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DP/ID/SER.A/863
3 July 1987
English

16395

PESTICIDE DEVELOPMENT PROGRAMME IN INDIA

DP/IND/80/037

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

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Vienna

295

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ACKNOWLEDGEMENT

I wish to take this opportunity to express my great satisfaction for having occasion to come, again, to this hospitable and interesting country and to work on ambitious project going on in PDPI.

In particular I would like to express thanks to Dr. S.P. Dhua, CMD, HIL, Dr. M. K. Hussein, UNDP, SIDFA, Mr. M. Lal, HIL, (GM(P), Dr. S.K. Khetan and Mr. Satpal from UNDP for their activity which allowed me to come to INDIA and take a part in International Workshop.

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, Dr. R.K. Khandal and Eng. V.N. Dutta with whom I had pleasure to collaborate directly. To all of them I wish many success 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.

CONTENTS

SUMMARY

In this report the attention has been drawn towards some of the projects which started during my last mission. The problems faced in these projects have been discussed with the responsible officers and conclusions and suggestions for further work on them have been made. The next task, in accordance with Term of Reference of present project, concerns to the methods of preparing new type of formulations - **WATER DISPERSIBLE GRANULES (WDG-s)** and **MICROEMULSIONS.** The plan of experiments has been prepared.

Being informed about some of the other projects, undertaken after my last mission, I was especialy interested in the following projects : purification of the carboxin sewage by flocculants; preparation of concentrated emulsions of butachlor and testing of different clays for water dispersible powders. The discussion on some of the problems of the mentioned projects were held and some suggestions have been given. The other tasks arising from the Term of Reference were the lectures being delivered and attendence in International Workshop concerning Pesticide Formulation. During my mission I have occasion to discuss in general about the PDPI project with CMD, HIL, Dr. S.P. Dhua, who expressed interest to get suggestions about directions of further research work on PDPI projects. Some of such suggestions have been given in this report also.

Similarly as in my previous report I have drawn a special attention towards the methodology of conducting experiments. I emphasise that, if it is not a necessity then at least it is very advantegeous to conduct some of the experiments according to **Factorial Design Methods.** I am trying to justify also the carrying out of the **model-scale experiments** which are proposed by me.

The recommendation concerning the purchasing of some of the research instruments indispensable for testing of raw materials and ready products has been also given.

FINDINGS AND RECOMMENDATIONS

1. THE PROJECT EXECUTED DURING THE PREVIOUS MISSION OF EXPERT

1.1 BIOCIDE FORMULATION

I am satisfied that the type of formulation had been changed in accordance with the recommendations given in my previous report (page 7 points i - x). The new formulation, elaborated by Dr. Ramdas characterised by spontaneous spreading over the surface of water and excellent distribution of biocide on water surface. The activity against larvae of different species of Anopheles staphensi mosquitos is also good. The results already obtained allow to prepare by pilot production the new formulation in biger amount for field tests. Such tests performed in different field and weather conditions will make possible to find some drawbacks of formulation (if there are any) and eventually to remove them by modification of composition. Some small drawbacks should not, in any case, delay the preparational work for starting of the production.

1.2 FLOWABLE CARBOXIN AND OTHER FLOWABLES

The composition of flowable carboxin has been elaborated and is presently tested in the field. The similar product but mixed with some amount of oil has not been elaborated because of foreseen problems with its registration. (The multicomponent products are not approved to the use.)

It is assumed that after registration of Flowable Carboxin it would be possible to introduce on the Indian market the packing, which will comprise two components - flowable carboxin and oil; May be it is not a bad solution. The best however would be to elaborate the composition of dry premix from which the water flowable or water/oil flowable could be prepared by local formulators. This premix would be produced by HIL Co. The further research work on this problem should be continuated so that more flowables of some other pesticides could be by similar method (from premixes) prepared. It seems, that on Indian conditions, where many Small Scale Formulators are engaged in production of pesticide formulations, it will be easier for them to produce flowables from premixes, produced and distributed by one big factory, simply by mixing the premixes with water or oil, than to instal in each small factory costly pearl mill for small scale production. It is necessary however to keep in mind that not each pesticide can be produced in flowable formulation by this method i.e. from dry premixes.

1.3 CHARACTERISATION OF EMULSIFIERS AND OILS

It is commonly known that properties of Emulsifiable Concentrates as well as Emulsion Concentrates and Microemulsions are dependent on the composition of formulation as well as on the physico-chemical characteristics of their components. Therefore, it is very important to know the methods to characterise emulsifiers as well as different oils which are to be emulsified.

In previous report I gave some suggestions (p.11 i-iv) as to what kind of characteristics should be determined for finding out the correlation between these characteristics and the properties of ready products.

The proposed, as well as some other methods of testing of oils and emulsifiers are very important, not only for better understanding of different phenomena of emulsions, but also for more skilful, better and more economical elaboration of new emulsifiable or emulsion formulations.

The previous suggestions concerning the above mentioned work had been performed only in confine scope and should be in the nearest future intensified.

The EC, as well as WP-s are, and most probably will, for the next several years, constitute the bulk of pesticide formulations in Indian and Pacific Regional markets. And we know that it is yet many different problems of quality of these products. Therefore, the know-how on the basis of which, fast and proper solution of problems could be executed is of great importance.

For performing the project according to the above recommendations, it is necessary to collect the set of standard emulsifiers as well as different solvents.

