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INDIA

Technical report: Findings and recommendations*

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Dr. Stefan Mosinski,
Expert in pesticide formulation

United Nations Industrial Development Organization

Vienna

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ACKNOWLEDGEMENT

I wish to take this opportunity to express my great satisfaction for having occasion to come, second time, to this hospitable and interesting country and to work on ambitious project going on in PDPI. My thank are due to those who invited me to work in this place.

In particular I would like to record my thanks to **Dr.S.P.Dhua, CMD, HIL, and Dr.M.K.Hussein, UNDP, SIDFA,** for their keen interest in my work as well as for holding fruitful discussions on several critical aspects of the work. Also I thank **Dr.K.D.Paharia, Advisor** of HIL for his valuable comments concerning some projects being carried out in PDPI. I thank **Mr.M.Lal, HIL, GM(P) and Mr. S.Pal** from UNDP for their help whenever it was seeked.

I would like to express my appreciation for **PDPI Scientists** and **Technical Staff** for their devotion and dedication work, especially to **Dr. S.K.Khetan, Dr. P.K. Ramdas and Dr.R.K.Khandal** with whom I had pleasure to collaborate directly. To all of them I wish many successes in the ambitious work in which they are engaged at present.

I thank also **Mr. R.R.Pillai** for his patient typing of my draft report, often not easily readable.

Explanatory note

In my report I have drawn attention towards methodology of conducting the experiments. This is not because a right methodology is not accepted by Scientists of PDPI, but because of the apprehension that, in many other similar pesticide formulations laboratories mainly the **trial and error methods** are used, which of course can not and do not assure the best results. Besides this, I would like to emphesise that for getting a modern pesticide formulations of high quality **the knowledge of some basic relations between physico-chemical properties of raw materials and the quality of ready products is necessary.**

CONTENTS

INTRODUCTION

In accordance with Term of Reference my task is to cooperate in finding out the solution of some of the problems which have been or will be undertaken, in due course of time, in PDPI Centre. After discussion with Dr. Khetan, the Manager and Head of PDPI, it was decided that I would be guiding the following projects:

1. To find a suitable laboratory method of finding out effectivity of a new Indian biocide formulation, anticipated for production and for using against malaria-carrier mosquito (Anopheles stephensi).

2. To check out a laboratory method for preparation of flowable formulation of carboxin.

3. Characterisation of solvents and emulsifiers.

4. To develop laboratory method for finding out the composition and the parameters necessary in preparation of water dispersible granules.

5. To give direction for initiation of project work in the pilot plant.

6. To prepare lectures on different aspects of pesticide formulation and deliver them during the training course meant for Small Scale Formulators of India.

The research progress in particular projects, specified in p.p.1-5 together with comments and suggestions has been given here as well as general conclusions which should help in carrying research work at a higher level. The details about the lectures prepared and presented are also given.

FINDINGS AND SUGGESTIONS

1. BIOCIDE FORMULATION

1.1 Problem retrospection

There can be several types of biocide formulations for combating mosquitoes, depending on the habitats and behaviour of the target mosquito, level of control and duration of residual activity that are desired.

According to the L.A. Laccy (1) some of the formulation objectives for microbial-control agents of mosquito larvae are as follows:

i Ease of handling and application;

ii long shelf life;

iii stability in field conditions after application;

iv good distribution of toxin in larval feeding zone;

v the highest prolonged contact with larvae.

Different kinds of formulations such as wettable powders, granules and water flowables of the biocide Bacillus thuringiensis, are available in the market. However, in case of Bacillus sphaericus, the main biocide against mosquito, all but one formulation are produced yet in experimental batch. The reason for this is that all its formulations settle too rapidly in water, which is a major factor responsible for their lack of residual larvicidal activity. The two different approaches have been taken in trying to solve these problems:

by preparing flowable formulation having very small particles which will settle much slower than those of wettable powders; and by preparing powders, pellets or granules which can float on the surface of water and release to it the biocide.

However, both the above mentioned methods have some advantages and disadvantages.

The flowables in which particle sizes are or can be smaller than the ones in wettable powders will perform longer activity but of course not as long as could be expected owing to vitality of bacteria, because of falling of particles and their disappearing from the surface habitant zone of larve. The **floating powders**, low specific gravity **pellets or granules**, get easily drifted after application and the distribution of biocide near the surface of water can be uneven. This inequality can also be caused by wind, which can concentrate the reservoir of biocide within a smaller surface of treated area. Such phenomenon can be advantageous only when the mosquitoes larve are concentrated mainly in some part of the pond and the wind is blowing in its direction, which can happen only by a chance.

