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PESTICIDES 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

United Nations Industrial Development Organization

Vienna

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ABBREVATIONS

Technical

CMC		-
CMC	-	Critical Micel Concentration
CRP	-	Control Release Pesticide
D	-	Dust
DD	-	Driftless Dust
EC	-	Emulsifiable Concentrate
F	-	Fungicide
Fm	-	Fumigant
G	-	GRanules
H	-	Herbicide
HLB	-	Hydrophilic Liophilic Balance
I	-	Insecticide
KL	-	Kiloliter
MPS	-	Micron Photo Sizer
MT	-	Metric Tonne
OM	-	Operational Manual
OP	-	Organo Phosphoric
PF	-	Pesticide Formulation
PGR	-	Plant Growth Regulator
PIE	-	Point of Inversion of Emulsion
R	-	Rodendicide
SC	-	Suspension Concentrate
TGP	-	Technical Grade Pesticide
TIE	-	Temperature of Inversion of Emulsion
TPA	-	Tonnes per Anum
WDG	-	Water Dispersible Granule
WP	-	Wettable Powder

Administration

AFCDC	-	
CSIR	-	Council of Scientific and Industrial Research
DGTD	-	Directorate General of Tech.Devl. Govt. of India
Excel	-	Name of Company
HICO	-	Name of company
ICAR	-	Indian Council of Agri.Research.
ISI	-	Indian Standard Institution

PDPI	-	Pesticide Development Programme India
PSSSU	-	Private Sector Small Scale Units
RC-G	-	Research Centre,Gurgaon
SAIC	-	State Agro Ind. Corpn.
SIDFA	-	Sr.Ind. Dev. Field Advisor
S.S	-	Small Sector
SSFs	-	Small Scale Formulations
UNDP	-	United Nations Dev.Programme
UNIDO	-	United Nations Indl.Dev.Organisation.

ACKNOWLEDGEMENT

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A. Methods of testing of some adjuvants and preparing of some PF-s

B. Lectures on Training Courses

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INTRODUCTION

One of the first object of the Pesticides Development Programme for India (PDPI), which is realised by Hindustan Insecticides Limited (HIL) under UNDP assistance, was to set up a Central R&D Complex at Dundahera, near Gurgaon in the State of Haryana. The specific aims of research work which are to be conducted in this complex are:

i)Support the formulations industry(especially of that ones belonging to Small Sector Industry) in manufacture, quality Control, safety packaging and to develop new pesticide formulations and methods of testing; ii) to find and utilise the local raw materials for pesticide formulations iii) scaling up and commercialisation of new production technologies iv) train the staff of Indian pesticide Industry.

As a part of its contribution, UNIDO in the period form 1.7.1981 purchased and delivered to PDPI Centre many modern and sophisticated machines and instruments;organised a dozen or so fellowships for Indian research workers in leading foreign research centres and provide a number of experts, as short term consultants, for project. The range of activity of previous experts concern : marketing of pesticides, application of pesticides, environmental protection, method of pesticide analysis, direction of development of new PFs. One item of expertise which has to be performed by author ,being in the setting up of pilot plant and prototype formulation production facilities for imparting suitable training for the counterparts and trainess. According to the Term of Reference the following programme was expected to be performed by author:

1. Identify which items of equipement, machinery and other facilities will be required for the project;

2. Recommend other infrastructure facilities requried for developing the production of specialised pesticide formulations;

3. Identify the manpower required;

4. Train the counterpart in the area of specialisation.

Because however, the term of reference had been prepared before 9.04.1982 part of the above programme (primerly point 1 and 2) has been already executed directly by the Indian experts working in the project. In relation to that, only that machineries and equipments which up till date were not purchased and which according to the opinion of author should be acquired had been identified and recommended to buy.

From the same reason the programme of consultancy has been expanded on the following subjects:

5. To elaborate the programme for the more important research projects.

6. To take part in preparing training courses organised for three groups of experts from Small Scale Industry.

(In the scope of the last point the author gave four lectures.)

The Technical Report presented is divided in three parts to facilitate its perusal. The first entitled "Findings and Recommendations" contains nine paragraphs, whereas the second one twenty one of recommendations. Their arrangement is not according to the priority but rather in accordance with arrangement of the first part of the report. In the third part, the author informs about his activity.

Other data referred to in the body of report have been included in the Appendices.

It is necessary to emphasise that the author is aware, that as the project is in realisation and has not been finished, it is not excluded that some of the conclusions, suggestions and recommendations given by the author would be achieved by the research staff of R&D Centre.

1. FINDINGS AND CONCLUSIONS

1.1 PESTICIDE INDUSTRY IN INDIA

Findings

Production and import of TGP-s for agriculture and public health

Demand of TGP-s in the years 1983-84 was assessed, by Working Group on Pesticides, on around 1.13.000 tonne.

As on April 1, 1984, the licensed capacity in the country for TGP-s was 99,155 MT. Out of this 97,765 MT has been installed. In addition to this, letters of intent for a capacity of 15,210 MT and DGTD registration for 16,980 MT have been issued, which are in various stages of implementation. Production achieved during the years 1983-84 was 58,798 MT.

Details for various kinds of TGP-s are shown in Table.1.

Table 1

Percentge of capacity of production for various kinds of TGP-s (as on April 1, 1984*)

Category of Pesticides	Licensed	Installed	Letter of Intent	DGTD
Insecticides	86,7	85.4	66.8	54,3
Fungicide	9,4	10.3	13,5	2,9
Herbicide	3,4	3.2	19.7	39,6
Others	0,5	1.1	-	3,2
Total %	100	100	100	100
Total MT	99,155	97,765	16,980	15,210

*Source: Min. of Chemicals & Fertilizers, Govt. of India.