Some of the following of them are recommended:

Nonylphenol (NPOE) and Octyl phenol (OPOE) adducts of $E+_20$

	Et_2O Nr.	HLB
e.g : NPOE	NP 4	8.9
	NP 8	12.3
	NP 10	13.9
	NP 15	15.0
	NP 30	17.0
OPOE	OP 10	1.36
	OP 16	15.6
	OP 40	17.9

Sorbitan esters of C_{10} - C_{22} fatty acids (SPANS) of HLB - 2.1 - 8.6, Uipophylic surfactants not soluble in water;

Polioxyethylene esters of SPANS (Tweens), hydro-phylic surfactants soluble in water.

Polyethylene condensates of C_{10} - C_{22} fatty acids or fatty alcohols of different HLB number.

As oils the following individuals and their mixture are recommended:

O-xylene, cyclohexane, hexadecan, hexane, octane, cyclohexanon, 2etoksyethanol, dioctylphthalate, parafinic oil and different technical solvents used for production of EC-s as : Aromasol, Solvent Napta, mixtures of mezytylene with ksylene, methyl naphtalene (Sol Vesso 200) and others.

The relations between the characteristics of these solvents and their mixtures (as many characteristics as possible) and the composition of emulsifiers giving the best result should be found out and if possible all of these information should be put into the memory of computer.

2. THE PROJECTS CONSULTED DURING THE CURRENT MISSION

2.1 MICROEMULSIONS AND WDG-s EXPERIMENTS

The programme of experiments as well as their theoretical basis have been elaborated and provide for execution (see p 16)

The main objective of experiments with microemulsions is to get experience with preparation of these systems and to find some relation between some characteristics of the components of systems and the characteristics of systems. Therefore, the model systems are recommended. Having the basic knowledge about preparing microemulsion systems, some of similar pesticide formulations can be eleborated. It is however, necessary to keep in mind, that such formulations will be in general more costly than others. Therefore only in special cases the production of pesticide microemulsions will be justified. This can have e.g. a place then, when activity of rather expensive pesticide will be much higher than other clasical formulations. Most probably the microemulsion p. formulations will be at the beginning mainly sold in small packings and used in glass houses or for sanitary use. The another aspect which should also be taken into account for getting good formulation is that it is necessary to have at disposal a big assortment of various kind, very often not typical emulsifiers. E.g. for synthetic pyrethrum microemulsion formulation the following emulsifiers are recommended:

A. DISTYRYL PHENOL ETHOXYLATE AMONIUM SULPHATE (5 moL Et_2O)

B. DISTYRYL PHENOL ETHOXYLATE

C. CALCIUM DODECYL BENZENE SULPHONATE

Taking into account the above requirements it appears proper not to extend this direction of work too much and rather concentrate the efforts on projects concerning emulsifiers as well as concentrated emulsions.

The WDG-s seems to be much more perspective pesticide formulations, having many advantages in comparison to WP-s and being not too much, if any, more costly. Because the process of granulation of dry powders is very susceptible as well on components of powders as on different parameters of process it is

recommended to conduct the experiments according to FACTORIAL DESIGN METHOD. This method is more and more often used e.g. in finding the optimal compositions of pharmaceuticals. Because it is expected that Analytical Laboratory of PDPI Centre will be soon equipped with JBM PC AT INTEL 80283 MICROPROCESSOR it will be possible to use it for processing the data. Therefore, it is also recommended to colaborate with an Indian Specialist Group from some of the higher schools in this subject. It would also be good to PDPI Centre to engage a mathematical statistician who will be responsible for preparing of programmes of experiments as well as for drawing out of precise (statistically proved) conclusions from obtaining data. It does not means that all experiments must be conducted by this method, but only that ones which can or should be done. The plan of experiments had been elaborated on Fluidized Bed (FBC-r) granulator and somebody can argue that may be it is not proper because in production more often the other type of granulators as e.g pan type are used. It is true, but choosing of FBG-r results from the fact that this type of granulator, owing to its versatile fittings, make possible to carrying out precisely parametized experiments. Knowing the basic parameters, responsible for quality of product, it will be easier to perform the process in other, more simple type of granulator.

2.2 EFFLUENT TREATMENT AND WASTE DISPOSAL IN A PESTICIDE FORMULATION PLANT

During the workshop concerning pesticide formulation the lecture prepared by Mr. Dutta has been devoted to purification of sewage from Carboxin production by using some of inorganic flocculants. The best result, according to which about 76.4% of Carboxin from sewage has been removed, can be achieved by using 1000 ppm of KOH, 1000 ppm. P.ALUM and 7000 ppm of Bentonite on sewage containing 500 ppm of Carboxin. The rest amount of Carboxin i.e. 23.6% is removed in second step by passing the supernatant of the first step through activated carbon.

Having experience with using some of organic flocculants from the group of polyacrylamide I made suggestion to check some of them, taking into account much lower concentration in which they are recommended to use (max. 250-500 ppm when they are using alone or much less when they are using together with mentioned inorganic flocculatns). The different kind of this type of flocculants are produced by many firms.

Dow chemical company e.g. recommend 12 flocculants for different area of application as well as for improve sedimentation of suspension as its filtration. One of this product SEPARAN AP 45 being in my disposal I hand over for testing. It has been found that an amount of 4 ppm of it improves the flocculation when inorganic flocculants were used. Further experiments should be carried out in order to lower the amount of inorganic flocculants. It is also recommended to supply the laboratory with others poliacrylamide flocculants and to test them. The booklet concerning organic flocculants has also been provided.

