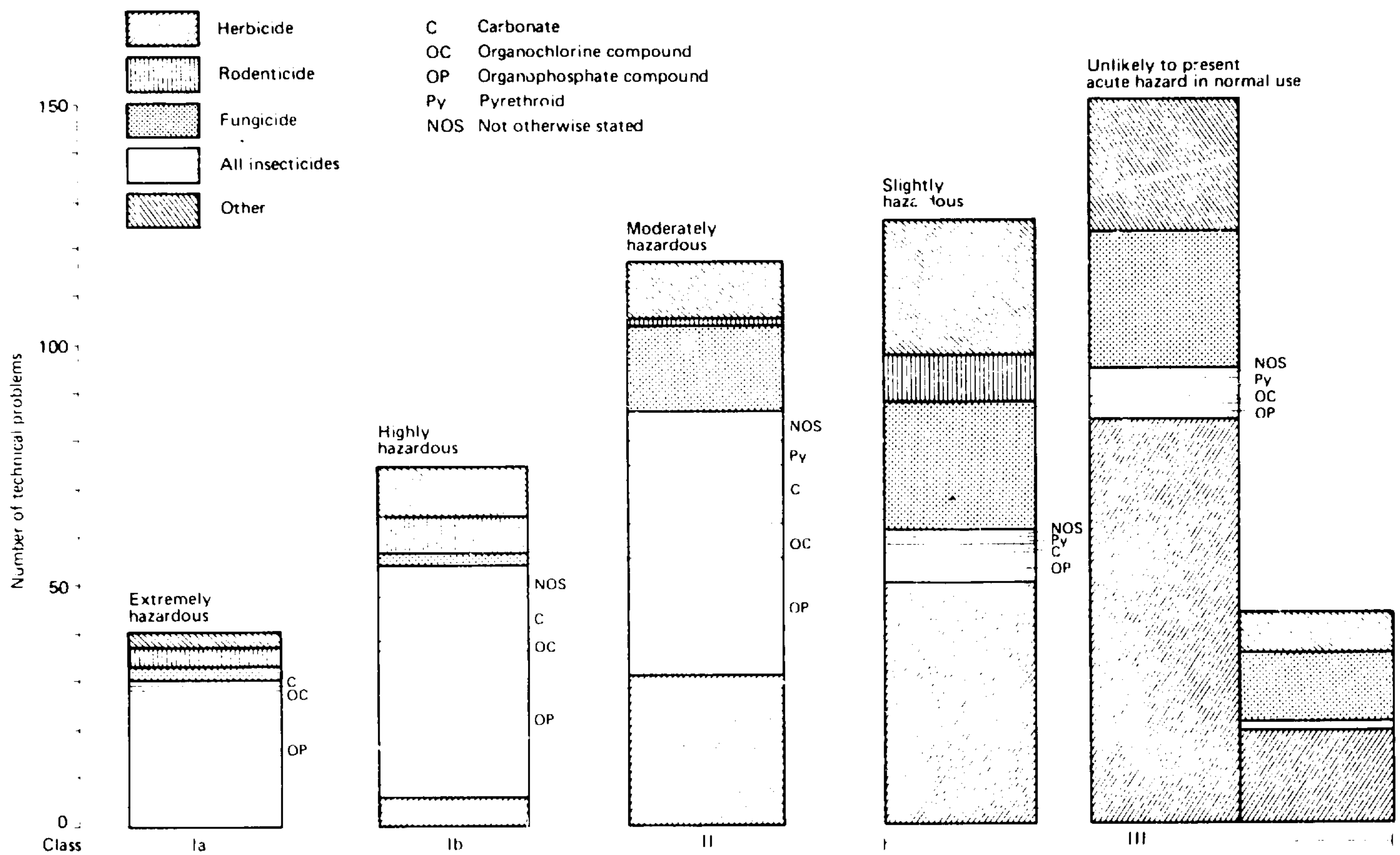
The aim should be uniformity in the statement on the nature of the risk (by phrase or symbol) on the label of the product, irrespective of the country of origin or use. Labels of products classified Ia and Ib should bear a symbol indicating a high degree of hazard, usually a type of skull and cross-bones, and a signal word or phrase, for example POISON or TOXIC. The presentation of the symbol and word or pharse, in particular their colour, size and shape, should be given sufficient prominence on the label.

By extension, the label for all products should carry additional warnings of the following type: "Keep out of reach of children"; and, for larger containers, "Keep product in original container", to avoid the danger of decanting the product into smaller unlabelled containers.

Precautionary statements

The part of the label containing precautionary statements indicates the ways in which the product may be harmful to humans and to animals and lists the steps which must be taken to avoid poisoning. The latter may include recommendations

Figure III. WHO classification of pesticides by hazard



		Class	Ia	Ib	II	[illegible]	III	
LD_{50}	Oral	Solid	< 5	5–50	51–500	> 500	(>2 000)	(>10 000)
		Liquid	< 20	20–200	201–2 000	> 2 000	(>3 000)	(>10 000)
	Dermal	Solid	< 10	10–100	101–1 000	> 1 000	—	—
		Liquid	< 40	40–400	401–4 000	> 4 000	—	—

Source: J. F. Copplestone, "Education and safe handling in pesticide application", Studies in Environmental Science 18 (Amsterdam, Elsevier Scientific Publishing, 1982).

for controls at the place of work, personal hygiene and protective equipment. For class Ia and Ib products, the symptoms and immediate treatment of poisoning should be described. This part of the label also provides information on practical treatment (first aid) and any physical or chemical hazards which may pose a special fire or explosion problem.

Restricted and general classification

Highly toxic pesticides such as parathion have been designated under United States law as restricted-use pesticides which can be used only by certified pesticide applicators. All other pesticides are in the general-use category and are available to all users.

Storage and disposal

Each pesticide label gives proper procedures for storage and disposal of the product and empty containers (see chapter XI).

Safety requirements during transit

The subject of safety during transit is fully covered in chapter XI. However, with regard to label information, there should be an easily recognized symbol or word on the label indicating the severity of the toxicity caused by accidental spillage or leakage.

Re-entry statement

The re-entry statement indicates the period after which it is safe for people or animals to re-enter an area which has been treated with pesticides for normal farm use.

Innovative label designs for regions of low literacy

The problem of low levels of literacy or illiteracy in certain regions was referred to above. The use of graphics to convey information to the user of pesticides has been found to be of great assistance in such circumstances. Label material which is an integral part of the package can also be supplemented by posters and films. The art of cartooning has been well developed. The message needs to be conveyed in a simple, recognizable and graphic form that explains the level of hazard, targets pests and crops, and methods of application. Some examples of such an approach are illustrated in figures IV, V and VI. An organization in the Ivory Coast specifies container sizes corresponding to a portion of cotton insecticide suitable for an area of 0.25 ha. The typical application method for cotton insecticides in that region is by ultra-low volume (ULV) using hand-held applicators. The label is overprinted with representations of the crop, applicator and pest (see figure IV).