Data concerning production and import of TGP-s are shown in Table 2 and Table 3

Table 2

Production and import of TGP-s in 1983-84*

	MT	%
Production	58,798	89,4
Import	6,978	10,6

*Source : Directorate of Plant Protection, Quarantine and Storage.

TABLE 3

Import of various kinds of TGP-s in 1983-84.

	MT	%
Insecticides	1346	19,3
Fungicides	265	3.8
Herbicides+PGR	1576	22.6
Acaricides	111	1,6
Insecticides for Public Health	3860	52,7
Total	6978	100

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*Source : Directorate of Plant Protection, Quarantine & Storage.

From the data regarding the import of pesticides it is seen that in the years 1983-84 the import was smaller by 20,0% and 35,5% than that in the years 1981-82 and 1982-83 respectively.

TABLE 4

Possible increase of production capacity of TGP-s in the coming future.

Category of Pesticides	Installed Capacity(MT)	Letter of intent+DGTD(MT)	Increase in %
Insecticide	81,035	19,360	23.9
Fungicides	9,795	2,550	26.0
Herbicides	3,085	3,000	97.2
Others	1,050	550	52.3
Total	94,965	25,460	26.8

Demand forecast for TGP-s in the years 1984-1990 are shown in Table 5.

TABLE 5

Demand forecast for TGP-s in the years 1989-1990*

Insecticides	93,720
Fungicides	19,182
Herbcidies	4,460
Others	1,810
Total	1,19,172

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*Source : Working group for VII Plan Pesticide information Vol,7, No.2 July-Sept, 1984.

Conclusions

i) Installed capacity of 94,965 MT in the years 1983-84 for the production of TGP-s was only partly achieved. The production, amounted to 58,798 MT, was only 62% of the installed capacity.

ii) Forecasted increase of installed capacity of production of TGP-s by 26,8% will assure the production of 1,20,426 MT. The latter is a little greater than that one of forecasted demand for TGPs, which in the year 1990 is expected to amount to 1,19,172 MT.

iii) By comparison of data in Table 4 and 5 one can see that the installed capacity is fully achieved in the case of fungicide production. However, the present rate of production can not cope with the rise in demand which is expected to be 19,182 MT by the year 1990.

1.2 PRODUCTION OF PESTICIDE FORMULATIONS

Findings

A range of conventional formulations is being produced and used in India. It includes seed dressing, often as WP-s and dusts: chiefly BHC and DDT as dusts and DDT and Carbaryl as WP-s. A high proportion of the fungicides is also formulated as dusts and WP-s. Besides these two common formulation EC-s, especially the O-P insecticides and granules, for example carbofuran and phorate, are also produced. Most of the herbicides are liquid formulations.

Manufacturing industry consists of a few firms who manufacture TGP-s which they sell on to the formulators. However, these manufacturers also formulate their own products. An unique feature of the Indian market is the very large number of local formulators, to became established by virtue of the government's policy of encouraging small scale industry for promoting competition. The position of these formulators is strengthened by the fact, that manufacturers of TGP-s are compelled to let non-associated formulators have 50% of what they make.

There are approximately 400 such small scale formulators. No company is involved however, in producing the newer kind of formulations such as e.g. driftless dust (DD-s) suspension concentrate (SC-s), water dispersible granules (WDG) or Control Release Pesticide (CRP).

The companies engaged in the manufacturing of formulations of pesticides in India are as follows:

Government Large House Producer of TGP-s or TGP-s and PF-s

Private Indian Large House Producers of TGP-s and PF-s

Private Indian Large house producers of PF-s

Multinational Large House Producers of TGP-s and PF-s

Multinational Large House Producers of PF-s

Small Scale Formulators.

State Agro Industries Corporations(SAIC)

The largest volume of pesticide formulations are dusts followed by wettable powders, emulsifiable concentrates and granules.

The production figures for formulations of pesticides are shown in Tables 6 and 7.

Table 6

Production figures in MT/KL for various kinds of formulations in 1982.

Formulation type	Production capacity	Total production	S.A.I.C	Small scale sector
Granules(MT)	90,00	17,083	-	900
Dusts	10,80,00	3,98,248	23,400	1,44,000
Wettable Powders(MT)	2,25,000	60,788	-	11,500
Emulsifiable Concentrates(KL)	2,70,000	26,713	700	5,900
Others	-	5,407	-	-
	16,65,000	5,05,239	24,100	1,62,300

Table 7

Production figures in MT/KL for variou formulations based on pesticide category (in 1982)*

Formulation Type	Insecticide	Herbicide	Fungicide
Granules(MT)	12,773	1350	-
Dusts	3,91,340	-	6908
Wettable Powder(MT)	54,483	695	5,609
Emulsifiable Concentrate(KL)	25,251	1,302	160
Others(MT/KL)	2,889	1,239	339

Conclusions

1. The production of various PF-s in the year 1982 was much lower than installed production capacity. The percent achievement of installed production capacity for particular PF-s was as follows:

For total PF-s - 30.34%, for granules 15.6%, for dusts 36.9%, for wettable powders 27.0%, for emulsifiable concentrate 9.9%.

ii) Of the total production of PF-s in 1982, 63.1% was produced by large industrial houses, including multinational sector and of the rest, 32.1% and 4.8% were produced by small scale sector and S.A.I.C. respectively.

iii) The installed capacity for the production of PF-s is quite enough not only to process the TGP-s, demanded for the year 1990 for different PF-s, but also to produce some of the newer PF-s. Some of the PF-s such as driftless dust, and water dispersible granules can be produced on the existing production lines with addition of some not too expensive local machines, for example: in the case of DD-s AIR SEPARATOR for separation of small particles of dust and in the case of WDG-s DISK, PAN or eventually FLUIDISED BED GRANUALATOR. For the work with suspension concentrates the CHANGE-CAN MIXERS and eventually (but not always necessarily) the BEAD or PEARL MILLS, the machines commonly used e.g. in paint industry. Similar mixers as above can be used for production of concentrate emulsions. For production of microemulsions no special machines are necessary(see recommendation 1).