TESTING OF CLAYS FOR WP-s FORMULATIONS

This project is important because the WP-s contribute the bulk of pesticide formulations. The main mineral carrier kaolin which is used in their production is mined from different deposits and its physicochemical properties are for his reason very often quite different. Such nonstandardised properties make problems in production of pesticide WP-s of high quality. The major defects of some of WP-s is its tendency to flocculate in "hard" or in "soft" water a tendency which very often can only be revealed after some period of storage of products. The research carrying on this problem by Dr. Khandal are very

systematic and accurate. His work is based on the assumption that the main reason of deterioration of self dispersility and suspensibility of WP-s is caused by the tendency to flocculation of clay carriers. Therefore in the first series of experiments the suspension stability of clays without pesticides in water of different hardness and temperature were tested. Some of the tested suspension revealed stability some other flocculation. It has also been found that if small amount e.g. 10% of clay of good suspensibility has been mixed with that one of high tendency to flocculation suspensibility of the latter was markedly improved.

After observing the experiments and after discussions of their results the following suggestions are given:

- the trying to stop the flocculation of clays in 5% "hard" water suspension by adding of some amount of sodium carbonate is not a proper solution because the concentration of suspension used in the field is lower (about 0.5%) and the amount of sodium carbonate in formulation will be not enough to stop flocculation,

- the flocculation of WP-s depends not only of tendency of clay particles to flocculation but also of particles of pesticide to flocculation. The wetting and dispersing agents proper for clays can not be such for pesticide. For that reason it is necessary to find surfactant system proper for mixture of clay/pesticide. This system can be different for different clay and different pesticide.

- it is easier to elaborate a good WP-s (of good suspensibility and self dispersibility) by choosing a proper surfactant system than by finding a methods of stabilizing clay suspensions,

- the good result for easily flocculated system in which anionic surfactants are used can be obtained while nonionic or anionic / nonionic system is used,

- because the physical properties of pure nonionic (based on Et_2O) make them difficult to distribute in powder of clay and pesticide it is recommended to use nonionic after their mixing with urea. Such a mixture has powder form and is easily distributed among the other powder components.

- the work on finding proper composition of WP-s would be more effective if faster and more precise detection of tendency to flocculation of tested suspension could be performed. The very good not very expensive apparatus for this is Sedimentation Balance.

3. VISIT TO PESTICIDES INDIA CO.

The visit took place on invitation of Mr. Singhal the Manager of the factory. The plant produce two pesticide - acaricide Ethion and insecticide Phorate and different formulations as EC-s, WP-s and granules. During the visit the different problems of the above production and eventual cooperation with PDPI Centre had been discussed. The Pesticides India is especially interested in checking the mineral carriers which is used for production of WP-s, because they have some problems with the stability of WP-s suspensions.

4. RECOMMENDATION CONCERNING THE PURCHASING OF THE NEW INSTRUMENTS

The PDPI Centre is already equipped in various very often expensive instruments but the same time there are lack of some ones, especially of that for testing of some basic physicochemical characteristics of raw materials and ready products. The following of them are recommended.

- Set of stalagmometrs for testing surface tensions of liquids and liquid solutions as well as interface tensions between the two different liquids. These characteristics are very important for research on **Emulsifiable Concentrates, Concentrated Emulsions and Microemulsions as well as on WDG-s**

- Device as e.g. telemicroscop for measuring contact angle between the droplet of liquid and solid. This instrument is very important for testing and choosing wetting agents for WDG-s (see p.p. 28.)

- Device for measuring tendency to flocculation of suspensions and for measuring their particle sizes. As the very good one and not to expensive the **Sedimentation Balance** (e.g. Mettler or Sartorius Co.) is recommended.

- Device for measuring zetapotensial of suspensions e.g. that one of Cambridge Instr. Co. This instrument is helpful to find reasons of flocculation of suspensions.

- More precise viscometer for measurement of rheological properties of suspension concentrates as e.g. that one produced by Haawke Rotovisco Co.

5. BOOKS, PATENTS AND PAPERS GIVEN TO PDPI

Book

Author : Dr. Attwood, Title : SURFACTANT SYSTEMS, Ed. 1983.

Patents

U.S. 4, 411, 692, Oct. 25, 1983, "Flowables Herbicides"

EU.P. 0142 485 Sept. 17, 1984, "ALOCHLOR EMULSION FLOWABLE"

Papers

- Basic of STATISTICAL EXPERIMENT DESIGN
- Design and analysis of industrial experiments.
- Making the medicine taste less nasty
- Do finer drops mean faster drying
- Spray-coating bulk drugs aids dosage form production
- The correlation between phase inversion temperature in emulsion and cloud point in solution of nonionic emulsifier.
- Study on the required HLB of oil-in-water emulsions by simple phase-inversion titration
- The determination of the required HLB of emulsions by an emulsion inversion point.
- The stability of Microemulsion system
- Micellization, solubilization, and Microemulsions
- Intermolecular Forees the long and short of it

- Properties of Hydrophobic sols
- Toward understanding microemulsion microstructure part I and II
- Interfacial phenomena in pesticide application
- Quantitative evaluation of the wettability of powders
- Application of the cohesive energy ratio (CER) concept to anionic emulsifiers
- water dispersible granules.
- The various separan products

6. SUGGESTIONS CONCERNING THE FURTHER DIRECTION OF RESEARCH WORK IN PDPI CENTER

Well equipped laboratories of PDPI Centre with modern Research Instruments makes it possible that this Centre will be the best in Asian and Research Work on Pesticide Formulations not only in India but also in Pacific Region. For getting however, such a position several conditions must be fulfilled and they will be if in parallel the following directions of work will be realised.