During the last 10 years, two new approaches have been used to evalue out a more efficient and more economical method of combating the mosquitoes larvae. The first one is by using a liquid formulation which, when put into the water will spontaneously spread on its surface creating monomolecular film. After testing more than 50 different organic liquids in laboratory, two of them were selected. First one is a biodegradable, nonpetroleum vegetable based oil used in cosmetic industry (isostearyl alcohol containing 2-oxyethylene groups (JSA-20E) and the second one in sorbitan monooleate (SMO) formulated with either 2 ethyl butanol (2EB) or 2 propanol (2P) (3).

These monomolecular organic surface films can modify the physical properties of water surfaces in ways which interfere with normal activities and development of mosquito eggs, larvae, pupae and / or emerging adults. These films can significantly reduce the surface tension of a mosquito habitat and subsequently kill larvae and pupae by inhibiting proper orientation of the air-water interface and / or by increasing the wetting of tracheal structures and by causing anoxia. For the most part, the effective surface dosage for larval control, have ranged from 0.32 - 0.48 gal / acre of JSA-2oE and 0,55-0,71 gal/acre of SMO - 75 (2EC).

If more dosage is used the excess liquid remains as a thick oil-like lens in equilibrium with the spread film. When portions of the film have been degraded or displaced by natural forces, the excess material in the lens or reservoir immediately and spontanously spreads to restore the equilibrium between the film and the excess bulk liquid, thereby, maintaining uniform coverge and film pressure. Tests in sewage polishing and settling ponds have indicated, that spray application of JSA-2oE can persist in certain field situations and kill mosquito larvae and pupae for a week or longer, when applied in dosage of 0,32 gal / acre.

The solid formulations which can slowly release stable and effective mosquito - controling film have been also elaborated. These formulations can release the effective film for several months under natural conditions.

The second approach to effective combatting of mosquito larvae is by using some biocides such as Bacillus thuringensis, which are most popular and Bacillus sphaericus which are also found effective. Several formulations of B. thuringiensis (H-14) are currently available for use against mosquitoes in a variety of habitats, whereas B. sphaericus is produced only by Stauffer as a wettable powder (Staufer MV 716 powder). The main disadvantage with WP-s and FL-s formulations of biocide, which create water suspension, is the lack of their residual activity. It is undoubtedly due mainly to the rapid settling of suspended particles and their disappearance from the surface of water - the feeding zone of larvae of some of the species e.g. Anopheles spp.

A formulation that enables flotation of spores near the surface over sustained period of time, would enhance residual larvicidal activity considerably.

One of the methods of testing, developed lately, is the one in which a water suspension of bacteria is used in mixture with o/w emulsion (2). The oil which produce monomolecular layer can be regarded as a formulation agent itself with complimentary insecticidal action.

The main role however of oil should be the uniform distribution of spores near the large area of water surface and keep them therefore a longer period of time. During the laboratory examinations G.M. Roberts & T.D. Burges (2) have found a suitable oil emulsion (based on ethoxylated derivatives of vegetable oils) and tested the activity of water suspension of B.thuringiensis on mixture ·ith this emulsion. In succiding experiments, in which some natural condition were to some extent simulated, they were able to find the following relations:

i) higher mortality of larvae was found when treated with a mixture of biocide and emulsion than that one treated with biocide suspension only; in the case of this mixture the mortality was 100%, and without oil emulsion only 4% after 18 hours;

ii) for lower level of water the effectiveness was contrary; the suspension of bacteria gave mortality 92% and in mixture with emulsion only 12% after 24 hrs;

iii) water suspenion of bacteria gave 100% activity up to - 0,5 meter, whereas in mixture with oil emulsion up to 2 m. This indicates better spreading of mixture on the surface of water;

v) if the mixture of suspension of bacteria with emulsion was used in the amount bigger than that one needed to create a monomolecular layer of oil, then excess of formulation: were floating on the surface in globules, from which the new monolayers could be created and replenished monolayers removed by simulated biodegradation;

vi) the vitality and activity of bacteria mixed with emulsion has not been changed after storage of the mixture at 25°C for 5 days;

vii) the laboratory results were verified in field conditions.

1.2 RESEARCH PROGRESS IN PDPI

The work have been conducted on two formulations - floating powder and liquid flowable. Both had been tested against larvae of B.sphaericus in laboratory. One sample of floating powder gave very good results but the second one taken from the same laboratory batch did not. The effectiveness of flowable sample have not been as high as that one prepared in laboratory in University - Madurai.