1.3 STANDARDS FOR TGP-s AND PF-s

Findings

Indian Standard Institution (ISI) has brought out more than 200 Indian Standards covering technical as well as formulated pesticides. These standards are generally formulated based on research and development carried out in the country. The specifications for TGP-s and PF-s are prepared by Pest Control Sectional Committee, AFCDC, which is composed of representatives of Ministry of Agriculture, Ministry of Defence, Ministry of Health and Family Planning, Several Research Institutes, and some of large house National and Multinational pesticide producers. The draft of the specifications elaborated by the above Committee is to be approved by the Agricultural and Food Products Division Council and the Chemical Division Council.

In the preparation of standards, due consideration has been given to the provisions of the Insecticides Act and the Rules framed thereunder.

The Indian Standards for TGP-s and PF-s decide the specifications for a required quality and suggest methods of sampling, testing, packaging and marking of products, very precisely. In this scope IS-c does not differ from international specifications as e.g. WHO, FAO or CIPAC. In contrary to international standards, IS-s allowed however the use of different simple analytical methods for quantitative determination of active ingredients, due to the fact that some of producers of PF-s are not equipped with modern analytical instruments.

In some of IS-s, there is no requirement for testing of products after accelerated storage. To get however registration for a product, the accepted and required properties of product should not be changed during 2 years, and in some cases during one and a half, one or even half a year. The producer of TGP-s or PF-s can use on the packaging of products ISI mark. Such marking indicates that the product meets ISI specification. However, it can be possible that there is no difference between the properties of products for which the ISI mark has been granted and of that ones which are not authorised to use it.

Conclusion

Each producer of pesticides which are admitted to the market may use ISI mark only after an appropriate payment. These marks however do not point out as which product is better or the best one (see recommendation 3 and 6)

1.4 QUALITY CONTROL OF PF-s

Findings

For testing of TGP-s as well as PF-s the State Insecticide Laboratories have been set up.

In each state of India there is at least one such laboratory and in some states there can be several such labs.

The Insecticide Inspector is authorised to draw samples as well from the factory as from the sellers of pesticide. The analyst is obliged to check the conformity of properties of product with approved specifications.

If it is found not as per specifications the producer is called to account and the selling of this bad product is banned.

It is happen that only the quantitative determination of active ingredient is done and not always the full physical parameters of PF-s are tested. There is no Central Register of factors responsible for not proper quality of pesticide products and for that reason it is very difficult to make out whether the amount of products of bad quality present on the market is serious, what of parameters most frequently differ from requirements and which kind of products and of which producers are most frequently complained.

Conclusions

Lack of statistical data concerning the defects of pesticide products being in trade turnover on Indian market, will make serious hindrance in eliminating the bad products from the market and the same improve the quality of crop protection, as well as sanitary of human being and domestic animals(see recommendation 7).

1.5 QUALITY OF RAW MATERIALS FOR PF-s

Findings

In contrary to TGP-s and PF-s there are no IS-s for mineral carriers, organic solvents, surface active agents and other adjuvants used in the production of pesticide formulations. The adjustment of quality parameters for these products are mutually done (but not always) by suppliers and formulators. However these adjustments not always take into account all parameters which can have influence on the quality of PF-s.

Some of the raw materials as e.g. mineral carriers, being of natural origin, are not refined or processed in other way, and their parameters may vary from batch to batch. Similarly, commonly used solvents used in EC-s production are technical products and the physicochemical properties of particular solvent can be different from batch to batch. Also the emulsifiers, which are delivered to formulators as a mixture of anionic and nonionic components, can have different characteristics from batch to batch. The pesticide formulators, especially those from the Small Scale Sector, are not in a position to control all the important parameters of raw materials.

Conclusions

i) Variable properties of some of the raw materials used for production of PF-s such as mineral carriers, solvents and emulsifiers can cause serious difficulties in production of PF-s of demanded quality standards.

ii) Uncontrolled properties of some of the carriers, solvents, emulsifiers and other adjuvants, used in production of PFs, can reveal their harmful effect on quality of PF-s, only after some period of time, when the product is already distributed in the market, or when it is in the hands of farmers, or when it has already been used.

These disadvantageous and harmful effects can be due to the deterioration of active ingredient, which results in its lower activity, higher toxicity, quick separation of floculated suspension or emulsion and bad distribution of pesticide after spraying, phytotoxity etc.(see recommendation 2).

1.6 RESEARCH AND DEVELOPMENT

1.6.1 Indian Research Centres dealing with pesticides.

Findings

The R&D work related to pesticides is being carried out in CSIR laboratories, ICAR laboratories, Agricultural and other universities and R&D Centres of Industrial Houses.

In particular, R&D Centres of CSIR are engaged in the following areas of research.

Name of R&D Center	Kind of R&D
Regional Research Laboratory in Hyderabad	Synthesis, analysis & engineering(Pilot Plant)
National Chemical Laboratory in Pune	Synthesis
Regional Research Laboratory in Jorhat	Synthesis
Central Food Technological Research Institute in Mysore	Residue analysis
Central Drug Research Institute in Lucknow	Toxicology
Hopkins Research Institute in Bombay.	Toxicity

Much of the work on pesticides toxicology evaluation on pests is being carried out in ICAR laboratories and Agricultural Universities. In Indian Agricultural Research Institute, New Delhi, some research work is being conducted on new PF-s. All the large Industrial Houses, government and private, possess excellent infrastructural facilities for R&D work.

The wide scope of considerable work concerning toxicology of pesticides, their residues and their quality control is being carried out at Central Insecticide Laboratory in Faridabad. The Center employs about 100 persons and is equiped with modern research apparatus.