1. The research work with the objective of improve the quality as well as the economy of production of currently produced product in the region. The following tasks should be solved in this direction.

- elaboration of new composition fo PF-s;
- finding and testing of new components for PF-s like new solvents, mineral carriers, surfactants and other adivants,
- checking the new composition of PF-s in pilot plant;

2. The research work with the objective of elaborate new pesticide formulations.

The following tasks should be solved in this direction;

- the analysis of advantages and disadvantages of new product in comparison to the old ones;
- elaboration of compositions and methods of producing in laboratory and pilot scale;
- eleboration of analytical and physico chemical methods of testing of new PF-s;
- eleboration of biological methods of testing;
- elaboration of standards for new products

3. The research work on methods of testing of raw materials for / and PF-s and on relation between the characteristics of raw materials and properties of ready products

The following tasks should be solved in this direction:

- methods of testing of characteristics of mineral carriers such as particle size, sorbitivity, grindibility, suspensibility, surfactant, adsorptivity;

- methods of testing of characteristics of solvents such as hydrophobity (water numbers) pesticide solubility, dielectric constants, surface tensions, interface tensions;

- method of testing of surfactants and their solutions such as HLB, surface tensions, wetting and spreading contact angle between droplet and solid;

- methods of testing of stability of suspension and emulsions;

- methods of testing of rheological properties of suspensions and emulsions;

- methods of testing of microemulsions;

- methods of testing of wDG-s;

- methods of testing of Control Release Pesticide Formulations.

- finding out relation between characteristics of components of PF-s and properties of ready products as e.g : suspension stability and zeta potential; stability of concentrate suspension and its rheological properties, relation between different thickners (organic and inorganic) and SC stability; influence of wettability of carriers and pesticide by solution of wetting / dispersing agents on properties of WDG-s.

The scope of the research work on different directions will be dependent on the priority of current tasks, and of the specialization and numbers of research workers. However, the best solution would be if all directions of work could be made in parallel by separate group of specialists working in different laboratories.

The results of the research works hould be patented and published in specialized journals. There is a need for collaboration with other Research Centres dealing with the physicochemical problems of suspensions and emulsions such as Pharmaceutical Research Centre, Cosmetic Research Centre, Paint Research Centre, and Agricultural Research Centre.

It is also advisable to programme the experiments with the help of some of Computers Research Centres.

7. PLAN OF EXPERIMENTS

7.1 MICROEMULSIONS EXPERIMENTS

Remark (acc to L. Prince)

"At the outset it must be explicitly stated that there are limitations to the nature of oils that have been emulsified and there are always product specification which decrease the range of emulsifying agents that can be employed in given formulae. Few oils in their natural form seem to be chemically constituted to form there stable system with water. It is particularly so of the o/w system. Most of oils do not microemulsify regardless of how much excess of emulsifiers is employed".

General rules of preparation of microemulsion (acc to L. Prince)

There are several ways of blending of ingredients of microemulsions. These systems consist of at least 10% of emulsifier on the weight of the oil, usually 20-30% is present. The techniques for w/o systems are simpler. They are prepared by blending the oil and the emulsifier with a little heat if necessary and then adding water. When emulsifier is found that present of the desire water uptake, it may be convenient, from a processing view point, to add the mixture of emuisifier and oil to the water. Again warming the system may speed the mixing process. The order of mixing does not effect the end result. Another technique is to make a crude macroemulsion of the oil and one of the emulsifiers (e.g. soap). By using low volumes of water a gel is formed. This gel is then changed into a clear solution by titration with a second surfactant (cosurfactant). This system may be then transformed into an opalescent o/w microemulsion of the desire concentration by further addition of water.

By far the most common method of making of an o/w microemulsion especially in trial and error method, however, is by the so called inversion process. Accordingly, this method of preparation is the prefered one for initial exploration.

Usually 100% emulsifier on the weight of the oil is employed. After carefully blending with heat, if necessary, water is added to the blend in the beaker. That is done in small aliquots. If the chemistry

is right, a clear, transparent w/o dispersion first forms. This is fluid. AS more water is added, at about equal volumes of water and oil emulsifier blend, the system becomes to be more viscous. As more water is added it becomes very viscous. Ultimately becoming a heavy gel. At this point it is frequently helpful to apply heat to thin the gel and facilitate passage through this stage. With the addition more water, the gel eventually thins out to fluid o/w microemulsion which can readily be identified by its clarity or opalescence.

The highly viscous intermediate gel stages are obviously not microemulsions but are sometimes so called. These systems are actually LIQUID CRYSTALINE PHASE.

The appearance of the highly viscous stage which may be clear or opalescenent is good evidence that the formulation is done to matching this oil and emulsifier. Unfortunately in many systems a clear w/o dispersion forms at first and begin to pass into the gel stage but fails to invert to a fluid o/w microemulsion.

If the emulsion is to viscous, the HLB should be slightly increased.