1.3 COMMENTS AND SUGGESTIONS

The selection of method and biocide formulations is correct. The method in which only monomolecular layer of some hydrophobic liquid is used seems to be not proper for Indian conditions. It would be difficult to find the appropriate oil and if it could be done most probably it would be too expensive. Besides, for using such an oil, ground or aerial system of spraying must be used which can very often be difficult to realize. The choice of formulations for biocide seems also proper. Both can be produced with relative easy method and application will not need more sophisticated equipment, and even could be applied by hands. Both formulations could also be used as the basic ones for preparation of other more sophisticated ones like slow release granules, water dispersible granules or encapsulated formulation.

Those formulations which have been already prepared in laboratory can be treated only as very preliminary ones and for that reason they are burdened with some deficiencies. The difference between the activity of two of these dust samples can be attributed to the heterogenity of mixture of biocide with mineral carrier. The homogenity of these two samples has not been checked.

It is however more difficult to explain the lower activity of flowable samples of very good physicochemical characteristics of suspension in comparison to the other flocculated one-quickly sedimented suspension. It was expected that the first one would be more effective but it was not so. Because the composition of two samples were different it may be that some components of the first sample could reduce the activity of biocide.

The given explanation concerning different activity of tested samples is valid only if the biotest had been performed according to standard condition.

It is not good that testing of activity of biocide formulation is performed in other laboratory located for away from PDPI Gurgaon, when there are possibilities to execute such tests in Entomology Laboratory of PDPI Research Centre.

The proposals regarding the continuation of research work on biocide formulation are the following:

i) to concentrate the work on flowable formulations which seems to be more effective and more comfortable to use than dust formulations;

ii) during the search for the best composition of formulation, to verify the successive samples by biotest in own Entomology Laboratory; the samples of high activity can be additionally tested in other specialised laboratory;

iii) after getting the results of biotests, the relation between the composition of samples and their physico-chemical characteristics shou i be found;

iv) for finding spreading ability of flowable formulation on the surface of water, the area of biocide activity should be tested;

v) for getting flowable formulations of good spreading ability and tendency to keep maximum biocide near the water surface, some hydrophobic liquids should be tested and selected; as hydrophobic liquids some biodegradable vegetable oils, or some of the synthetic ones should be tested.

In this connection, the following characteristics of oils must be taken into account :

- physico-chemical characteristics (see app.1..)

- compatibility with biocide;

- Cost performance;

vi) in selection of oil, the method of testing used by Roberts & Burges (2) should be used;

vii) it is recommended to be acquainted with some papers, where criteria for selection of oils and other adjuvants, used in preparing flowable formulations, have been given;

viii) for comparison of effectiveness of elaborated formulations by laboratory tests, a recommended formulation should be used as a standard or such a standard should be prepared using known recommended adjuvants e.g. the one used by Roberts & Burges (2);

ix) the activity of elaborated formulation must be tested after its storage in different climatic conditions (low and high temperature);

x) the field test on elaborated formulation should be performed after getting positive results of tests according to p.p. viii and ix.

2. FLOWABLE CARBOXIN FOR SEED DRESSING

2.1 RESEARCH PROGRESS IN PDPI

Using surface active agents and thickeners available in Indian market, several samples of flowable formulation have been prepared and criteria of selection of components as well as methodology of using Dyno-Mill have been worked out. The prepared samples looked quite well and some of their characteristics e.g. thixotropy measured on Brookfield viscometer were also correct. Unfortunately, lack of several adjuvants which are recommended in literature made it impossible to compare the properties of samples worked out in PDPI laboratory with those prepared by using recommended adjuvants. For similar reasons, a formulation containing as one component parafinic oil,which increases effectiveness of seed dressing,can not be worked out.

2.2 COMMENTS AND SUGGESTIONS

Having now at disposal recommended assortment of components, the following experiments are suggested;

i) using the water solution of polymeric thickeners as well as some of the mineral thickeners to find their proportion and concentration giving the desired thixotropy expressed in terms of yield value;

ii) using the single polymeric thickener and its mixture with mineral but of the same yield value. as the single one, to prepare carboxin flowables and compare their characteristics;

iii) using one of the domestic polymeric thickener and recommended mineral one, as well as recommended polymeric thickener and domestic mineral one, and at last both domestic thickeners to find their proportion and concentration giving the desire yield value;

iv) using selected composition of domestic thickeners prepare carboxin flowable and compare its characteristics with that one prepared using recommended thickeners;

v) using the fine powder of carboxin or its water suspension mixed with parafinic oil, select the best combination of dispersing agents and emulsifiers for getting stable emulsio-suspension and then find the optimum combination of thickeners.