The main problems as concern PF-s which are put in the future plans of this centre are given below:

i) Physical and chemical analysis of PF-s against accepted standards.

ii) Studies on deterioration of pesticides on storage and methods to prevent the same.

iii) Development of new analytical methods and critical evaluation of the existing techniques.

iv) Development, in collaboration of other infrastructures, of safer, cheaper and more effective formulations of pesticides.

v) Training of analytical chemists for Regional and State Insecticides Laboratories.

vi) R&D work on modern instrumental methods for pesticides analysis.

vi) Training of analysts in modern techniques of pesticide analysis.

Conclusions

There are quite a lot of Government institutions which are carrying out research on different aspects concerning pesticides. A large number of them are engaged in laboratory and field tests of pesticides, in analysis of pesticides and in toxicological tests. A few are engaged in synthesis and engineering problems and very few with the problems concerning production and testing of PF-s. The research work conducted on PF-s is however, fragumentary, and not comprise any of questions, solution of which would seriously improve the quality of PF-s as well as economy of their production. The more complete work is probably done by Industrial Houses Laboratories. Considering however competition between these companies it is normal, that the results of their researches are not always rendered to, and the same utilised by, other producers of PF-s.

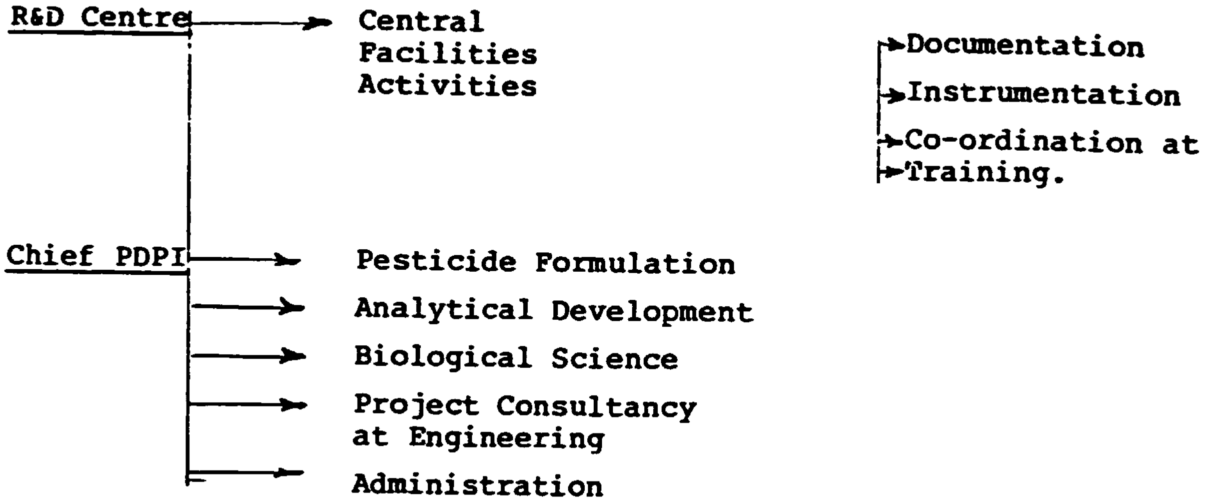
The SSF-s are in general using receipes of pesticide formulations elaborated and rendered to them by suppliers of TGP-s. But as already has been mentioned the raw materials used for production of PF-s have in general no standard quality and very often it is necessary to modify their properties. But this procedure is not possible without having properly equipped laboratory as well as good knowledge and experience in the scope of PF-s.

Taking into account the above mentioned difficulties and drawbacks in production and development of PF-s, at least in some sectors, a new Research Center for PF-s development by Government of India and UNIDO has been called into living. Development of comprehensive research on PF-s in this Centre will fulfill the existing gap and would act as a guide in bringing improvements in quality and effectiveness of all PF-s produced by SSF-s and introduced on the market as new generation of PFs.

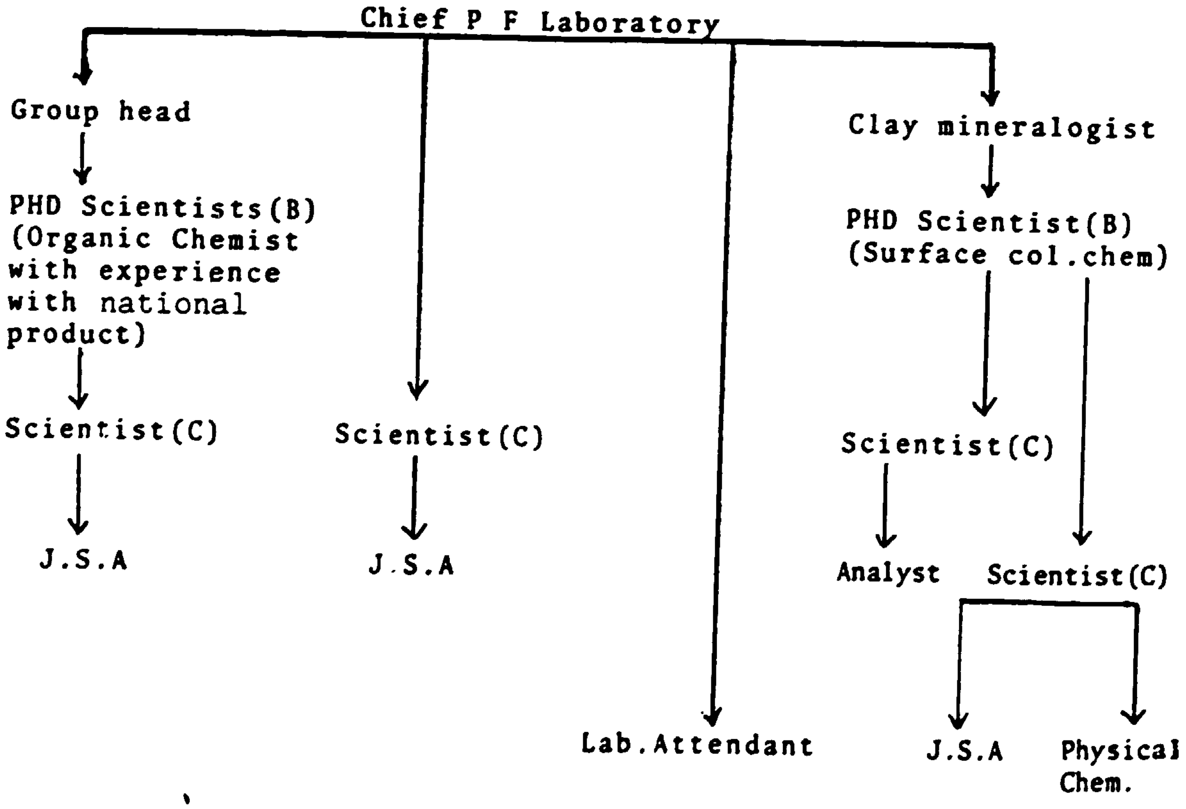
1.6.2 Organisation of PDPI Centre in Gurgaon