If the emulsion particles are to large (and system potentially unstable) the HLB should be lowered.

Improper matching results in failure to achieve any one or all of the above mentioned stages.

Experience has also shown that an oil can be matched to a given emulsifier by blending with other oil.

Visual and optical streaming beirefringent observation with polarizing plastic sheets are made after each water additions. The composition points of systems are identified by different colours and shapes of points.

a) transparent (clear), isotropic w/o and o/w systems

b) translucent (opalescent) isotropic w/o and o/w systems

c) opaque and unstable isotropic w/o and o/w systems

d) visually heavy and beirefrigent thin gels of cylindrical liquid crystalline phase

f) viscous, non-beirefringent macroemulsion inversion stage.

Calculation of Amount of Surfactant in preparation of Microemulsion (acc to H.L. Rosano)

It is assumed that all the surfactant molecules will be at the o/w interface. The total interfacial area A will be equal to:

$$A = n \times 6 = a \times 4\ r^2$$

and the total volume of the dispersed phase will be equal to:

$$V = a \times 4/3\ r^2$$

Where:

n - number of surfactant molecules

b - cross-sectional area occupied by the surfactant molecule at the o/w interface

a - total number of droplets of dispersed phase

r - radious of the sperical droplet

Combining the two equations gives:

$r = 3V/nxb$

For water/benzene microemulsions stabilized by potasium oleate and p-methyl cyclohexanol, the calculated droplet size agreed with those by light scattering if $b = 70A^\circ$ is used.

Using equation 1 to calculate the weight of sodium lauryl sulfate (SDS) to microemulsify 5 ml of H2O in - hexadcane the following values were used: $r = 500\ A^\circ$ or $b = 50A^2$ per molecule. Therefore, $n = 0.6 \times 10^{21}$ molecules which corresponds to 0.287g of SDS.

The cosurfactant plays two major roles: firstly it effects the packing of the surfactant molecule at the interface and secondly it brings the necessary reduction in interfacial tension. Addition of cosurfactant increase the volume of the packed surfactant molecules without affecting the length and hence it enables the geometrical packing. The using of cosurfactant is essential in the case where ionic, very hydrophylic surfactants are used. In case of nonionic which can be prepared with different HLB the using of cosurfactant can not be necessary.

It is however, evident (from the phase diagram) that nonionic surfactant is a good solubilizer at an optimum temperature range e.g. in case of cyclohexane + water, containing 5% of $C_{12}H_{25}O(CH_2CH_2)_{5.3}H$ the 20% microemulsion was stable between 33 - 35°C, and when more hydrophylic oxyethilene adduct was used having 9.7 oxyethylene groups, the microemulsion of the same concentration of oil phase was stable between 45-50°C. In lower temperature e.g 25°C the concentration of oil phase in stable microemulsion is lower. For 5-(Et_2O) emulsifier this concentration = 8% and for 9.7(Et_2O) emulsifier = 3-4%. On the other hand ionic surfactant are stable to temp. change but need higher concentration.

A mixture of nonionic and ionic (not hydrophylic) seems to be ideal. The region of microemulsion becomes more stable to temperature change by adding an ionic surfactant. The advantage of blending (mixing of surfactant) is that a nonionic surfactant is the main solublizer and the small amount of oil solube ionic surfactant is added to adjust of PIT or HLB of the mixture as well as to increase the stability and solubilization. Consequently, the appropriate combination of a balanced ionic surfactant and nonionic surfactant favour effective solubilization and temperature stability.

Some problems concerning CMC should also be clarified. If the size of the hydrophile and lipophile groups of the solubilizer increases, the CMC will decreases, the aggregation number will increase and solubilization power will be enhanced.

e.g. using two surfactants:

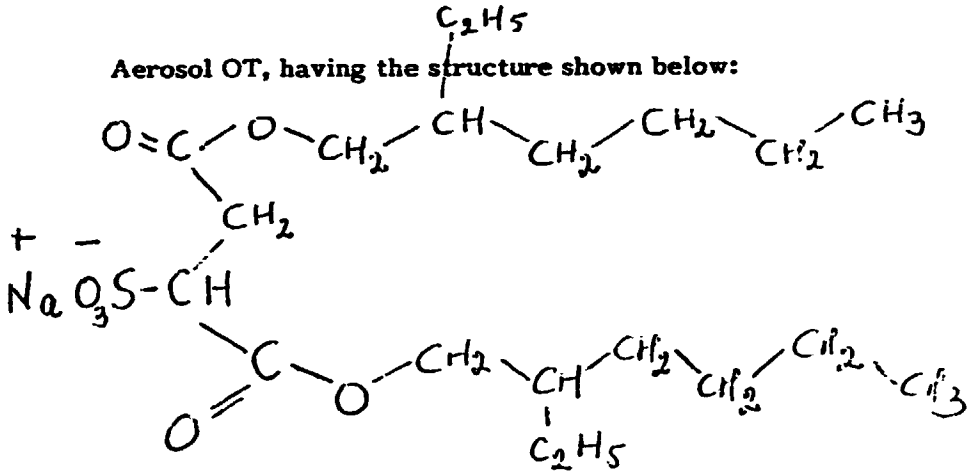
$C_9H_{19}C_6H_4(CH_2CH_2O)$

and $C_{12}H_{25}C_6H_4(CH_2CH_2O)$ 9.7

To summarise the preparation: 0.287 g of SDS is dissolved in 5 ml of H2O, 25 ml of n-hexadecan is added, then titrated while stirring with 1-pentanol until clarity is achieved. 1-pentahol is not too soluble in oil or in water and is an efficient cosurfactant with w/o system.