In Malaysia, the regulations call for a coloured strip covering 20 per cent of the area of the label to be printed on all packages. On the two most hazardous classes of pesticide, a skull and cross-bones symbol is overprinted (see figure V).

Figure IV. Sample pesticide label illustrating applicator and target pest and crop

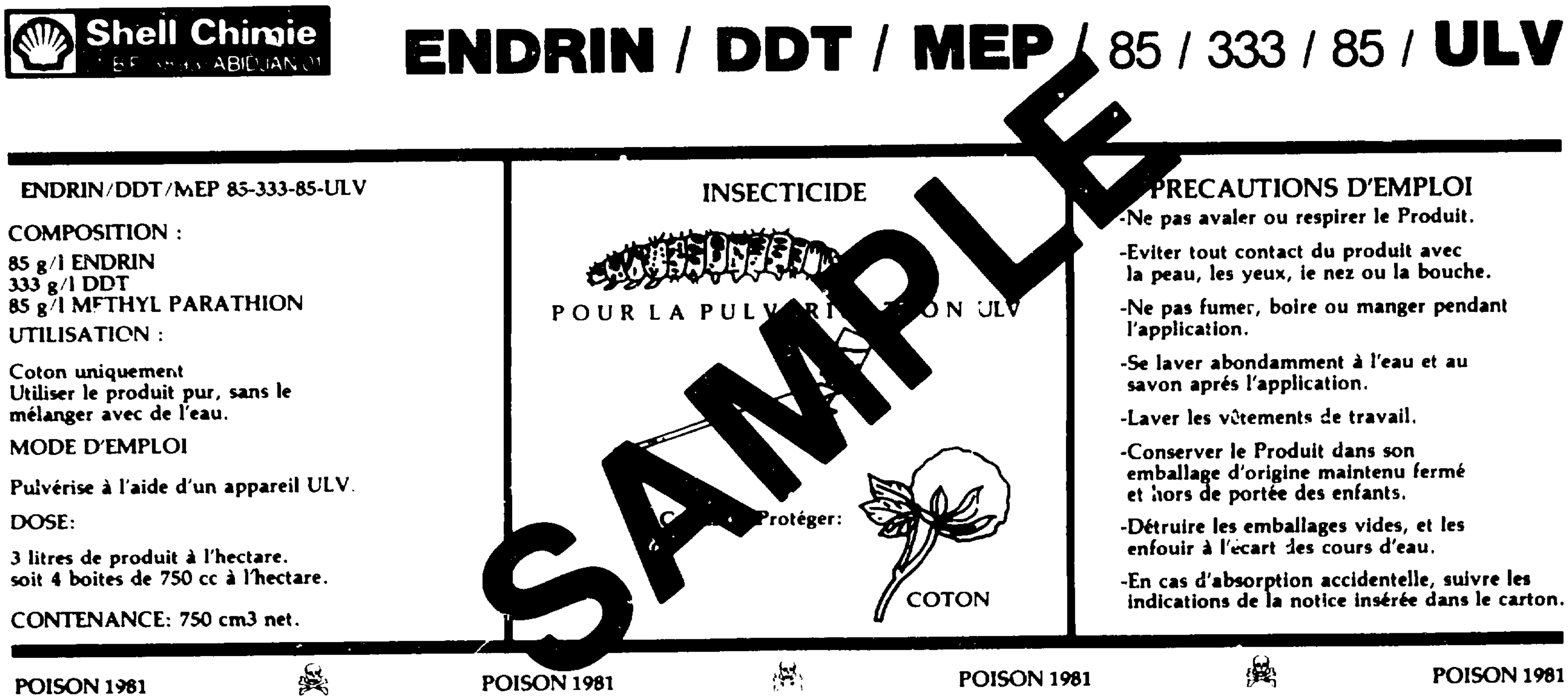
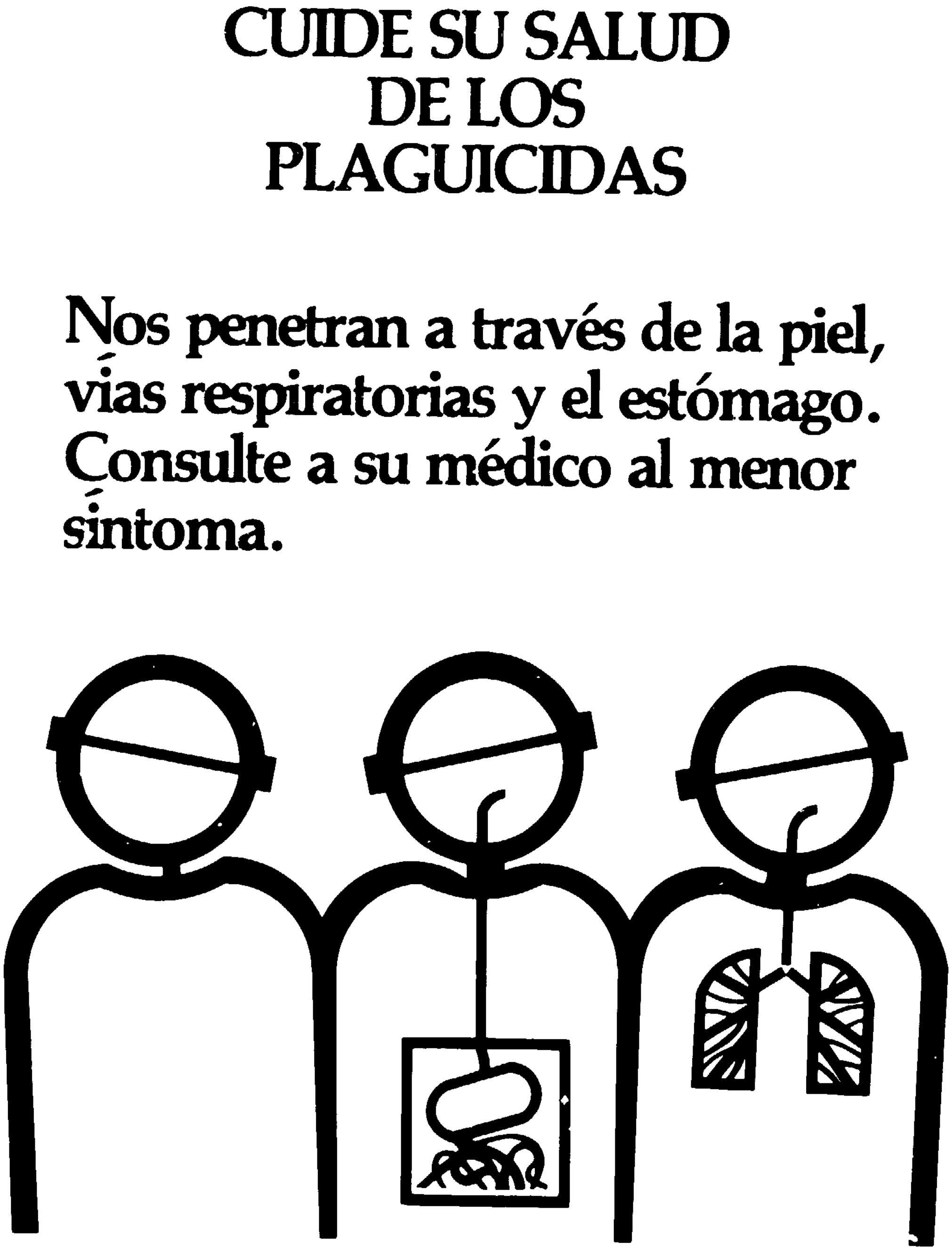