Remark 1. The Uni Royal, producer of carboxin and its flowable formulation, produces the dry premix which can be mixed with some amount of water or water/oil and ethylene glycol, by local formulators in order to prepare water or water/oil flowable formulation. The proportion of components in the mixture is as follows:

Premix	Ca 42% (W/W)
ethylene glycol	Ca 21 %
Oil	Ca 7%
Water	Ca 30%
or	
premix	Ca 24%
ethylene glycol	Ca 21%
thiuram	Ca 21%
Oil	Ca 18%
Water	Ca 30%

It can be assumed that production of premix by some company e.g. HIL, which wants to produce technical carboxin, would be the most economical solution. This permix can be delivered to Small Scale Formulators, who can prepare its flowable formulation by a simple way on the basis of prescribed recipe. The premix should contain dispersing agents, thickener, emulsifying agents and some amount of mineral carriers. The particle size must be very small and for that reason it should be prepared in jet-o-mill.

vi) It is recommended to elaborate the composition of premix. As a dispersing agent the sodium lignosulfonate is recommended.

3. CHARACTERISATION OF EMULSIFIERS

3.1 RESEARCH PROGRESS IN PDPI

The collection of samples of various emulsifiers from different domestic suppliers have been done. Some preliminary tests of their characteristics have been also performed.

3.2 COMMENTS AND SUGGESTIONS

The main problems in producing Emulsifiable Concentrates (EC-s) in India, as well as elsewhere, result from nonstandard properties of emulsifiers and solvents and some times also from the nonstandard technical pesticides. The difference in quality of emulsifiers and solvents are in general difficult and tedious to determine. These factors caused serious problems especially for some of Small Scale Formulators who have to produce EC-s in accordance with accepted standards. The situation could be, to some extent improved, if it is possible, by relatively simple and quick methods, to test the emulsifiers and solvents and to find the characteristics different from that ones of samples which are conventionally accepted as standards and also to find the influence of these deviations on the optimum composition of EC-s. In order to solve these problems and to elaborate the instruction for Small Scale Formulators as to how to proceed, the following experiments are suggested :

i) determine the following specific characteristics of particular emulsifiers and solvents :

- water number
- cloud point;
- Tanaka number;

and take some of these individuals as standards;

ii) find the optimal composition of standard solvents and emulsifiers for particular EC-s of pesticides;

iii) check the same characteristics as in point i) for some of the solvents and emulsifiers obtained from other batches.

iv) find the relation between characteristics specified in p.i. and the optimum composition of EC-s.

4. WATER DISPERSIBLE GRANULES

4.1 PROGRESS OF WORK IN PDPI

The work has not yet been started.

4.2 PATENTS AND LITERATURE REVIEW.

Water dispersible granules (WDG) are relatively a new type of formulations used in the same way as wettable powders, i.e. to prepare water suspension for spraying. Their main advantage is that being non-dusting they are more safe for users and environment. Moreover, they are easier to handle and to measure.

The process of preparing WDG-s depends on blending the main component, pesticide of very fine particle sizes, with carriers, surface active agents and binders and then to agglomerate the powder.

A variety of processing equipment are available including disc, pan, drum, fluidised bed units, compactors or extruders.

In all of these equipments, except the two latter one's, the dry powder is granulated with small amount of water or with water solution of some adjuvants. Such prepared granules are then dried and if necessary, too small and too big fraction of particles are separated, using the sieves or by air separation.

Two most important characteristics of WG-s are:

- the degree of dispersibility of WG-s in water on the primary particles (similar test as for WP-s);
- good integrity of granules and their resistance on abrasion which will counteract to produce an undesirable dust.

The realisation of these two requirements depends as well on the used carriers, dispersing, wetting agents and binders as on parameters of the process. The typical composition of WDG formulation is as follows:

Components	% w/w
Pesticide	50-95
Dispersant	1-7
Binder	0-2
Carrier	0-45
Wetting agent	0-2

Very important for good dispersibility of granules is their proper wettability. The type and level of wetting agent used in the system is determined by matching the solid surface tension of pesticide with the surface tension of water solution of wetting agent (see appendix 2) The next key component is binder or adhesive agent, a synthetic or natural gum, to provide good strength and integrity of granules. Not less important is the type of carriers. That ones of high sorbtivity are not recommended, what is due to the fact that high amount of water is required for granulation process and moreover its presence affects the integrity of the granules. The following components are recommended in producing dispersible granules.