Findings

The organisation of R&D Centre as well as PF-s Laboratory is as follows:



PF-s Laboratory



Conclusions

i) The organisational scheme of R&D Centre mentioned above is rather general and is not giving idea about the tasks and scope of activity of particular Division, Section of Sub-Section. It is not clear as to which division the Pilot Plant is subordinating.Most probably it appears to be to the Section or Division of Project Consultancy and Engineering but in the Scheme it is not clearly shown.(See recommendation 9)

1.6.3 Scope of activity of PDPI

Findings

There is no official document yet in which the short and long range tasks for P&R Centre would be presented. From the discussions however with the senior scientists of the Center and from own considerations the following objectives can be precised:

i) Testing of PF-s which are distributed in domestic market, specifying those PF-s not meeting the prescribed quality and to find reasons of the same.

ii) To give technical advice and assistance to the small pesticide formulatiors, localized all over the country, regarding improving the quality of some of their products and lowering their cost of production.

iii) To investigate carriers, solvents, surface active agents and other domestic PF-s additives and to decide which of them are suitable for production of PF-s of particular technical pesticides.

iv) To elaborate such simplified methods of testing of PF-s adjuvants which should be easily adopted by SSEs.

v) To elaborate the Vademecum (guide book) for Pesticide Formulators in which the reasons for not being able to acquire enough good quality of PF-s should be clarified and conditions of producing good products should be presented.

vi) To elaborate a range of new spray adjuvants which when added to the suspensions or emulsions, would increase the effectiveness and economy of usage of PF-s.

vii) To claculate the cost of production and cost of performance of new PF-s.

ix) To elaborate data about the scope of usage of new PFs and their advantage over the ones being currently produced.

x) To adopt elaborate chemical and physicochemical methods of analysis of TGP-s and raw materials used for the productin of TGP-s and PF-s.

xi) To carry out the laboratory, green house and small field tests of the new PF-s.

xii) To train the SSF-s in production and testing of modern PF-s.

xiii) To produce some of the pesticides of high purity used as standards for analytical work.

xiv) To carry out the laboratory work on technology and recipes of PF-s used in pressurised aerosol containers.

Conclusions

The scope of research projects presented above ought to be treated as a prospective one. Its full realisation will depend not only on the well equipped laboratories and highly qualified research personnel but also on the methodology of research posses by them and adopted for different kinds of problems.

1.6.4 Space utilisation for work on PF-s

Findings

There are two rooms already used for work with PFs, of the global area of about 60m². In both of them the following short comings have been observed:

i) The floors, benches and instruments were covered by dust.

ii) The apparatus for grinding, mixing and testing of powders were localised in the same place. The mills which, during work, create dusts were not placed in protective plastic boxes.

Conclusions

i) There are in PF-laboratory several instruments of high precision which were not protected against dust and dirt and because of that are subjected of faster waste.

The origin of dust can be the mills located at the same place or even openings where exhaust fans are installed.

ii) It seems that the space provided for PF-s research is not big enough for all the work which is planned to be done, and also that ones which are expected to be done in case of full operation of Pilot Plant.
(See recommendations 11,13 and 14)

1.6.5 Employment in PDPI Centre

Findings

The R&D Centre in Gurgaon is in the course of organisation and only part of specialists are currently engaged in the work. All of them have full qualifications to carry out research work or to implement its results to practice. The selection of people is very clear sighted and possiblity of selection of really good ones is very considerable. Each of scientific worker has documentary evidence of professional acheivements. Several research workers have experience of carrying out research on practical problems in international research institutes. All of them are very enthusiastic in their work. The Research Center employes the following groups of employees - Ph.D-s-9; M.Sc-1; Engineers-3; B.Sc-s-4

The employment in particular section of PDPI is as follows:

Division	Posts
Chief of PDPI	H and R&D.M (1)
Centralised Facilities & Activities, Head	R&DM (1)
Documentation	L (1)
Central Instrumentation	I.S(1)+E.E.(1)
Coordination & Training Cell	G.L.(V.1)
Pesticide Formulation	G.L(1) + A (3)
Clay Mineralogist	G.L.(1) + A (V.1)
Analytical Development	G.L.(1 Vacant) +
Biological Sciences	G.L(1)+J.E(1)+F.S.(1)+L.A(1)
Project Consultancy & Engineering	G.L.(2) + S.S.A(1)
Administration	O.S(1) + A.S(1) + C (2)

Abbrevations explanation

A - Analyst; A.S. Accounts Superintendent; C-Clerk; C.E-Chemical Engineer; F.S-Field Supervisor; G.L.-Group Leader; H-Head; I.S-Instrument Supervisor; J.E-Junior Entomologist; L-Librarian; L.A. Laboratory Attendant; O.S.-Office Superintendent; R&DM-Research & Development Manager; S.S.A.-Senior Scientific Assistant.