Figure V. Sample label for highly poisonous pesticide

A third significant example of work in this area comes from Costa Rica, where an insurance company has produced and distributed large numbers of posters illustrating procedures for the safe handling of pesticides. A similar example is shown in figure VI.

Figure VI. Sample pesticide poster using graphic illustrations and written explanations[a]



[a] Legend reads: Protect your health against pesticides.
They enter the body through the skin, the respiratory tracts and the stomach.
Consult your doctor at the slightest symptom.

The subject of labelling clearly needs re-examination. The well-written and legally effective labels applied to pesticide containers do not necessarily serve the needs of the user, especially when levels of literacy are low or non-existent. Moreover, it will be clear from the above sections that the amount of information which has to be conveyed is very considerable. In order to avoid overloading the label, it may be convenient to provide directions for use, including crop information etc., as a separate leaflet to accompany the individual package, reserving the label itself only for those items which are essential to immediate safety. It is of interest that in India, where the problem of the number of written and spoken languages occurs in an extreme form, the instruction leaflet may have to be printed in 12 different scripts and tongues, including English. Communication with the user is of prime importance. The sale in a vendor store of an incorrect and inadequate amount of pesticide to an illiterate farmer must be prevented. The cause of such an error will continue to exist until a means of communication is developed.

Label specifications

Labels become detached or fade. Printed labels on packaging need specifications as to the qualities of adhesion and also of the colour fastness and weather resistance of inks. The severity of the problem is exacerbated by the use of similar packaging for different pesticide products, for example herbicides and insecticides. The internationally accepted test methods such as ISO 105 and BS 5609 may be used, but they involve special equipment and testing should be carried out for 65 hours. If the equipment is not available, a satisfactory substitute may consist in simply exposing to the elements a sample bearing the actual adhesive. Samples of ink printed on the substrate should be observed under worst conditions for at least 21 days. This period is often sufficient to indicate stability. In case any visual change to the sample occurs during that period, corrections should be made.

Packaging of pesticides

Of special importance to the successful local packaging of formulated products is the supply of locally available and good-quality packaging materials. Good quality is necessary because the very nature of pesticides puts higher demands on packaging. Those special demands are often not generally known to packaging manufacturers unless they have been specially trained, since the total volume of packaging used for pesticides is probably less than 2 per cent of their overall business, and is unlikely to exceed 5 per cent of a particular type. The pesticide formulator may therefore be called on to give guidance to the packaging manufacturer with regard to the required packaging specifications.

In some countries there is an adequate range of choice of both suppliers and package types and a willingness and desire by both packagers and vendors to meet quality requirements. But in countries which may be new to the formulation of pesticides, there should be an awareness of the problems of defective packaging, the resulting negative effects on sales, the considerable problems and cost of rework and disposal, and the hazards that may be caused by the user if the package fails.

Package size

Package size is dependent on the needs of the market-place. Large farms often require packages in the volume range of 30 l to 200 l of the product. However, in many developing countries, packages of smaller size, in the range of 125 ml to 750 ml for insecticides and up to 5 l for herbicides, are often preferred for small farmers.

There is considerable merit in the use of small packages, although economically they may not always be as advantageous as large packages. Their use is frequently encouraged by Governments and agencies for the following reasons:

(a) They can be conveniently designed for only one product application for a given area, and may sometimes be incorporated into an application system. For example, some insecticides are sold in a plastic container which can be used directly with a ULV applicator. The user simply removes the closure from the container, which is then screwed on to the applicator. At no time is it necessary for the user to come into contact with the product;

(b) When large-sized packages are used, the product must be dispensed, which leads to difficulties in measurement where literacy is low. In addition, needed cash is tied up when some of the product is left over and cannot be used until the next season;

(c) Used containers are seldom thrown away, but kept for a variety of secondary uses, such as farm scarecrows or water vessels. Undoubtedly in the past, numbers of people incorrectly used pesticide containers for the carriage and storage of drinking water, with sometimes terrible results. Small containers, however, are not generally used as water vessels, which is an additional advantage of their use;

(d) Another advantage is the reduction or elimination of the dispensing of loose pesticide, which is still a common practice in many countries. This method not only leads to the use of unauthorized and unlabelled containers, but contributes to the practice of adulteration. In addition, the presence of large stock containers from which small containers are filled results in contaminated pesticides stores which are not infrequently adjacent to and unprotected from food stores.

Package standards

International experts have made useful suggestions on standards and specifications for pesticide containers which will serve as guidelines for those concerned with newly established pesticide formulation plants. Such suggestions, if they reduce the number of accidents due to spillage, leakage or reuse of containers, will be applauded by both government authorities and users of pesticides.

Some general package requirements are outlined below:

(a) Packages should comply with the national standards and regulations in force and, where required, with international transport regulations such as those recommended by the United Nations Committee of Experts on the Transport of Dangerous Goods;[4]

(b) The shelf life for a container and product should be established as two years. If shorter than that, the expiry date should be shown clearly on the package;

(c) Pesticides should be packaged only in clean and dry containers designed to provide protection against deterioration, compaction, weight change or other spoilage. Containers must withstand all anticipated levels of handling, storage, stacking, loading and unloading conditions and should not become adversely affected by changes in atmospheric conditions, pressure, temperature and humidity. Standards of performance should be established through accepted test procedures (see annex to this chapter);

(d) The inner surface of containers or closures may be coated or lined with substances or materials which have been tested to resist corrosion. When such coatings, linings or materials are used, they should not contain substances which could mix with the contents, form other compounds or weaken the overall structure. Manufacturers of technical material will be able to advise on compatibility questions;

(e) Outer surfaces of pesticides containers must be constructed of, or coated with, materials which resist corrosion or other deterioration, and which will accept either printed label copy or the attachment of a printed label. Labelling should be positioned so as to be readily identified, and should remain legible and attached throughout the anticipated shelf-life;