Dispersing agents

- Sodium or calcium lignosulfonate (commercial unrefined product containing 18-23 weight percent of hexoses and pentoses (largely mannose, glucose and xylose) and lesser amount of arabinose, fructose and galactose) with 5% of polymerized sugar (polysacharides, degenerated cellulose and hemicellulose);
- sodium dibutyl napthylsulphonate;
- sodium N-methyl - n - oleyl taurate

Wetting agents

Sodium dodecylbenzensosulfonate;
nonyl or octyl phenol/ethylene oxide condensate;
sodium dioctyl suicinate;

Binders

- Polyvinyl produced by 86-91 mol percent hydrolysis of polyvinyl acetate (molecular weight 18000-25000);
- polyvinyl pyrrolidone (molec. weight 30,000-50,000)
- methyl cellulose (av. mol. weight between 13,000-16,000) of which 2% water solutions having viscosity 10-17 can be mixed with succrose
- hydroxymethyl cellulose (av.mol.weight 20,000-23,000);
- starch;
- sorbitol;
- polysacharides.

Carriers

Kaolin;
bentonite (swelling clays);
chalk;
precipitated silica (in small amount);
fumed silica(" ");

Other adjuvants

Sodium sulphate (for improving dispersibility);
sodium hyperphosphate (for improving dispersibility)

The process parameters are different for various methods of preparation.

Control of the moisture level spray is critical for proper granulation of dry powders. Also, the droplet size are equally important. The speed of mixing the powders during granulation should be optimum. Rate of drying and temperature at which it is drived are also critical to the quality of the finished product. Low temperatures for drying will produce soft granules, whereas high drying temperature produces hard non-dispersible granules. Usually the temperature range of 50-60°C is recommended.

4.3 COMMENTS AND SUGGESTIONS

The experiments should be carried out to find out the relations between the composition of WDG-s and process parameters and their properties. Knowledge of these relations will be helpful in elaborating of WDG-s of various pesticides. The following steps in experiments are proposed.

CHARACTERISATION OF COMPONENTS

i) find the relation between concentration of dispersing (DA-s) and wetting agents (WA-s) and surface tensions of their solutions in water.

ii) determine the flow points of DA-s for selected powders;

iii) determine the adsorptions isotherm for selected powders and DA-s, acc. to (1);

iv) determine contact angles between liquids of known surface tension and solids;

v) determine the sorptive capacity of powders;

vi) determine the suspension stability of powders using different DA-s of the same concentration (making a paste).

PRELIMINARY METHOD OF PREPARATION OF WDG-s

The dry powders of carriers, pesticides or mixture of both will be mixed with the water solution of selected DA-s, DA-s + WA-s and DA-s + WA-s + binders (B-s) in order to get dense paste. The time of mixing should be sufficiently long to assure a good covering of solid particles with solutes. The paste can be then extruded through a 14 mesh sieve and obtained "noodles" can be dried with ventilated air at 50°C.

The amount of water in dried product should be less than 2%. The "noodles" are then crushed and screened through 14 mesh and then through 40 mesh sieves. A fraction collected between these two sieves is proper one. The size of granules should be between 1,4 mm and 0,4 mm.

SELECTION OF INGREDIENTS OF WDG-s

To select the proper ingredients for WDG-s the granules obtained by preliminary method will be evaluated. The following properties of WDG-s will be tested:

i) **suspensibility**, or degree to which the WDG-s remain suspended in dilution with water. The method of testing is described by CIPAC : MT-15;

ii) **desintagration rate**, while conducting the suspensibility test; the rate of disintegration is observed and the results are rated qualitatively on a three point scale : slow; fair; quick.

SELECTION OF PROCESS PARAMETERS

After selecting the components, the optimal process parameters will be found. They will be dependent on the used production techniques. In case of extrusion press granulation, followed by drying, the following additional properties will be tested:

iii) **Storage stability**

Samples are stored in sealed bottles at 10°C, 20°C, 40°C and some times at 50°C for several months. They are tested periodically to determine whether the initial suspensibility and desintegration rate have not been changed.

iv) **Attrition**

Granules are shacken or rotated in a sealed container, with steel balls and without them, after which sieve analysis is carried out to determine the finest content, before and after test.

v) **Sieve analysis**

Two hundred grames of granules are sieved for 10 minutes and the amount of granules of size between 14 and 40 mesh is determined. The more granules the best product.

By using pan granulation or fluidised bed granulation techniques the influence of all process parameters on the particular properties of WG-s must be tested.

CLASSIFICATION OF GRANULATION PARAMETERS

Type of process	Apparatus Parameters	Process Parameters	Components Parameters
Extrusion process	Type of mixer	Mixer filling Mixing time Drying temperature	Type of DA-s Type of WA-s Type of BA-s Type of mineral carriers Paste concentration Concentration of grqnulating solution
Pan or drum process	Angle of inclination Nozzle type Nozzle location	Granulator filling concentration of granulating fluid Spray angle Liquid flow rate Atomising air pressure Droplet size Drying temperature	Type of DA-s Type of WA-s Type of BA-s Type of mineral carrier Type of binder solvent Concentration of granulating fluid
Fluidized bed granulation process	Air distribution plate Shape of granulater body Nozzle type Positive or negative pressure operation.	Bed load Fluidising air flow rate Fluidising air temperature Fluidising air humidity Atomisation - Spray angle - Liquid flow rate - Air flow rate - Air pressure - Droplet size	Type of DA-s Type of WA-s Type of BA-s Type of mineral carrier Type of binder solvent Concentration of granulating fluid.