Anionic and nonionic emulsifiers and cosurfactant (acc. to Tadros)

Aerosol OT, having the structure shown below:



is favourable for formulation of a w/o microemulsion, without the need of adding cosurfactant.

As a result of the presence of a stumpy head group, and large volume to length (V/L) for the nonpolar group, the interface tends to bend with the head groups facing inwards, thus forming o/w microemulsion. It has been assumed that V/L > 0.7 is necessary for microemulsion formation.

With ionic surfactants for which V/L is <0.7 microemulsion formation needs the presence of a **cosurfactant.** The letter has the effect of increasing V without effecting L (if the chain length of the cosurfactant does not exceed that of the surfactant).

According to other authors the nature of the microemulsion depends on the packing ratio $V/a_o l_o$ where V is the partial molecular volume of the surfactant molecule, a_o is the head group area of surfactant molecule and l_o is the maximum chain length. The packaging ratio is affected by many factors including hydrophobicity of head group, ionic strength of solution, pH, temperature, cosurfactant. With Aerosal OT $V/a_o l_o$ is >1 since both a_o and l_o are small and this molecule favourable formation of w/o microemulsion.

of similar PIT or HLB the 3% of the second surfactant seems sufficient to yield a similar microemulsions realm as in 5% of the first surfactant.

In order to increase the amount of solubilization as well as the size of micelle, ionic and nonionic surfactant, whose hydrocarbon chain lengths are long should be used e.g. longer chain sodium alkyl sulfates require smaller amount of alcohol (cosurfactant). Since the polyoxyethylene chain is not strongly lipophylic the CMC in the oil phase is not small. Substitution of a polyoxy ethylene compound with a suitable mixture of sucrose monoester and sorbitan monester in the oil phase will decrease CMC and increase solubilization of water because both sorbitan monester in the oil phase will decrease CMC and increase solubilization of water. Both sorbitan monoester and sucrose monoester posses efficient hydrophylic groups of different size.

It seems that for o/w microemulsion the more efficient solubilization effect can be get by using not to hydrophylic nonionic surfactant e.g. $C_9H_{19}C_6H_4O$ (CH_2CH_2O) 7.4H and not to hydrofobic ionic surfactant e.g $C_{12}H_{25}C_6H_4SO_3$ $1/2C_a$.

Surfactants used in preparing microemulsions

Nonionic

Sorbitan esters of C_{10} - C_{22} (SPANS) HLB - 2.1 - 8.6 Polioxyethylene - sorbitan esters C_{10}-C_{22} (TWEENS) up to 80% Et_2O

Polyoxyethylene of alkyl fenols 6-20 aioms C upto 8% $E+_2O$; diethylphenol ethoxylate; polyxyethylene of factty alcohols or fatty acids; Pluronics - polyoxyethylene polyoxypropylene block polymers.

Anionics

Potasium oleate, sodium laurylsulfate, sodium dodecyl sulphate, petroleum sulphate, $R_{12}OCH_2CH_2SO_4Ca_{1/2}$; $C_{12}H_{25}C_6H_4OSO_3$ Cal/2, petroleum sulphonate, distyrylpheno ethoxylate amonium sulfate (5 mol Et_2O)

Experiments

Type of mitroemulsion : O/W

Oil phase : cyclohexane, para-xylene, cyclohexane,

Water : distilated

Surfactants : Conc. in oil (w/v) = 30%

nonionics : oxyethylene nonylphenol, HLB^{10} - 12, 15

Span / Tween HLB 10, 12, 15

anionics : $C_{12}H_{25}C_6H_4OSO_3$ 1/2 C_a

Amount of oil sample titrated with water 5 ml.

Temperature : room t.

Series 1 of experiments

Oil phese : xylene

Surfactants : Span/Tween

Ratio S/T : 0.5/4.5, 1.0/4.0; 1.5/3.5 (S:10 HLB, T:15 HLB)

Surfactants : Nonylo (N)/ Calcium (C)

Ratio N-12/C, 4.5/0.5; 4.0/1.0, 3.5/1.5

Ratio N-15C, 3.0/2.0; 2.5/2.5; 2.0/3.0

Titration of samples with water and observations (magnetic mixing)

Series 2 of experiments

Oil phase : cyclohexane

Surfactants. Span/Tween

Ratio S : T 0.5/4.5 , 1.0/4.0, 1.5/4.5 S : HLB 10, T : HLB 12

Surfactants : N/C N : 12 HLB

Ratio N/C 4.5/0.5; 4.0/1.0; 3.5/1.5

Series 3 of experiments

Oil phase X/C. 1:1

Types and proportions of emulsifiers will be settled after the and 2 series of exp.

All samples should be kept after titration in closed tubes. The solution of dodecylobenzene sulfonate of Ca should be prepared after drying of butanol solution of this salt.

7.2 WATER DISPERSIBLE EXPERIMENTS

Before starting to agglomerate the powder mixture containing pesticide, surfactants, binders and carriers it is recommended to find the conditions of aglomerate hydrophylic carrier e.g. Kaolin and then to check the influence of hydrophobic components e.g waxes or pesticides (DDT) on the parameters of grannulation. It would be interesting to find how the parameters are changed when the granulated powder mixture contain more and more hydrophobic solid.