Conclusions

1) The Pesticide Formulation Division is the basic research unit of PDPI. In this division the following projects will be conducted:

Elaboration of method of testing and criteria of selection of raw materials and adjuvants used for production of pesticides.

Improvement of quality of currently produced PF-s.

Elaboration of compositions and method of producing of new types of formulations as driftles dust, suspension concentrates, emulsion concentrates, microemulsions, control release granules, water dispersible granules.

Collaboration with Pilot Plant as well as with other institutions dealing with PF-s and their testing.

Preparing lectures and demonstrations for training course.

It is obvious that the above enumerated tasks will not be realised by such a small group of workers as is currently employed in this division.

ii) Taking into account the range of work which will be carried out in PDPI as well as in R&D from one side and very good outfit of Analytical Laboratory from other, it is clear that the amount of employed people is absolutely not enough - not only to realise the tasks resulting from the work of different divisions but also not to the full and proper utilisation of existing very expensive, modern analytical instruments. (See recommendation 10)

1.6.6 EQUIPMENT IN PDPI CENTRE

Findings

The equipment for laboratory and pilot plant work which already have been purchased are listed in table 8 and 9.

Table 8

LIST OF EQUIPMENT

(Already purchased for PDPI)

1. PESTICIDE FORMULATION LABORATORY

No.	Description	Supplier
A.	FOR PREPARATION OF PF-s	
1.	Colloid Mill "ICM"	Alpine Ang, FRG
2.	Lab.Grinding Mill "ISIOK"	Condux, USA
3.	Homogenizer	Schott, FRG
4.	Lab.Tumble Mixer "529/0"	Netzsh G,6H,FRG
5.	MIcronizer 4	Sturtevent Mill Co.,USA
6.	Dyno Mill	
7.	Extruder Type Granulator Mod EXK-1	Dudji Paudal,Japan
8.	High Efficiency Lab.Kneader	JKA-Werk,FRG
B.	FOR TESTING PF-s	
1.	Auto Fraction Collector "Linearri"	Reichert Chemic Technik,FRG
2.	Rotavapor Evaporator "RE-120"	BUCHI, FRG
3.	Selective 5000 Ton Analyser PM 123509"	Beckman, US
4.	"Spectronic 20" Spectrophtometer	Bausch and Lomb,US
5.	Redwood Viscometer	Karl Kolb, FRG
6.	Homogenizer	SCHOTT, FRG
7.	Analytical Balance Mod.2434	Sartorius, FRG
8.	Top Loading Balance	SARTORIUS, FRG
9.	Moisture Determination Balance Mod.No.6010H	Ohaus Scale corp.,US
10.	Refractometer Abbe "3L"	Bausch and Lomb,USA
11.	Automatic K-F Titrimeter Mod.392	Fisher Sci.Co. USA
12.	Potentiometric Titrator Mod.DL 40 RC	Mettler, CH
13.	Micron Photosizer Mod.SKN-1000	Scishin Ltd., Japan
14.	Powder Characteristic Tester	Hosokawa Iron Works Ltd.,Jap.

Table 9

LIST OF EQUIPMENT
(Already purchased)

2. **PILOT PLANT**

No.	Description	Suplier
1.	Lab Grinding Mill LV15M	CONDUX, US
2.	Lab.Blast Mill "CGM100"	CONDUX, US
3.	Hammer Mill "LHM 20/16"	CONDUX, US
4.	Cone Crusher	Siebtechnik, FRG
5.	High Efficiency Lab. Kneader Mod. HKD	JKA-Werk,FRG
6.	Lab.Ball Mill "1226C"	Guwina-Hofman,FRG
7.	Ball Mill	Guwima-Hofman, FRG
8.	Universal Lb.Mixer Mod. NTHK 15	G.Papenmeyer GmbH,FRG
9.	Mixer "FM50/12	Lodige, FRG
10.	Ultraplex Universal Mill, B160 UPZ	Alpine AG.,FRG
11.	Micro-Jet Mill Mod 8MJ	Fluid Energy Proc & Eq.Co USA
12.	Air Compressor	Champion, US
13.	Ribbon Blender, "M-20s"	S. Hoves,US
14.	Ultrafine Mill, US"	Society Ultrafine,France
15.	Filling Machine "AJ-232"	Nat.Instr.Co.,USA

Conclusions

i) Concerning laboratory equipments

As it is seen from the lists 8 and 9, the list of laboratory equipments is considerably modest in comparison with the list for pilot plant. It is not in accordance with the rules, because the main parameters, essential for technology of formulation of pesticide should be mainly established on laboratory equipments, whereas the pilot equipments are used for checking the established parameters in larger scale and for preparing the large amount of products for field tests. To fulfill such a function the pilot plant equipments should have their equivalents among the laboratory equipments as e.g. in the case of air-jet-mill. However, some of pilot equipment like e.g. Ultraplex Universal Type 60 UPL, Ultrafine mill, Lodige mixer, Ribbon Mixer have no laboratory equivalents. Taking the above into account, as well as the fact that for more efficient work some of additional equipments will be needed it is proposed to made up the existing laboratory equipment.

ii) Concerning Pilot Plant Equipment

Similarly as in the case of laboratory outfit there is no equipment on which the technology of new PF-s could be checked or find out and on which larger amount of products, for field trials could be prepared.

iii) Concerning testing apparatus

There is lack of several, very important apparatus necessary for testing of PF-s. One of these is that one for determination of particle size and stability of suspension. The existing Micron Photo Sizer is not the proper one. The procedure of testing of sample is tedious and time consuming. Besides, the some required conditions for testing of samples, limited the informations only to the particle sizes where as more important are others like suspensibility and tendency to flocculation of tested suspensions, rate of desintegration of WDG-s. Such informations can be easily however obtained by using Sedimentation Balance . Another disadvantage of using MPS- is, that only very diluted suspensions can be tested and some times the use of organic solvents (not water) are to be used to prepare suspensions. In the case of testing pesticides the use of these solvents is not advisable because of solubility of pesticides in the solvent. Also the dilution of suspension can not be recommended in the case of PF-s, as a very diluted suspension of PF-s has a tendency to flocculate.