(f) Containers of a specific design which have met the required standards through tests performed for one specific product must be retested if they are to be used with another product, or with a new formulation of the existing product;

(g) Inspection procedures should be established at container filling sites which ensure that the quality of pesticide containers is maintained;

(h) All liquid containers should have an ullage of at least 5 per cent that is, they should not be filled above 95 per cent of capacity;

(i) Reused or reconditioned packaging should be used only when it can be tested as being equal in performance to original packaging;

(j) Closures and seams must be thoroughly tested for leakage and corrosion-resistance, and containers with their closures in place must undergo standard drop tests, for example ASTM D-775 of the American Society for Testing Materials (ASTM), to withstand accidental droppings from trucks and pallets;

(k) Finally, an item that might be overlooked is the design of closures and containers proof against tampering by children, a practice that has generally been accepted in the dispensing and packaging of pharmaceutical products. The United

[4] *Transport of Dangerous Goods* (United Nations publication, Sales No. E.77.VIII.1).

States Environmental Protection Agency (EPA) has developed guidelines for the requirements of child-proof containers, and other countries might avail themselves of the results of such work by writing to EPA.[5]

Package specifications and testing

Specifications are not only a useful form of communication between vendor and buyer, but also an essential factor in the purchase of pesticide containers. Table 2 (in the annex) lists items which should always be specified in the purchase of pesticide containers. Of particular importance is item 22, test values. A means of testing or measurement should always be established, using agreed written methods or standards such as those developed by internationally recognized bodies.

The performance of tests on containers is a useful means of determining the probability of the containers providing the level of protection required. Following the production of the containers tests should be carried out to confirm the validity of the original work. The use of specific test procedures improves communication between interested parties such as regulatory bodies and container manufacturers and users. Test procedures can be developed with varying levels of complexity, depending on the facilities and personnel available. However, well-established test procedures such as those published by ASTM or other internationally recognized bodies should be used for general reference purposes. Useful test procedures may be based on United Nations recommendations on the transport of dangerous goods[6] examples of which are presented in the annex, those listed by the United Kingdom or United States Departments of Transport, or those published in *Chemistry and Industry*, No. 4, dated 18 February 1978, pp. 111-115.

Selection of packages for different product groups

Solid products (powders, dusts and granules)

Small packages, usually up to a capacity of 3 kg, can generally be selected from ready-made packaging, such as bags, pouches, canisters, cans and glass or plastic jars. Bags or pouches should be manufactured so as to be leak-proof through the bottom and sides. The top will be open for filling and must subsequently be sealed so as to become leak-proof, usually through a combination of heat and pressure using a standard heat-sealing device. Bags and pouches are often manufactured with more than one ply of material. The inner ply will usually be polyethylene film, which is useful for sealing, provides an excellent moisture barrier and is resistant to attack by most chemicals. The thickness of the film should not be less then 0.02 mm. Thicker films of up to 0.05 mm are often needed to achieve leak-proof seals after filling.

[5] Enquiries should be addressed to the Director of the Registration Division, United States Environmental Protection Agency, Washington, D.C., United States of America.

[6] *Transport of Dangerous Goods* ..., chapter 9.

Canisters and cans should be manufactured with leak-proof bottoms and tops for filling. Canisters are made with layers of paper to form the body, which may be embedded with polyethylene or other materials, such as aluminium foil, to develop necessary barrier qualities. Canisters may have a round or rectangular section.

Cans are normally manufactured from tin plate, thin steel sheet coated with tin on both sides, and may also be round or rectangular. Tin plate normally provides good environmental and chemical protection, making it a useful packaging medium. Corrosion occasionally occurs, and is preventable through the use of inner coating. Such coatings can only be satisfactorily applied to round cans. When required, outer coatings of paint or varnish may be applied.

There are a variety of closures for canisters and cans, the replaceable plug being the most useful for solids. When controlled application is needed, sifter tops in tin plate and plastic are available. Screw-on closures are also available.

Glass or plastic jars are one-piece containers comprising bottom and body, manufactured for top filling, and often available in standard sizes. Glass is seldom corroded by pesticide formulations but is little used for packaging solids. Plastic jars made from polyethylene are particularly useful, due to their moisture barrier and shatter-proof characteristics. Other plastics may be used for jar manufacture at some cost to overall packaging qualities. Closures for glass and plastic jars should be of the screw-on type, unless an alternative closure is shown to have sufficient retentive capability.

Large packages with a capacity of 10-30 kg may be selected from sacks, fibreboard, plastic or steel drums and corrugated boxes. Sacks may be manufactured entirely from polyethylene film or from layers of paper and film or other barriers. They should be made leakproof and may be filled through an open top which is closed by sewing or heat-sealing. Sewn tops are not leakproof for dusts and powders and do not provide moisture-resistant seals unless special taping-over methods are employed.

Fibreboard, plastic or steel drums are usually in standard sizes. Linings are often used in the form of polyethylene bags either for moisture protection or to reduce drum contamination and ease cleaning for reuse. The drums have full-size removable heads that should be capable of being locked on after filling, so as to withstand rough handling

Fibreboard drums are manufactured from layers of paper and have polyethylene or other barriers such as embedded aluminium foil. Plastic drums are manufactured from polyethylene, providing an excellent moisture barrier. Steel drums provide maximum protection and can be shielded against corrosion by use of either coatings or polyethylene bags.

The use of any of the large rigid drums provides excellent protection against compaction. They can all be closed using a variety of heads. Since gasketing is frequently used, it is important to check compatibility.

Liquid products

Small containers with a capacity of up to 5 l can generally be selected from available stock packaging. The types used are cans, either flat or screw-top with neck, and glass or plastic screw-top bottles with neck. Cans should be manufactured with leakproof ends that have gasketing compounds at the interface with the body. Side seams should be welded or soldered. Cans manufactured from tin plate usually provide excellent protection to liquid formulations. In the event that additional internal protection against corrosion is required, coatings may be applied to round cans.

Since some liquid formulations such as acids will corrode the base tin plate in storage, inorganic nitrite salts have been added as corrosion inhibitors. However, dimethylamine formulations of, for example, 2,4-D have been shown to produce the potential human carcinogen, dimethylnitrosamine, which can be prevented by the use of plastic-lined metal containers.

Care should be taken to ensure that minimal volumes of water are present in cans or formulations at the time of packaging to avoid the development of rust and pin-holes. Defective compound and side-seaming and the presence of water are major causes of can failure.