5. Directions for works in Pilot Plant

The main directions for works in Pilot Plant are given below:

i) to control and to modify the process parameters which had been established in laboratory scale;

ii) to produce the bigger amount of products for field trials;

iii) to check the effectiveness of various pilot instalation and to find the optimal parameters for processes used in production of PF-s, such as mixing, grinding, milling, granulation, spray drying, encapsulation.

iv) to modify the construction of production equipments.

The actual outfit of Pilot Plant makes it possible to perform all but not spray drying and encapsulation process. Regarding the tasks specified in p.iii the main attention should be given to these processes which presently are most commonly used in PF-s industry i.e. mixing and milling process and also to those which in the near future will be introduced to the industry i.e. wet milling and granulation processes.

The main goals of the experiments of grinding, milling and mixing of solid materials would be to find the effectiveness of particular machines in these processes. The investigations should be conducted at first using model materials and then to check these result on pesticide formulation components.

The effectiveness of grinding and milling can be tested by using mineral carriers of different hardness or abrasion index, alone, and their mixture with some of materials or synthetic waxes of different melting points.

For testing particular machines in the process of mixing it is recommended also to use model mixtures. Some of them can be composed from the following components in various proportions:

- Kaolin / dye
- Kaolin / chalk
- Kaolin / Sorptive carrier / DDT

The homogenity of mixture will be estimated on the basis of analytical results and using standard deviation method (1.2). For comparison of effectiveness of particular machines, the following costs must be included: amortization, overhaul and maintenance, labour costs (frequency of cleaning and standstill time, must be taken into account) and energy cost (3). The comparison of costs of dry and wet milling should also be performed in similar way. But for comparison of costs of production of WP-s and LFL-s the costs of adjuvants and packages must be included.

Similarly for making the cost estimates while comparing different granulation processes such as pan or drum process, extrusion, spray drying or fluidized bad processes, these points should be kept in mind.

6. General Conclusions

1. The physico-chemical properties of the materials used in preparation of PF-s are extremely important and it is highly essential to carry out a study by which it is possible to relate these properties to PF-s quality. Once these effects are quantified it may be possible to predict process performance and final quality of multi-component systems from a number of fundamental measurements. For that reason the modern pesticide formulations laboratories of leading companies are equipped not only with pilot plant equipment but also with many sophisticated instruments for testing different properties of raw materials as well as ready products.

2. The work conducted to elahorate new product should be more and more based on pricesely established relations of physico-chemical properties (quality) of the ingredients rather than on trial and errors method, especially when the need to produce safe products is gaining importance day by day. An investigation of the fundamental factors, which influence the properties of PF-s, would enable to make quicker and more rational formulations.

3. Taking into account rising trends of going in for the modern PF-s more often only the products of very high quality are accepted to use by government institutions.

4. It looks that PDPI Centre will be the leading institute in the work of PF-s not only in India but in South Asian region and will be able to improve the standards of actually produced PF-s by elaborating the more safe and more effective products.

5. It is necessary to equip PDPI research laboratories of PF-s in the following instruments:

- for measuring zeta-potential of suspensions; Rank Mark II Particle Microelectrophoresis Apparatus (Rank Bross, Bottisham, Cambridge, UK)

- for measuring contact angle of liquid; telescope fitted with goniometer eyepiece for projecting image of drop profile:(Rome - Hart Inc)

- for measuring cloud point (Cloud Point Apparatus (Wesean)

- for exchanging clays with Cations cation Exchange Colums.

6. It is necessary to engage colloid-chemist who will be able to introduce physico-chemical methods and will be carrying out examinations of physico-chemical characteristics of components and ready PF-s.

7. The methods of improving quality of PF-s and elaboration of new ones should be based more and more on fixed physicochemical characteristics of components of PF-s and less on the trials and errors methods.

8. For preliminary testing of elaborated or improved PF-s, some basic biotests should be adopted and used in Biological Laboratory of PDPI.

9. The research workers should be motivated to publish and patent the results of their work, because this is the only way to assure effectiveness and high level of researches.

10. To get more information about conditions how to conduct manufacturing process in a safe way it is necessary to organize special laboratory and equip it in specific instruments for testing ignition point, flash point, temperature of explosion etc.