Informative experiment could also be a such one in which, pure "or nearly pure" hydrophobic solid is aglomerated.

In the first series of experiments the following parameters should be fixed.

The kind and consentration of dispersing and wetting agents on the rate of agglomeration and the range of the sizes of granules).

Before starting the agglomeration process the following parameters should be fixed.

- the load of powder mixture,
- the concentration of dispersing agent,
- the concentration of wetting agent,
- the concentration of blending agent,
- the temperature of air,
- the rate of air flow,
- the time of granulation.

In each series of experiments one parameter will be changed e.g. type of dispersing agent, its concentration, type of wetting and blending agent and so on. It is recommended however, to find for one dispersing / binding agent e.g for calcium lignosulfonate the optional parameter for granulation of hydrophylic and hydrophobic solids and after that to check there parameters which are responsible for wetting and disintegration of granules.

For finding the influence of different temperature of granulation and properties of granules, it is recommended to end the process of granulation on such a point in which some amount of water (5%) will be contained in granules. Then samples of granules (e.g. 10g) will be dried in temp. 80, 100, 120 to the amount of water 0.5 - 0.8% and wettability and suspensibility will be tested. In these tests the maximum acceptable temperature of drying will be fixed.

Because many parameters have been related with preparing of WDG it is recommended to conduct the experiments in accordance with FACTORIAL DESIGN EXPERIMENT.

The degree of granule buildup in a fluidised bed is a function of the ability of droplets of granulating solution to wet the powder particles, and for these particles subsequently to stick together. If a hydrophobic component is present in the system, granulation becomes more difficult.

The important factor is the wetness of the bed during granulation.

The wetness of the powder at any time depends upon many apparatus, process and product parameters. The factors which can affect the initial wetting of the bed include:

- type of binder,
- binder solvent,
- concentration of granulating solution,
- temperature of granulating solution,
- spray nozzle type,
- liquid addition rate,
- atomising air pressure,
- atomitincy air flow rate,
- droplet size,
- powder hydroflobility.

The subsequent rate of evaporation of the moisture from the granules is a function of:

- fluiding air flow rate,
- fluidising air temperature,
- fluidising air humidity,
- quantity of granulation solution.

As any one time the moisture content of the bed, and therefore the rate of growth of the granules, is a function of the balance between the two groups of factors. In general a combination of parameters which result in the bed being kept a wetter for longer / e.g a greater quantity of granulating solution added at a faster rate, a low fluidising air temperature and flow rate /slower evaporation) and larger droplets has been found to produce the largest granules.

It has been concluded that certain properties of the raw materials, for example hydrophobility, may exert a strong influence upon the process. In case when mixture of powder (e.g. hydrofobic and hydrophylic) is more hydrophobic the granual size are smaller. A lineral decrease in mean granule size was observed with increasing the hydrophobic material content.

From that what has been said above it is obvious a need to be able to quantify the degree of powder hydrophylicity/ hydrophobicity and to quantify the degree of wetting within a fluidised bed. An indication of the degree of wettability of a powder is given by a contact angle measurement with a specific liquid.

A contact angle Θ of 0° infers full wetting, 180° represents no wetting at all, thus a low value of Θ indicates a relatively easily wetted solid/liquid combination.

During the wettability of fine particles, or granules containing such primary particles, the liquid meets the solid at a contact angle Θ which is determined by the values of liquid, solid and solid-liquid interfacial tensions viz. γ_L and γ_S and γ_{SL} according to the Young-Dupre equation.

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\Theta \quad (1)$$

As the liquid penetrates the empty capilaries into the aggregates the solid-air interface (immersional wetting) and the wetting process will proceed more readily the higher the adhesion A which is defined as:

$$A = \gamma_S - \gamma_{SL} = \gamma_L \cos\Theta \quad (2)$$

The conditions for spontaneous penetration is $\cos\Theta > 0$ i.e. $\Theta < 90°$.

The type and level of wetting agent used in system is determined by matching the solid surface tension γ_S of the toxicant with the liquid surface tension γ_L of the wetting agent at the field dilution rate. The surface tension γ_L of water solution of wetting agent should be slightly less than the solid surface tension γ_S of the toxicant and the change in γ_L as a function of concentration approaches zero i.e. $d(\gamma_L)/d(\text{conc}) \cong 0$.

For calculating the γ_S the Antonov's rule is used according to which:

$$\gamma_{12} = \gamma_1 - \gamma_2 \quad (3)$$

Where: γ_1 - surface tension of liquid 1,
γ_2 - surface tension of liquid 2,
γ_{12} - interface tension between liquid 1 and 2

The Antonov's rule is not of general validity however, for non-polar substances in which only the dispersion forces are of significance for their surface tensions, Antonov's rule is experimentally valid (acc. to Fowkess' postulate). Then the following relations can be used for finding γ_S:

For drop sessile on solid, when all forces are in equilibrium the following equation is valid:

$$\gamma_S = \gamma_{LS} + \gamma_L \cos\Theta \quad (4)$$

taking into account Antonov's rule:

$$\gamma_{LS} = \gamma_L - \gamma_S \quad (5)$$

substituting equations (5) in equation (4) leads to:

$$\cos\Theta = (2\gamma_S/\gamma_L) - 1 \quad (6)$$

$$\gamma_S = \gamma_L(1+\cos\Theta)/2 \quad (7)$$

$$\gamma_{LS} = \gamma_L(\cos\Theta - 1)/2 \quad (8)$$

Measuring e.g. contact angles of droplets of water solution of sodium oleate in concentrations between 0.003 and 0.05% as well as their surface tensions, the surface tension of paraffin wax was calculated in the range between 24.5 - 26.4 and γ_{LS} from 11.3 (for 0.003%) and O (for 0.05%)

When γ_L is plotted v.s.cos Θ a substantially strait line is obtained.