Glass or plastic bottles with necks are useful for liquids, since they can be poured without spillage. Glass bottles are excellent for chemical packaging because of their characteristic inertness, but are more liable to break or shatter during a typical life cycle. Plastic bottles, usually made from polyethylene, are useful for containing formulations without solvents. Plastic bottles, however, are liable to environmental stress cracking as a result of structural defects or incorrect resin selection. Special care must also be taken in the design of outer containers for small plastic bottles, in order to protect them from becoming crushed when stacked during storage. Under such conditions, cracks readily develop and leaking occurs. Large liquid containers, typically in the capacity between 10 and 200 l are usually of standard varieties, such as steel or plastic jerry cans and drums. Liquids should always be packaged in containers with closed heads, and in the case of drums, the head should be seamed or welded on to the body. Individual openings for dispensing from large liquid containers should not exceed 63 mm in diameter but two openings may be placed in the head.

Steel containers provide very high levels of strength, with consequent resistance to damage during handling, transport, storage and stacking. They may be coated internally with a variety of materials which provide resistance to corrosion. Internal coatings should be used and selected with great care to avoid incompatibility. In addition, consideration should always be given to the risk of coating failure arising from incorrect manufacturing procedures.

Seaming compounds are used to seal the interface between drum ends and body, while rubber, elastomer or plastic gaskets are used to seal the closures. As with small containers, care should be taken to avoid the presence of water when filling.

Large plastic containers, usually constructed from polyethylene, are self-supporting or require an overpack in the form of a steel drum or a corrugated cardboard box. Such containers provide excellent protection against moisture, especially because of the weight or thickness of the walls. The thickness often provides an adequate barrier for the packaging of solvent-based formulations, particularly when the vapour pressure is low.

Pressure packages such as aerosol containers

Containers which are filled under pressure at ambient temperatures must be designed to be pressure-resistant. The gauge of the metal used for the body and heads, the means of sealing and the construction of the valve are particularly important. The design, selection and testing of pressure containers is complex and should be undertaken only by trained persons using carefully calibrated instruments. The shelf-life of pressure containers is often less than two years, and packers are well advised to limit production in co-ordination with consumption.

Overpacks

Overpacks are used to accommodate one or more containers. They provide extra protection for the inside containers from handling, stacking and shipping damage. Overpacks may be constructed from film bags, shrink wrappings, paper bags or corrugated boxes, depending upon the level of protection required. The most commonly used overpack for pesticides is the box, particularly due to its ability to provide low-cost, economic protection. In extremely severe transport conditions, it is advisable to accumulate a number of boxes within a wooden crate.

Closures

Selection of the correct closure is extremely important to successful packaging in rigid containers, especially when they hold liquids. The closure size for liquid containers should be determined from the required pouring rate and the viscosity of the formulation. Closure sizes for liquid containers should not exceed 63 mm, and it is useful to limit smaller sizes to 38 mm for the purpose of standardization.

Closures for rigid containers carrying powders or granules may be larger than 63 mm and similar in size to the diameter of the jar or drum. Tamper-proof features built into the closure to indicate whether a container has been opened are particularly useful. Other tamper-proof methods are available, such as shrink-on seals. Closure liners should be carefully selected since they greatly influence overall performance. Inadequate liners are often found to be the cause of defective containers.

Closures are not designed to be in constant direct contact with the product, only with the vapour phase, and should not be expected to contain liquids when the container is inverted. They should be applied to containers at a torque sufficient to maintain a seal. It is customary for the torque originally applied to lessen with time, usually within 24 hours. The correct method of measurement for closure torque is to measure the opening force.

In conclusion, it may be fairly stated that without the provision of proper packaging and labelling, the establishment of a pesticide formulation plant should not be undertaken.

ANNEX

CONTAINER SPECIFICATIONS AND TEST PROCEDURES

Examples of container test procedures[a]

Preparation of packing and packages for testing

Tests should be carried out on packaging and packages prepared as for dispatch, including inner receptacles in the case of combination packagings. Inner or single receptacles should be filled to not less than 95 per cent of their capacity in the case of solids and 98 per cent in the case of liquids. The substances to be dispatched in the packages may be replaced by non-dangerous substances except where this would vitiate the results of the tests. If the substances to be dispatched are replaced for test purposes by non-dangerous substances, the substances used should be of the same specific gravity as the substances to be carried and their other physical properties (grain, size, viscosity) should correspond as closely as possible to those of the substances in question.

Paper or fibreboard packaging should be conditioned for at least 24 hours in an atmosphere maintained at 50 ± 2 per cent relative humidity and at a temperature of $25 \pm 2°C$. They may alternatively be conditioned for at least 24 hours in an atmosphere maintained at 65 ± 2 per cent relative humidity and at a temperature of $20 \pm 2°C$ or $27 \pm 2°C$.

Steps should be taken to ascertain that plastics materials used in the manufacture of plastics receptacles are chemically compatible with the substances the receptacles are destined to contain. This may be done, for example, by submitting sample receptacles to a preliminary test extending over a long period, for example six months, during which the samples would remain filled with the substances they are destined to contain. At the end of such a test, the samples should be submitted to drop, leakproofness, stacking and, where applicable, internal pressure (hydraulic) tests.

Stacking test

All packages other than bags should be subjected to a stacking test using three test samples per design type and manufacturer and the test method outlined below.

The test sample should be subjected to a force applied to the top surface of the test sample equivalent to the total weight of identical packages which might be stacked on it during transport. The minimum height of the stack including the test sample should be 3 m. The duration of the test should be 24 hours, except that plastic drums and jerrycans intended for liquid should be subjected to the stacking test for a period of 28 days at a temperature of not less then 40° C. A stacking height of 2 m should be allowed for in the case of tin-plate and light metal receptacles.

The criteria for passing the test are as follows. No test sample should show any deterioration which would adversely affect transport safety or any distortion liable to reduce its strength or cause instability in stacks of packages. Stacking stability may be considered sufficient when, after the stacking test, and in the case of plastics receptacles, after cooling to ambient temperature, two receptacles of the same type placed on the test sample maintain their position. No test sample should leak in composite or combination packagings, and there should be no leakage of the filling substance from the inner receptacle or inner packaging.

[a] *Transport of Dangerous Goods* (United Nations publication, Sales No. E.77.VIII.1).

