CHAPTER I
INTRODUCTION

Ever since Man's attempts at cultivation to secure adequate and reliable food supplies, he had to suffer competition from pests, diseases and weeds. One of the main reasons for failure to find a permanent solution to this problem lies in the ability of our biological competitors to adapt to almost any change in environment and there lies the invention of much more efficient pesticides to take care of this problem.

Pesticides are synthetic organic chemicals used to control weeds in fields and lawns, and unwanted or harmful pests, such as insects and mites that feed on crops. Pesticides are divided into categories according to the target organisms they are designed to control (e.g., insecticides control insects). A pesticide product consists of two parts: active and inert ingredients. Active ingredients are chemicals, which actually control the pest. Inert ingredients are primarily solvents and carriers that help deliver the active ingredients to the target pest; they serve to enhance the utility of the product. The combination of an active ingredient with a compatible inert ingredient is referred to as a formulation. The active ingredients in pesticide products come from many sources. Some, such as nicotine, pyrethrum, and rotenone, are extracted from plants. Others have a mineral origin, while a few are derived from microbes. However, the vast majority of active ingredients are synthesized in the laboratory. These synthetic active ingredients may have been designed by an organic chemist or discovered through a screening process of chemicals generated by various industries. Regardless of their source, pesticide active ingredients have different solubilities. Some dissolve readily in water, others only in oils. Some active ingredients may be relatively insoluble in either water or oils. These different solubility characteristics, coupled with the intended use of the pesticide, in large measure define the types of formulations in which the active ingredient may be delivered.

An adjuvant is any compound that facilitates the action of pesticides or modifies characteristics of pesticide formulations or spray solutions. They become the major part of inert ingredients found in pesticide formulation. The terminology for pesticide additives is sometimes contradictory. It is often assumed that any material that lowers the surface tension of water (i.e., a surfactant) in the spray mixture or increases the wettability of the spray solution on surfaces is an adjuvant.

Chemist's involved in pesticide research today have to face the challenge of finding new pesticides that are both highly effective and with a potential market large enough to bear the high development costs. In addition, they must ensure that such pesticides satisfy all the safety criteria for mammalian toxicology and environmental behavior. Pesticides products play a major role in optimizing the production of agricultural products. There are many reasons to develop product, which are taken up more readily by the target plant.

Mathematical Models can provide a big help for the search after products with improved properties. The use of mathematical models can help to reduce the number of experiments that are necessary to investigate the efficiency of products. Both research expenses and time to market can be considerably reduced. Mathematical modeling of pesticides is a relatively new field of research and has the potential of increased attention if the models are able to reproduce the real behavior of pesticide formulation on plants.

The present work deals with the development of a general-purpose mathematical model and its ability to predict pesticide uptake in plant. The modeling work is based on previous developed models by Muro-Sune (2002) and Rasmussen (2003). These models have be improved and further developed. The project is made in collaboration with Syngenta, UK, who has provided necessary information related to actual pesticide formulations and their application. Tools from the ICAS software package developed at CAPEC were used; Model Testbed (MoT) was used for solving the model equations whereas ProPed estimated the physical parameters.

1.1 Chemistry & Technology of Agrochemical Formulation

Enormous changes have taken place in the chemistry and technology of agrochemicals over the last 20 years or so, particularly in the discovery of new active ingredients, their formulation, packaging, use, regulation and general management.

Similarly, the formulation additives and adjuvants supply industry has developed new products to meet the needs of the agrochemical industry for products having greater safety to the user, much lower environmental impact and improved biological efficacy to the specific target pest. Great strides have been made in understanding the modes of action of both pesticides and adjuvants, so that molecules can now be designed for activity at the target site only, and which are effective at low doses and have low toxicity to mammals and other non-target life forms.

Agrochemical products have been used widely for many years to increase the yield and improve the quality of food and fiber crops and to improve public health all over the world. The agrochemical industry has become a major business producing products with a total world sales value estimated in 1997 at over US$30 billion, and it plays an important part in the economies of most countries. The agrochemical business represents a significant opportunity for surfactants and other essential formulation additives as well as adjuvants for spray applications. Although the agrochemical industry markets have reached maturity in North America, Western Europe and Japan, there is still considerable scope for new, more environmentally friendly active ingredients and formulations. Developing areas, especially the Asia-Pacific region and South America, have a rapidly increasing need for safe agrochemical products to increase crop yields. Indeed, the market for agrochemical products in the Asia-Pacific area (including Japan) is now almost as big as that of the Western European market and in the future could rival that of North America. Changes in the population of the world and increasing urbanization and industrialization of communities are placing a great demand on the efficient use of available land for agriculture. For example, the United Nations has forecast that if present trends continue, the population of the world will increase from about 5 billion now to about 10 billion by the year 2040, and the fastest rate of growth will be in the less developed areas, particularly the Asia-Pacific region (Sugavanam, 1990). There will, therefore, be an increasing need for agrochemical products as an important input to the management of food and fiber crops to improve their yield and quality.