11. It is recommended to use part of PDPI budget for purchasing samples (each of 1-5 kg) of some of standards components like mineral carriers, dispersing agents oils, emulsifiers, thickners, binders etc.

12. It is recommended to elaborate in solving some of the problems with other Indian Research Centres as well as with some of the foreign centres where similar problems are being worked out. The results of investigations would be mutually rendered as well as published or patented.

Such cooperation of PF-s field could have taken place between PDPI Centre and IPO Warsaw and also with the similar Research Centres of other countries e.g. that one of Hungary.

13. Taking into account the fact that only a small portion of the PDPI budget, allotted for training its scientists in various research centres in India and abroad, has been utilised, it is recommended that scientists and technical staff of PDPI should be sent to various centres to get acquinted themselves with the advancements in specific areas of pesticide formulations. For this purpose, some of the centres where internationally renowned scientists are engaged in doing work on PF-s are listed below:

- Department of Physical Chemistry,
  University of Bristol, BS 8 1 TS; dr B.Vincent
  Specification : testing and investigation coloidal and dispersion systems including clay suspensions

- Agriculture University, Dept. for Physical and Colloid Chem.,
  De Dreyen 6,6703 BC Wageningen, The Netherlands
  Specification : testing and investigation colloidal and dispersion systems such as clay suspensions
  Dr. E.G.M. Pelssers

- Institute of Colloid Chemistry, Sreged, Hundary
  Specification : testing of clays Prof. F.Szanto

- Research Institute for Technical Chemistry of the Hungarian
  Academy of Science, Vesprem, Hungary
  Specification : granules technology
  Prof. L. Armos.

- School of Pharmacy, Leicester Polytechnic, P.O.Box 143, Leicester
  LE 19 BH, England. Specialization : Fluidised Bed Granulation
  dr. M.E. Aultan.

7. **LECTURES**

1. EMULSIONS & EMULSIFIERS, pages 14, 5 references.
2. SUSPENSION CONCENTRATE, pages 14, 8 references
3. PHYSICAL AND PHYSICO CHEMICAL
   FACTORS AFFECTING EFFECTIVE
   MESS OF PESTICIDE FORMULATIONS,pages 9, 7 references.

Appendix 1

1. CRITERIA FOR SPREADING OF ONE LIQUID ON ANOTHER.

1.1 COHESION AND ADHESION OF LIQUIDS.

$$WC = 2\ V_a \qquad (1)$$

Where : WC - Work of cohesion of liquids;
Va - Surface tension of liquid A expressed in erges per square centimeter.

Work of cohesion is a measure of the tendency of liquid to cohere, i.e. the resist comminiution. For two insoluble liquids A and B, which create interfare A/B, the work of adhesion is :

$$W_A = V_a + V_b - V_{ab} \qquad (2)$$

Where : V_{ab} - the interfacial tension

W_A is work of adhesion - the tendency of the two liquid surfaces to adhere to each other.

1.2 SPREADING.

Liquid will spread smoothly over the surface of the s .strate (solid or liquid) or it will remain in the form of a single, floating, lens-like droplet. The liquid will not spread when its work of cohesion is greater than its work of adhesion to the substrate, and conversely it will spread when the work of adhesion exceeds that one of cohesion. Spreading coefficient is defined by the relation:

$$S = W_A - W_c \qquad (3)$$

The spreading will occur when S>0. If we combine equations (1), (2), (3) we obtain for the condition that liquid A spread on liquid B, the following equation.

$$S = V_b - V_a - V_{ab}$$

Since all of these quantities can be measured, the spreading coefficient may be calculated.

In case of emulsions, the influence of spreading coefficient on the stability of emulsion can be illustrated in fig. 1

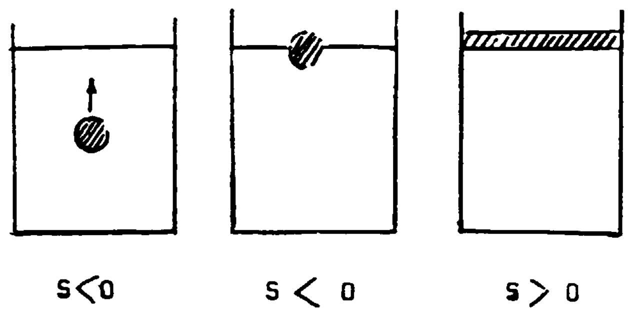

fig 1

For O/W emulsion used with biocide suspension S is >0

2. CRITERIA FOR COLLECTING SOLID PARTICLES AT THE INTERFACE O/W

The amount of solid particles (e.g. biocide) which will be collected at the O/W interface or around the globules of oils in O/W emulsions is dependent on the contact angle of the solid and the two liquid surfaces. If this contact angle is close to 90 degrees the most solid particles will be collected around the oil globules. For smaller and bigger contact angle, the particles will be concentrated out of interface - in oil or in water phase. This phenomena is illustrated in fig. 2.