TABLE 2. SPECIFICATIONS REQUIRED IN THE PURCHASE OF PESTICIDE CONTAINERS

	Packaging item															
Specification item	*Bags*	*Sacks*	*Pouches*	*Poly-ethylene bags*	*Ad-hesives*	*Pallets*	*Fibre drums*	*Poly-ethylene drums*	*Steel drums*	*Steel pails*	*Tin cans*	*Poly-ethylene jugs*	*Labels*	*Clo-sures*	*Boxes*	*Book-lets*
1. Outside length or height	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X
2. Outside width or diameter	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X
3. Outside depth	X	X		X		X					X	X			X	
4. Inside length															X	
5. Inside width															X	
6. Inside depth															X	
7. Nominal capacity				X			X	X	X	X	X	X				
8. Actual capacity							X	X	X	X	X	X				
9. Number of pages																X
10. Flute															X	
11. Thickness	X	X	X	X			X	X	X	X	X	X	X			
12. Minimum average weight	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X
13. Coatings							X		X	X	X					
14. Yield (m^2/kg)																
15. Substance weight (g/m^2)	X	X	X	X									X		X	X
16. Opening								X	X	X	X	X		X		
17. International Maritime Organization class							X	X								
18. Valve description		X														
19. Catalogue numbers				X	X		X	X	X	X	X	X		X		
20. Drawing numbers						X	X	X	X	X	X	X		X	X	
21. Materials of construction	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
22. Test values	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
23. Assembly			X	X											X	
24. Special features			X				X	X				X				
25. Outside decoration			X				X		X	X	X			X		
26. Printing	X	X	X	X			X	X	X	X	X	X	X		X	X
27. National freight designation	X	X	X	X			X	X	X	X	X	X			X	

XIII. Regulatory procedures for pesticides in developing countries

*Jan de Bruin**

Need for regulatory procedures

The correct and timely use of suitable pesticides can be of great importance to agriculture, especially in countries where the climate promotes the rapid development of agricultural pests. Faulty methods of application and the use of unsuitable pesticides may, however, be very dangerous or cause considerable damage. Many countries, especially those with highly developed technologies, have therefore set up regulatory procedures to control trade practices and the production and use of pesticides.

The elaborate regulatory procedures of developed countries are strengthened by a comprehensive enforcement system. Such a system and the regulatory procedures it is designed to enforce put high demands on equipment and manpower, demands which developing countries will often find it impossible to meet.

However, developing countries have a less urgent need to introduce elaborate regulatory schemes to control pesticides. The innovative process leading to the formation of new pesticides has hitherto been limited to a number of technologically advanced countries where the basic laboratory work (toxicology, analytical methodology etc.) has been done, and where the results of such work are evaluated as part of the regulatory procedure. Once evaluated, those results are valid world-wide and may be considered transferable. Developing countries can therefore use such data as inputs, without having to produce them independently.

Developing countries should design regulatory procedures suited to their specific needs, and not attempt to adopt all the elements of regulatory schemes used in developed countries. The standards for acceptance of a pesticide in one country, such as an industrial food-exporting country with a temperate climate, an abundance of fertile land and advanced agricultural technology, would not necessarily be applied in another country with different agricultural practices and a different climate and economy. The benefit-risk ratio may differ widely from country to country, especially between developed and developing countries. The

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failure by experts to achieve consensus on a model law further confirms that regulatory schemes cannot be simply transferred from one country to another. Only when transferred data are supplemented by data specific to the country concerned (for example, efficacy against local pests, differences in exposure of workers, climatic variation) can meaningful regulatory decisions be made at minimal expenditure of local resources.

Designing a regulatory procedure

First step: definition of scope

In designing a regulatory procedure the first step must be to define the subject matter. A useful definition is the following: A pesticide is any substance or mixture of substances intended for preventing, controlling or mitigating the effects of any unwanted species of insect and plant (including fungi), or intended for use as a plant growth regulator, crop protectant, defoliant or desiccant. The term pesticide also includes any substance or mixture of substances used for the control of pests during the production, storage, transport, marketing or processing of food for humans or animals, or which may be administered to animals for the control of insects and arachnids on their bodies. It does not apply to antibiotics or other chemicals administered to animals for other purposes, such as to stimulate their growth or to modify their reproductive behaviour; nor does it apply to fertilizers.

The second step: definition of objectives

The second step should be carefully to define the objectives to be reached with the introduction of a regulatory procedure, taking into account, where appropriate, specific national problems. Possible objectives are outlined below:

(a) *Quality control.* The pesticides which become available to the agricultural community should be of good quality. The concept of quality covers three aspects, namely the pesticide itself, the package and the label;

(b) *Protection of the user.* Users of pesticides are exposed to immediate hazards. They open the package, apply the product, clean the application equipment used, and deal with any unused material and empty packages;

(c) *Protection of the consumer.* Pesticides must be so applied that the consumer of food derived from the agricultural product is protected against any untoward health effects due to the presence of undesirable high pesticide residues;

(d) *Protection of crops.* Damage to the treated crop should be absent or at worst minimal. However, neighbouring crops should also be protected, for example against damage by spray drift of herbicides and damage caused by persistence in the soil of phytotoxic residues of a pesticide used on a preceding crop;

(e) *Protection of livestock.* The main risks to domestic livestock are the inadvertent consumption of freshly treated food crops and contamination from fumigation and rodent control operations. Even when it does not lead to the loss of animals, it may lead to the presence of unacceptable levels of pesticide residues in milk, meat etc.;

(f) *Protection of the environment.* It is generally accepted that the application of biologically active chemicals on limited areas can also have a considerable impact on beneficial species, but in most cases there is a complete recovery of population within a relatively short time, provided threatened or scarce species are not involved and sufficient untreated habitat remains. Particular attention should be paid to the aqueous environment. Water is a valuable resource; residues of pesticides which can travel over long distances, such as persistent pesticides in running water, can be a threat to the supply of drinking water and, in the case of herbicides, defoliants etc., to water used for irrigation purposes. Edible fish from contaminated water, especially ponds, may accumulate pesticides and so build up unacceptably high levels of pesticide residues;

(g) *Protection of export interests.* Some countries derive a significant part of their foreign currency from the export of agricultural products. Great care must be taken that such exported goods do not contain too high a level of pesticide residues. If they do, the importing country may refuse to admit the goods.

Third step: assessment of enforcement potential

The third step is a careful assessment of the enforcement potential. As has been stated above, the real value of a regulatory procedure is largely dependent on the practicability of enforcing it.

An inventory should be made of the laboratories, field stations, workers and other personnel who can assist in enforcing the regulations. The necessary time should be allowed and equipment made available to perform enforcement duties.

Fourth step: deciding the form of regulatory procedure

The fourth step is to decide on the form of regulatory procedure, taking all the above factors into account. There are several possibilities, including the following:

(a) *Voluntary scheme.* No legal force would be required with such a scheme, under which regulation is based on mutual trust and understanding. There must be some guarantee, however, that the scheme cannot be undermined by non-participants;

(b) *Preventive scheme.* In principle, it would be forbidden to produce, sell, use or otherwise dispose of pesticides, unless explicitly allowed. When properly enforced, such a scheme is practically foolproof, but it involves elaborate bureaucratic procedures and considerable resources;

(c) *Retrospective scheme.* Within the framework of a set of basic rules, there would be freedom to produce, sell, use or otherwise dispose of pesticides, but companies and individuals would be held responsible and called to account for what they did or neglected to do if mishaps occurred. Such a system is much simpler to operate, but has the great drawback that action will usually be taken only after an incident has occurred. Moreover, it presupposes a certain level of education and sense of responsibility of everyone concerned;

(d) *Government scheme.* Only the Government or bodies empowered by it would be allowed to produce, sell, use or otherwise dispose of pesticides. The drawbacks of the scheme are that it involves considerable bureaucracy and limits individual initiative;

(e) *Regional scheme.* Under such a scheme, two or more countries of similar agricultural and political background would have a common regulatory procedure and share resources.