In the case of Sedimentation Balance the measurement is made in the range of suspension concentration similar to that one used in practice and the water of different "hardness" and different temperature can be used for measurement.

The other testing instruments needed for work with PFs are that one for quick testing of average particle size and surface area of solid particles and that one for separation of particular fraction of particles.(see recommendation 12).

1.7 ENVIRONMENTAL PROTECTION

Findings

There is no ventilation system both in the pilot plant as in the laboratory and there is no installation for sewage treatment. The electrical installations is not explosiv-proof.

Conclusions

All dust filters connected to the pilot and laboratory mills are localized inside the laboratory or pilot plant. Such system is dangerous for workers, because of toxic atmosphere, as well as for workers and all equipment and buildings, because of eventual possibility of explosion and fire.(see recommendation 14).

1.8. SCOPE OF WORK ON PF-s IN LABORATORY AND PILOT PLANT

LABORATORY

1. To find carriers, solvents, surface active agents and other adjuvants for particular PF for a chosen TGP.
2. To find method and apparatus for getting the product of best quality.
3. To assess the quality of product.
4. To assess occupational safty while working with PF.
5. To calculate preliminary cost of raw materials and packaging.
6. On the basis of the results of biological testing of PF to calculate the cost performance of using new PF in comparison to the cost performance of the one which is already being used.
7. To prepare a report of research for Pilot Plant with all data indispensible for check and eventual modify the parameters of process.
8. To check eventual modification sugested by Pilot Plant.
9. To test product prepared in Pilot plant.
10. To prepare, in eventual cooperation with other division, the paper for publication and if possible patents.
11. To carry out some of interwential work commissioned by other insitutions.

Pilot Plant

1. To check a method proposed by PF laboratory and find eventual faults of method because of scale up.

2. To propose modifications (concerning parameters of method or apparatus).

3. To check proposed modification given by PF-s laboratory.

4. To calculate the preliminary cost of production.

5. To elaborate brief foredesign.

6. To prepare biger amount of product for field tests.

7. To prepare, in eventual cooperation with other division, the papers for publication and if possible patents.

8. To carry out some of interwential work commissioned by other institutions.

1.9 PROJECT PROMOTION

The lack of electricity in R&D Centre Gurgaon made, for nearly 4 months of my mission, impossible to begin regular work on some of more important projects, by PDPI personnel. After this period the research work also cannot be carried out by them in full scope, because they were engaged in organising three training programmes as well as preparing several lectures. It is necessary to emphasise at this junction that all training courses were prepared very efficiently, what taking into account, very short intervals between succeeding trainings, was a result of organising capability of R&D Centre management. This capability as well as very good disposition of scientific personnel to rather difficult type of research work, give hope that planned research projects will be performed equally efficiently. However for fulfilment of this hope several drawbacks, which will hamper quick progress, should be if possible, rapidly removed. These drawbacks are the following:

i) Lack in PF-laboratory several basic instruments which made impossible to perform full cycle of ne ry tests; they are : Brookfield Viscometer; Sedimentation ce and Fisher Sub-sieve Sizer.

ii) Lack of different raw materials and ready PF-s of high quality, which could be used as a standards for similar products.

iii) To modest scientific personnel in PF-s laboratory and in Analytical laboratory.

The faster the above main drawbacks will be removed the faster will be positive results of work and full utilisation of specialised, very modern, very sophisticated and very expensive instruments and machines with which R&D Centre in Gurgaon have been equipped.

Assuming however that after some, not too long period of time, R&D Centre will be equipped with missing research instruments and chemicals, as well as additional Scientific personnel will be recruited, can we be sure that the progress in research work will be fast and effective? I think that probably not if the next conditions will not be fulfilled.

iv) Well constructed plan of research work in which the aim of particular projects would be precisely given. The tasks of the particular projects should be supported by full analysis of the problem. It would be desirable if such a plan could be assessed by some of authorised Indian experts from institution of related to PDPI speciality.

All experiments should be carried out in such a way that, when the project is over, the results be published or patented either partly or fully. This condition is obvious, but unfortunately very often is not realised. It happens that because of use not improper research technique, specific for each field research, or lack of precisly planned experiments, the results, of often long-lasting investigations, can not be fully utilised.

2. RECOMMENDATIONS

2.1 The laboratory and pilot plant studies on the methods of production of new pesticide formulations, more safe, more effective and more convenient to use, should be carried out.

The higher cost of some of the new PF-s, in comparison to that ones currently prouced, cannot be an argument against production of the former. This may be explained as follows:

The performance cost of the new formulations, i.e. cost of production + cost of usage can be lower, in spite of the higher cost of production, than the cost performance of the conventional PF-s.

Moreover, production of new, better products is expected to be more expensive in the beginning of manufacturing, but after some period of time its cost goes down. The new PFs should be prepared in bigger amounts on Pilot Plant Scale and then should be distributed to different users for testing and assessment.

2.2 The intensive work in testing of indigenous mineral carriers, solvents, emulsifiers and other adjuvants should be carried out and criteria of selecting them for different PF-s should be worked out.