The ability to protect growing crops from weeds, pests and diseases has been known since ancient times in the Old World of the Middle East, Asia and

China. However, the greatest improvements in crop protection efficiency and productivity in terms of crop yield and quality have occurred mainly in the West and within the last century. Simple emulsifiable oils and soaps have been used as agricultural sprays to control insect pests for many years. The modern era of weed control can be said to have started in the 1940s with the development of the phenoxy acid herbicides such as 2,4-D acid. Since then, and particularly since the 1960s, many new synthetic pesticides have been introduced to combat a very wide range of weeds, pests and fungal diseases. A great deal of research and development has been carried out by all the major agrochemical companies and other organizations to produce new active ingredients and formulations which can be applied easily to crops and which will optimize the activity of the pesticide (Green, 1987). Although in the last few decades there have been remarkable developments in new agrochemical active ingredients and formulations, most companies are now reviewing their product-pack strategies and government regulatory authorities are introducing controls and legislation which are leading to the introduction of reduced-risk active ingredients, and safer and more environmentally friendly formulations in more convenient packaging. There is also a need to reduce the total amount of active ingredients applied per hectare. The cost of the development of new products is becoming increasingly high and it is estimated that it can cost US$150-200 million to develop one new active ingredient with a development timescale of 7-10 years from initial discovery to first registered commercialization of the product. This is causing the industry to consolidate by mergers of companies or research joint ventures between companies. Generic manufacturers are also able to introduce off-patent products without the initial high cost and risk of research and development. Research and development is, therefore, concentrated on the major world crop and pest problems, and patenting of new active ingredients and formulations is very important to protect intellectual property rights in all the important markets of the world. Because of the variety of active ingredients, which are available, many different types of formulations have been developed depending mainly on the physico-chemical properties of the active ingredients (Tomlin,1997).

In the past most formulations were simple solutions in water, emulsifiable concentrates in a solvent, or dusts and dispersible powders. The current trends are to eliminate petroleum-based solvents as much as possible and to replace them with water in water-based suspensions and emulsion formulations. At the same time, there is a move away from dusty powders towards essentially dust-free water-dispersible granules. Controlled release formulations and seed treatment formulations (also usually water based) may enable better control and placement of the active ingredient. In particular, flowable seed treatment formulations can be supplied in bulk containers, are safe to the operator and, because they are applied directly to the seed, they reduce wastage of pesticide and environmental impact in the field. The wide variety of agrochemical formulations which is available requires a range of different formulation additives to produce safe and usable products. Probably the most important of the formulation additives are surface-active agents. Surfactants have been obtained from natural products by extraction or modification for thousands of years. Examples of surfactants that are well known are soaps for cleaning, greases and tallows for waterproofing, and glue, egg white and natural gums as dispersing and emulsifying agents. Synthetic surfactants, which have been specially synthesized in order to obtain surface-active effects, represent a relatively modern development, which may be said to have evolved from the 'sulphonated oils' of the 19th century. The early period of the 20th century was a very active phase in the development of sulphated and sulphonated anionic surfactants with long hydrocarbon chains. In the second half of the 20th century, the development of surfactants entered a more specialized phase with the introduction of amphipathic molecules for specific applications. Non-ionic surfactants became available in which the hydrophilic part of the molecule was based on condensed chains of ethylene oxide. A wide range of surfactant properties can be achieved by varying the ethylene oxide chain length. This development has led to a better understanding of the colloid and surface chemistry principles involved in the fundamental functional properties of wetting, dispersion, emulsification and solubilization in the formulation of pesticides. As a result of all this work, it is now possible for surfactant suppliers to prepare 'tailor-made' surfactants to suit particular functions.

For nearly all formulations the most important formulation additive is the surfactant in terms of preparation and production. The surfactant often determines the maximum concentration of the formulation that can be achieved, the particle or droplet size, long-term stability and sometimes even the biological activity of the formulation. Surfactants, either alone or mixed with oils, are essential components of adjuvants, which can enhance the biological activity of the spray mixture by affecting spray droplet size, retention and spreading on leaf surfaces or by assisting uptake, and translocation of the active ingredient into the crop. Many other additives are used for specific purposes, such as anti-settling, anti-freeze and anti-foam agents for water-based formulations, and fillers and disintegrants for powders and water-dispersible granules. Preservatives are also important additives to formulations to prevent biodegradation during preparation and storage, particularly where the formulations are aqueous based and contain carbohydrates, or where the products are exposed to the atmosphere after application, as in the case of baits and pellets (Knowles, 1995). Agrochemical companies are now paying increasing attention to the packaging of pesticides as part of the total 'delivery system' for convenient use and user safety. Rinsing and safe disposal of plastic bottles is becoming very important. In some cases this can be overcome by using bulk or minibulk containers, or small-volume returnable containers, all of which are returned to the manufacturers for cleaning and refilling. The move from liquids to granules allows the use of simple bags or cartons for ease of disposal. Powders and granules can also be supplied in water-soluble bags to eliminate operator contact entirely. Despite the extensive research and development which goes into the introduction of a new product, when the product is diluted and sprayed onto crops in the field it is likely that only 10-20% of the active material will reach the target site. This can be caused by many factors, such as poor spraying conditions, spray droplets missing the crop and hitting the soil, droplets bouncing or running off the crop leaves, general adverse weather conditions (Matthews, 1992) and poor formulation of active ingredient and adjuvants. There is, therefore, a great deal of scope for improving the efficiency of the spray application process, selection of optimum formulation for uptake process and also understanding the effect that active ingredients and adjuvants can have on them. This is an area where all the technologies of formulation, packaging and spray applications can work together to produce safer and more efficient 'total delivery systems'.