The final decision on a regulatory scheme will have to be based primarily on an assessment of the agricultural and economic structure of the country, but legislative and political factors will also play a role in most cases.

Fifth step: the responsible authority

The fifth step, if a voluntary scheme is not adopted, is to determine which authority should be responsible for designing, operating and enforcing the regulatory procedure.

Given the largely agricultural use of pesticides, the most appropriate authority would normally be the Minister of Agriculture. However, since aspects of the protection of public health, the environment and the economy are also involved, the ministers and executive authorities responsible for those fields should also have a role to play.

Once it has been determined under which ministry the first responsibility for the regulatory procedure should fall, one person should be appointed, together with a staff, to bear the daily responsibility. Such an executive will henceforth be called the registrar.

Sixth step: establishment of a regulatory procedure

The sixth and final step is to shape and initiate a regulatory procedure which takes into account all the above considerations.

Recapitulation of objectives

It may be useful at this point to consider in more detail the main objectives to be achieved, namely quality control and protection of the user, consumer, crops, livestock, the environment and export interests.

Quality control

Acceptable active ingredients

The basic rule is that no product should be used unless its active ingredients are acceptable. Their acceptability can be determined on an administrative basis. If the active ingredient in question is a component of registered and commercially used pesticides in one or more countries responsible for the innovation and production of pesticides, the product would be considered acceptable with the same use pattern approved in the originating country.

Blanket acceptance of a pesticide by a developing country on the basis of the registration of the pesticide in the country of origin is advisable only when the patterns of use (target crop, formulation and timing, frequency and rate of applications) are reasonably equivalent in the respective countries. As the use patterns diverge, the need for obtaining local field data becomes more important.

Acceptability as defined above could be ascertained through a written statement confirmed by a responsible authority in the country of origin. If such a statement cannot be produced, due consideration should be given to the fact that the benefit-risk ratio in the country of origin may be quite different from that in the receiving country. A country with a warm climate may be confronted with serious pest problems which are unknown in the country of origin of the active ingredient, and which require the use of that particular active ingredient. Moreover, environmental considerations may weigh less heavily, because, for example, degradation of active ingredient usually proceeds much faster in a hot climate.

The registrar, taking into account all transferable data on such matters as toxicity and degradation, and carefully considering the benefit-risk ratio, should then make the decision whether the active ingredient is acceptable for use in the receiving country. Assistance in making such decisions may be sought from FAO or WHO, or from national agricultural product boards where they exist.

Quality of active ingredients

When a formulating unit imports active ingredients for further processing, a rule could be laid down to ensure that such imported materials conform to FAO or WHO specifications, if available. The importing party should be held responsible for their conformity.

Registration of formulated pesticides

For formulated pesticides imported as such, the same rules can be followed as for the acceptability of active ingredients. The composition of each formulation should be divulged to the registrar who should treat such information as both privileged and confidential. The particular formulation can then be given a registration number with which it will henceforth be associated. The registration number should appear on each package of the formulation, and it should be a felony to sell or even possess pesticides bearing that number but having a composition different from that deposited with the registrar.

For locally formulated products and imported ready-to-use products which are not registered and commercially used in the country of origin, but which could be useful in the receiving country for reasons similar to those explained in the case of active ingredients, the following rules should be applied:

(a) The product should conform to FAO specifications;

(b) Any person wanting the product to be registered, henceforth called the applicant, should be domiciled in the country, or, if not, should file the application

through a person or company domiciled in the country and assuming legal responsibility for the product;

(c) Should no FAO specifications exist, the applicant should be required to prove to the satisfaction of the registrar that the product is of reliable and adequate quality.

The declaration of the composition of the formulation forms part of the procedure.

Quality control of imported formulated products

In the case of imported active ingredients, the time normally available between import and further processing may be used to exercise control and carry out the necessary formalities. That interval is not always available for imported products, which may be needed on short term to deal with a threatened outbreak of pests. However, caution is necessary. When tenders are made for the supply of imported formulated products, the quality of the product must be carefully specified. Tenders have sometimes been won with bargain offers involving concessions to quality beyond acceptable limits. The following measures may offer some safeguards:

(a) The lot should be checked by a sworn sampler prior to shipping;

(b) One sample should be analysed by a reliable and well-equipped laboratory in the manufacturing country. An official body in the manufacturing country should confirm the status of the laboratory;

(c) One sample should remain in the manufacturing country and two should be sent to the receiving country. One of the latter may be used for analysis in the receiving country, and the other should be kept as a reference sample in case of a dispute;

(d) The importer should be personally responsible for ensuring compliance with the above procedures, and if the Government itself is the importer, one official should be made responsible;

(e) Only on the written confirmation of the laboratory in the manufacturing country that the lot meets the required standard should the goods be released for unloading.

Methods of quality control

It is important that at least one official laboratory be charged with quality control of active ingredients and formulated products. Many standardized methods are available, such as those of the Collaborative International Pesticides Analytical Council (CIPAC) and the Official Analytical Chemists of America (AOAC). If a certain method cannot be used because of a lack of the prescribed sophisticated instrumentation, alternative methods can often be applied with simpler equipment.

Responsible manufacturers can usually provide good descriptions of appropriate methods of analysis of their products (see also chapters VI and VIII).

Quality of packaging

The quality of pesticide packages, including tamper-proof fastening and sealing, should be adequate. The packaging should not only provide protection during storage, handling and transport, but also be able to withstand adverse climatic conditions (high temperatures, humidity). Responsibility for such matters should lie with the formulator, for locally made products, or the importer, for imported goods. In addition, pesticides should only be delivered by a formulation plant or imported in sealed packages designed to be opened immediately prior to use (see also chapter XII).

Quality of labelling

Labels bearing clearly legible directions for use, warnings and warning symbols in the language or languages of the country concerned should be safely fastened to each package.

In some cases, illiteracy may exist in rural areas. Warning symbols should therefore receive due attention. The text should be concise, clear and logical. If it is difficult to understand, it may not even be carefully read. Label directions are especially important where cultural differences, for example in garments and footwear, may accentuate the potential hazard to the user. In such circumstances, the label directions may need to be supplemented by special training programmes (see also chapter XII).