S - solid

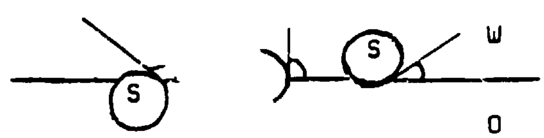

fig.2

The contact angle with the solid at the interface depends on the hydrophilic - lipophilic balance (HLB) of the solid particle surface and can be modified by surface active agents.

Remark. It is very difficult in the case of a biocide to predict what kind of emulsifier should be used to get the demanded effect. For that reason only a trial and error procedure can be used.

References:

P. Becher "The Liquid/Liquid Interface", Official Digest, 1962 p.p. 488-505

S. Friberg, J.Witton "Liquid Crystals - The Formula For Emulsions" American Perfumer and Cosmetics, 1970, Nr. 12, p.p. 27-30.

Appendix 2

CRITERIA OF SELECTING WETTING AGENTS FOR DISPERSIBLE GRANULES (DWG-s)

The type and level of wetting agent used in the system is determined by matching the solid surface tension Vs of pesticide with the liquid surface tension Vl of the wetting agent at the field dilution rate.

The solid surface tension Vs of the toxicant can be determined by:

1) transfer behaviour of particles in two immiscible liquids having two different known surface tensions, i.e.:

$V_L < V_S < V_{L_2}$ or

2) measuring contact angle θ between a liquid of known surface tension and solid on a goniometer and use relation:

$$V_S = \frac{(1 - \frac{\theta}{8})\ (\cos\theta - 1)}{2}$$

The type and concentration of the wetting agent in the formulation is determined from graphs of agueous surface tension values of the various wetting agents V_L vs concentration, where the V_L is slightly less than the solid surface tension V_S of the toxican and the change $d(V_L)/d(\text{conc.})=0$.

Reference :

J.F.Wright and N.I.Ibrahim "Steps of Water Dispersible Granule Development" Advances in Pesticide Formulation Technology. Ed. by Herbert B. Scher. ACS. Washington, DC. 1984 p.185-192.

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Conc. Biocide

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3. R.Lovy, W.D.CarretJ,J.Chiconitte and T.W.Miller Jr.,"Control of Culex spp. mosquitoes", Mosquito News 40:2735.

4. Burges,H.D. "Production, formulation, standardisation, and safety of microbial larvicides" pp 181-90 in F.Mich(ed), Basic biology of microbial larvicides UNDP/World Bank/WHO Publ.188pp.

5. Coutch, T.L. "Formulation of microbial insecticides : conventional formulation" pp 3-10, in C.M. Ignoffo and L.A. Falcon (eds) Formulation and application of microbial insecticides. Misc. Pub. Entomol. Soc. Am. 10(5), 180.

Conc. Suspensions

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2. Th. F. Tadros "Control and assessment of the physical stability of pesticidal suspension concentrates" chemistry & Industry, 15 March 1980

3. B. Vincent "The stability of particulate suspensions" Chemistry & Industry, 15 March 1980

4. Th. F. Tadros "Physical principles in suspension and emulsion processing"; Advan. Transport Processes 1984, 3, 1-34.

5. Th.F.Tadros "Dispersion Science and Technology in Pesticidal Formulations" Advance in Pesticide Science, (1983) 245-246

"The factors affecting fluidised bed granulation" Manufacturing Chemist & Aerosol News, December, 1978, 50-56 "Fludised Bed Granulation - Factors Influencing the Quality of the Product" Int. J. Pharm. & Prod. Mfr. 2(4), 24-29(1981)

6. R.J.Meyer "The Rheology of Natural and Synthetic Hydrophylic Polymer Solutions as Related to Suspending Ability" J.Soc. Cosmetic Chemists 10,143(1959).

7. A.Martin "Physical Chemical Approach to the Formulation of Pharmaceutical Suspensions" J.Pharm. Sc. 50, 6, 513 (1961).

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9. T.F. Tadros "Adsorption of lignisolulphonates on pesticides for Agueous Solution and the Stability of the Resulting Dispersions", Advance in Pesticide Science (IV Int. Cong.) part 3 p.820 (1978).

Conc. Testing of emulsifiers

1. Yutaka Tanaka "A new test method for nonionic surface active agents"

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3. M.Rosch "ProjeKtierung einer Anlage Zur Feinmahlung tiefschmelunder organischer substancen.Geigy-Kolloguium 5 Jun 1970 pp.32.

All the above referred papers are now available in PDPI Centre.