1.2 Formulations of Agrochemicals

Farmers and growers in all the main agricultural areas of the world rely very substantially upon crop protection chemicals to help them meet the ever-increasing demand for food and other materials such as natural fibers. The consumer continues to seek higher quality and greater variety of produce. Simple dusting powders and spray oil formulations have been used for many years to protect growing crops from weeds, pests and diseases. However, since the 1940s the chemical industry has endeavored to satisfy the demands of farmers and growers for increased crop yield and quality by the continuous development and introduction of crop protection chemicals into the international market place. Today, there is an effective herbicide, insecticide or fungicide to combat almost every significant problem faced by the modern farmer and grower. This development has led to a need for a wide range of product formulations, additives and process technology to accommodate the variety of physical and chemical properties of the pesticide active ingredients. For example, water-soluble active ingredients may be prepared as aqueous solutions or powder formulations, whereas oily liquid active ingredients are usually formulated as hydrocarbon solvent-based emulsifiable concentrates. Active ingredients, which have very, low solubility in either water or hydrocarbon oils may be formulated as suspensions, powders or water dispersible granules (Van, 1973). In the 1980s and 1990s, pressure from government authorities and the consumer highlighted a need for products and formulations which are safer and more convenient to use, more effective at much lower application rates, less toxic to non target species and more environmentally friendly. By far the most important method of application of agrochemicals is by spraying, usually with water but occasionally with oils as the principal carrier. Formulations are also made for direct application to the soil or for treating seeds before planting, and for protecting stored crops from various pests and diseases (fungi, insects or rodents), which in some countries could destroy as much as 30-40% of the harvest. Pesticidal active ingredients encompass a broad range of chemicals, each with its unique chemical and physical properties and mode of action. The main categories of pesticides are herbicides, insecticides, fungicides, plant growth regulators, molluscicides and rodenticides. A great deal of research work has been carried out into understanding the modes of action and physiological effects of active ingredients and the influence of formulation type on the biological performance of the pesticide [Chow *et al.*, 1983]. The successful use of any active ingredient depends on its correct formulation into a preparation, which can be applied for crop protection safely and with low risk to those applying the material, to non-target species and to the environment in general. The earliest pesticide formulations were based on simple dusts, powders, granules, aqueous solutions and mineral oil-in-water emulsions. In recent times, particularly during the period from 1970 onwards, there has been a rapid development of more sophisticated formulations based on the availability of more powerful surfactants and other additives, and a much better understanding of the principles of colloid and surface chemistry to improve formulation stability and biological activity. Processing technology has also developed over this period to give much smaller particle size for better stability and activity for water- and solvent insoluble active ingredients.

The main objectives of formulation can be summarized as follows: to provide the user with a convenient, safe product, which will not deteriorate over a period of time, and to obtain the maximum activity inherent in the active ingredient.

The formulation chemist needs to take into account a number of interacting factors in the choice of the specific formulation type for each active ingredient. The main factors, which need to be taken into account, are

- physico-chemical properties;
- biological activity and mode of action;
- method of application;
- safety in use;
- formulation costs;
- market preference.

Once these parameters have been determined, proper selection can be made of the final formulation type and the use of inert ingredients, including surfactants and other additives, to produce a stable formulation with at least a 2-year shelf life during storage under varying climatic conditions. The most common formulations are still soluble concentrates for watersoluble chemicals, emulsifiable concentrates for oil-soluble chemicals, and wettable powders and suspension concentrates for insoluble solids. Granules and seed treatments for direct application have also been produced for many years. In recent years the number of formulation types has increased enormously to meet the needs of operator and environmental safety or to improve the activity and persistence of the active ingredient. An international coding system was therefore devised by GIFAP in 1984 (in 1996 GIFAP was renamed GCPF - Global Crop Protection Federation, based in Brussels, Belgium). The major types of formulations and international codes are shown in Table 1.1.

Table 1.1 Major types of pesticide formulations

Formulation type	Code
Granules	GR
Solution concentrates	SL
Emulsifiable concentrates	EC
Wettable powders	WP
Suspension concentrates	SC
O/W emulsions	EW
Suspoemulsions	SE
Microemulsions	ME
Water-dispersible granules	WG
Microcapsules	CS
Seed treatments	DS, WS, LS, FS

The most common formulations are those, which are made for dilution into water in a spray tank. In these cases the choice of formulation additives is very important to ensure that the product mixes and dilutes easily. Sometimes products may be mixed together in the spray tank or may be mixed with spray adjuvants to enhance biological activity. Products such as granules or seed treatments are usually applied undiluted to the soil or to the seed respectively. A few products are formulated to be diluted and sprayed in oils, and there are many minor formulations such as baits, pellets, smokes and aerosols for special purposes.