Protection of the user

Good agricultural practice

The key requirement for protection of the user, is good agricultural practice, which has been defined by FAO as follows:

> "Good agricultural practice in the use of pesticides is the officially recommended or authorized usage of pesticides under practical conditions at any stage of production, storage, transport, distribution and processing of food and other agricultural commodities, bearing in mind the variations in requirements within and between regions and taking into account the minimum quantities necessary to achieve adequate control, the pesticides being applied in such a manner as to leave residues that are the smallest amounts practicable and that are toxicologically acceptable."[1]

The officially recommended or authorized usage is that which complies with the procedures, including type of formulation, dosage rates, frequency of application and pre-harvest intervals, approved by the relevant authorities.

Good directions for use are essential to ensure conformity with the official standards of usage. Application of the directions is largely a matter of education which falls outside the scope of regulatory procedures.

[1] Food and Agriculture Organization of the United Nations, *Guide to Codex Maximum Limits for Pesticide Residues*, first issue (Rome, 1978).

Establishing directions for use

The directions for use will very often be different from those applicable in the country of origin of the active ingredient. It is the responsibility of the applicant, either the local formulator or the importer, to propose directions suitably worded for labelling.

The elements included in the directions for use have already been mentioned in the definition of good agricultural practice given above. The necessary warnings and recommendations for the protection of the persons using the product should also be specified. A complication arises in that connection because safety measures, such as the wearing of impervious protective clothing, which can be observed without too much trouble in a temperate climate may create problems in hot and humid climates. It is realistic to assume that such safety instructions will often not be observed under those conditions. It may therefore be wiser not to register pesticides which would require unreasonable and unenforceable safety measures.

With regard to labelling, preference should be given to the international danger symbols, but care should be taken that any symbol used is really meaningful to the people who will handle the material.

When the directions for use have been proposed, the registrar should either accept them or indicate in which respects they need to be amended. It may be useful to request the advice of specialized agricultural testing stations or similar bodies, and of public health authorities dealing with the safety of the user.

It should be clearly understood that acceptance by the registrar of the directions for use should not imply acceptance of responsibility for their contents. The supplier of the goods should bear legal responsibility. In most cases, the registrar will not be in a position to bear such responsibility as he will lack the means to make independent investigations on which to base an opinion. Any attempt to do so may lead to great delays in registration, which will result in withholding new and improved pesticides from the agricultural community for perhaps a number of years.

Protection of the consumer

The objective is to protect the consumer from agricultural commodities containing excessive amounts of pesticide residues. Excellent guidelines for determining maximum residue levels are given in the list drawn up by the Codex Alimentarius Commission. The establishment of adequate pre-harvest intervals, that is, the length of the period which must elapse between the last application of a certain pesticide and the harvest of the crop, would ensure that maximum residue levels are not exceeded. That should be included as an essential element in the directions for use.

Protection of crops

Crop protection is also a matter of good agricultural practice. In the case of toxic or phytotoxic pesticides, measures should be taken against spray or dust drift. In the case of persistent pesticides, in particular those which persist in the soil and can harm subsequent crops, the appropriate warnings should be included in the directions for use.

Protection of livestock

Where appropriate, the directions for use should contain a warning to prevent the entry of domestic livestock into freshly treated fields or into recently fumigated or otherwise treated spaces.

Protection of the environment

Environmental protection can partly be covered by general regulations. These should prohibit the discarding of unwanted residual quantities of pesticides and empty containers in the environment, and the washing of used equipment in public waterways, especially in the case of persistent or phytotoxic pesticides (i. e. herbicides). It is best to have a general prohibition of such practices unless expressly allowed in particular cases, and to consider the infringement of such rules as a felony.

Protection of export interests

In principle, the problem is the same as that of protecting tne consumer. The objective is to prevent the occurence of unacceptably high levels of pesticide residues in agricultural commodities.

The maximum residue limits listed by the Codex Alimentarius Commission provide very useful guidelines for export products. At the national level, after careful consideration of the benefit-risk ratio, it may be decided to allow a higher level than the maximum residue level recommended by the Commission, provided it remains within the limits of toxicological safety. For export, however, the maximum residue limits must never be exceeded, or the exported goods may be refused by the importing country on the grounds that internationally agreed residue levels have been exceeded.

Registration of a new pesticide

It is clear that many elements are needed to determine what is good agricultural practice for the application of a given pesticide in a given crop. For a new pesticide, or a pesticide new for the country in question, the transition from non-use to full use involves a major change. Careful consideration should therefore be given to the possibility of operating a system of gradual registration. Such a system could consist of the following steps:

(a) *Step 1: trials permit.* A permit is issued to use a new product for experimental purposes. The basic transferable data, such as data on acute and subacute toxicity, and methods of product and residue analysis should be available. A limited number of qualified persons or institutions should obtain a permit to apply the new product experimentally in order to gain experience and data under the prevailing local conditions. Such a permit could be limited in time or in the amount of pesticide used and acreage treated;

(b) *Step 2: provisional registration.* When sufficient experience and data have been gained, the new product could be provisionally registered subject to certain limitations concerning the quantity of product that may be sold, regions where sales may be made, disposal of treated products etc., for a specified period and on the understanding that the applicant will make available additional data generated during the provisional period. If during that period sufficient experience has been gained and actual practice has shown that the product is useful and the benefit-risk ratio is positive, then the next step can be taken;

(c) *Step 3: full registration.* Full registration follows the steps outlined above, but without restrictions. However, there should always remain a possibility to revoke a full registration if some unexpected and unacceptable side-effect is observed. For legal reasons, revocation should always be in writing and the grounds for revocation clearly specified. Early consultation with the manufacturing company involved is strongly recommended, because any responsible manufacturer will want to give full support to all investigations into the possible causes of such unexpected occurrences.

Funding

It would be reasonable for the applicant to pay a certain fee when applying for registration. The fee should not be too high, however, or it may become an obstacle to the introduction of new pesticides and detrimental to the interests of the agricultural community.

It would be a good idea to levy a small fee periodically for extension of registration. That would prevent the registration files from becoming cluttered with records of products which are no longer on the market.

The re-registration time interval should not be so short as to cause unnecessary and time-consuming additional administrative work.

Conclusion

In an ideal world, each country in which pesticides were applied would have a properly enforced regulatory procedure. At the very least, qualified analytical chemists would monitor the quality of products found in the market and review the suitability of packages and the adequacy of labels, taking action where standards did not meet specifications or conform to minimum safety requirements. Negligence in the market or in the field brings the use of pesticides into disrepute and has harmful effects on agricultural production and public health.

The best safeguard remains an awareness of correct practices, respect for the minimum acceptable standards, and the existence of an authority that is both willing and able to take swift action against offenders in the wider interests of the user of the products, the consumer and the environment.

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