Extrapolating this line to COS Θ = 1 (θ = 0) γ_L = 25.8

Any liquid having a surface tension of 25.8 dyn/cm or less will spread spontaneously on paraffin wax. γ_L = 25.8 is the limiting surface tension for spreading or in Zisman's terminology the critical surface tension. γ_C .

Critical surface tension γ_C for captan = 58.7 dyn/cm . In case of WDG the concentration of wetting agent should be such that at the field dilution rate the γ_L value should be slightly less of 58.7 dyn/cm

In selecting the wetting agents, for WDG-s the two characteristics should be tested : surface tensions of water solutions of wetting agents and the contact angles of their droplets sessil on pesticide surface. The first characteristic can be measured on du NOUY tennsiometer. The surface tensions as well as interface tensions between two liquids can also be measured by droplet weight method by using stalagnometers. Concerning the second characteristics, contact angle, there are several methods which can be divided on direct and indirect methods.

Indirect method a liquid drop resting on a plane solid surface.

From indirect methods the two have been extensively used for powders - penetration method and droplet height method.

The most commonly used is however the direct method.

In this method the contact angle is determined by constructing a tangent to the profile at the point of contact with the solid surface. This can be done on a projected, image or photograph of the drop profile or directly using a telescope fitted with goniometer eyepiece. Advantages of the direct method are that it employs relatively simple instruments, it can be used on solids having a small surface area and it requires only small amounts of liquid. Large errors do occur when trying to define the exact position of the liquid solid contact point and is therefore preferably used by experienced operators. The powdered toxicant is compacted in a Weber hydraulic press at 6000 kg/cm^2.

The droplets, are created by Agla micrometer syringe. The drawing of apparatus for measuring the angle of contact and details conc. measuring are described in the paper of L.Carino and H.Mollet entitled "Wetting of a powder by Agueous Solutions of Surface Active Agents" pub. in Powder Technology, 11(1975) 189-194.

The relation between cos ( ) and can also be found, according to Fowkes theory, from the relation.

By extrapoluting data to cos ( ) - 1 one has a method to obtain.

Values for some materials

Cellulose (paper)	42-46 dyn/cm
Polyethylene	35 "
Paraffin wax	25.5 "
$C_{36}H_{74}$	21.0 "
Fluorodode canoic acid	10.4 "

PLAN OF WDG EXPERIMENTS

Second series of exp: INFLUENCE OF DISP/WETT Agents ON SELFDISPERSIBILITY OF WDG.

Code of Exper.	CONTENTS % A	B	C	D	E_1	E_2	E_3	TESTED PARAMETERS Selfdispersibility v.g.; g; p.	Suspensibility %
V/1	40	40	X1	X4	0.5	-	-		
2	40	40	X1	X4	1.5	-	-		
VI/1	40	40	X1	X4	-	0.5	-		
2	40	40	X1	X4	-	1.5	-		
VII/1	40	40	X1	X4	-	-	0.5		
2	40	40	X1	X4	-	-	1.5		

Explanations of symbols and comments: X4 - the % which will be found in Exp. IV; E1, E2, E3, - different wetting agents- v.g. very good, g-good, p-poor.

During all experiments the following parameters will be fixed:
loading = 250 grams; amount of water - 80g; time of introducing of water - first 10 minutes; rate of air: minimum rate which will assure the fluidisation of bed; humidity of air, temperature of air: during the first 10 minutes = 25-30°C, during the next 30 minutes 60°C, during the next 10'-80°C.

PLAN OF WDG EXPERIMENTS

First series of exp. INFLUENCE OF DISPERSING/BINDING AG. ON DEGREE OF GRANULATION

Code of experim.	COMPONENTS %					TESTED PARAMETERS	
	A	B	C	D	E	FRACTION BETWEEN 14 AND 74 MESH	
						Before attrition test	After attrition test
I/1	80	-	20	-	-		
2	90	-	10	-	-		
3	95	-	5	-	-		
II/1	-	80	20	-	-		
2	-	90	10	-	-		
3	-	95	5	-	-		
III/1	40	40	X1	-	-		
2	35	65	X2	-	-		
3	65	35	X3	-	-		
IV/1	40	40	X1	2			
2	40	40	X1	5			

Explanations of symbols and comments: A - hydrophylic powdered material e.g. clay; B-hydrophobic material e.g DDT/silica (80/20) C-Lignosulphonates (different refined and nonrefined grades), D-binding agents, E-WETTING Agents, The C, D and E should be so matched to A, B or A/B that premix will be characterised by very good wettability and suspensibility. For preliminary test of attrition it is proposed to rotated granules in a sealed cylinder for a some period with such a rate of revolution that granules will be sliding each on other. X1, X2, X3 the % of C will be matched acc. to results of exp. I and II.