It is recommended to collect samples of raw materials of high quality from different foreign countries. These samples can be used as standards for comparison of their properties with that ones of indigenous origin. By using the standard raw materials of high quality, the standard PF-s should be prepared and then, by using domestic raw materials, an attempt should be made to prepare products of similar high quality.

It is also necessary to develop simple methods of testing of raw materials and to find out the relationship between their properties and the quality of ready PF-s.

2.3 Samples of the PF-s of the world renowed companies should be collected and their characteristic properties should be estimated.

These mentioned samples should be used as developed standards for the new PF-s which will be developed by the workers at PDPI. In general, the product of world renowned companeis is characterised by much better properties than required by internatinal standards. Owing to that they are in general more effective and more purchased then other products of average quality.

2.4 The process of unit operation which are involved in PF-s production like; milling, powders mixing, paste mixing, granulation, fine particles separation, spray drying etc. should be studied by using different types of pilot machines.

It is suggested that the model mixtures of different carriers and some of the non-toxic substances of characteristics similar to pesticides, e.g. some mixture of natural waxes of different hardnes and different melting points, should be used for this purpose.

For preparation of model mixtures having different melting points and different hardness, a wax of high melting point, e.g. Carnauba Wax, can be mixed with the other one of low melting point e.g. paraffin. The complete results of studies will be getting by using **factorial design experiment.** The results of these studies will enable one to carry out pilot plant work on PF-s of particular TGP-s as well as to design production line for this products.

2.5 To get full information about the possibilities of SSPs to starting the production of new PF-s as well as about their difficulties with the current products, it is recommended to prepare and distribute the questionnaire with appropriate requires. The questionnaires should be annonymous. Information such as, the kind of machinery and type of raw materials used. methods of testing of raw materials and ready products, and problems which the producer met with production and quality control should be selected in these questionnaires.

2.6 For bringing out improvement in the quality, safness and effectiveness of usage of PF-s it is recommended to introduce the trade marks which would be put on the packing of PF-s.

The "Q" mark for products having quality similar to that of selected world best products and the "1" mark for products having quality better than what is required by IS-s, can be used for this purpose.

This grading system of products should however, not be a reason of increasing the price of the products.

Introduction of the proposed trade marks may generate competition between companies and favour the production of high quality PP-s.

2.7 In order to monitor the quality of PPs, data produced by analysts of CIL, on quality of PP-s should be compiled, preferably in Computer Based Information System, and be distributed to the interested institutions.

Taking into account that PDPI is obliged to find out the reason of bad quality of products, as well as the methods to improve their quality, it may be said that the most suitable location of proposed information system would be in PDPI.

2.8 The programme of colaboration of PDPI with other laboratories of CSIR and ICAR should be developed .

The colaborative work should be carried out on the following areas of research :

Chemical and physical methods of testing of PP-s and their residues.

Laboratory, greenfield and field tests of new formulations.

Preparation of new formulations.

Taking into account that some of the well organised laboratories are already carrying out work concerning the biological assessment of PP-s, as well as the residues analysis, this kind of work should be given lower priority in PDPI. The scope of cooperation should be elaborated and accepted by both sides.

2.9. It is proposed to elaborate for each division of PDPI the general scope of tasks, in such a away, that prospective improvement specialisation specification of division and persepective growth of specialisation of people, will be shown. The scope of internal cooperation between divisins should also be encouraged.

2.10. Both pesticide formulation laboratory as well as Analytical Laboratory should be strengthened by appointing qualified personnel. To realise the intentional programme of R&D the following workers should be recruited.

	Ph.D	M.Sc	B.SC
For work on granules dispersible granules and driftless dusts	1	-	2
For work on Control Release Pesticides	1	-	2
For work on microemulsion	-	1	-
For analytical work	2	2	2
For testing of surface active agents	-	1	-
For testing of mineral carriers	-	1	-

The person who will be engaged in testing of surface active agents should be trained in some of Indian manufacturers of these products e.g. in HICO in Bombay.

These laboratories are very well equipped with very modern and sophisticated instruments (See appendice F).

The work on Control Release Pesticides should be carried out in close collaboration with the specialists from Institute for Polymers and Plastics.

2.11 The actual space for laboratory work on PF-s and for testing raw materials should be increased, to have at least three additional laboratory rooms of full area of $60m^2$.

2.12 The following instruments and machines should be purchased:

For laboratory work:

i) Contraplex Labormill(Alpine)
ii) Laboratory lodige Mixer
iii) Laboratory Granulator (Aeromatic Co.)
iv) Minispray Dryer (Labor Co.)
v) Erweka Agregate
vi) Aeromatic bath and continuous fluidized bed processing units for drying, spray granulations, agglomeration, instanization and coating.
vii) Zig-zag separator for separation of solid particles in the size range 1-100 micrometers(Alpine)

For testing of PF-s..

i) Air jet sieve 200 (Alpine)
ii) Sedimentation Balance(Metler or Sartorius)
iii) Sub-sieve sizer with accessories(Fisher Sci.Co.)

For Pilot Plant

i) Zig-Zag separator for separation of particles in the size range 1-100 micrometers(Alpine)

ii) The Pearl Mill, but the same or similar to that ones which are used in India e.g. in paint industry, most probably the domestic production.

iii) The Pan Granulator

iv) The Fludized Bed Granulator (Uni Glatt System)
v) The Change Can Mixer

2.13 It is necessary to install in PF-s laboratory rooms airconditioners instead of fans. This will enable all the

instruments being protected not only againsts dusts but also against harmful humidity, particularly during the wet season. It is proposed to localise the set of apparatus used for grinding, mixing, granulation, separation and the like in separate laboratory room and all instruments used for testing of PFs is another one.

2.14 **All points where the danger of dust hazard can taken place should be connected to Central Exhaust installation.** The air polluted with dust of pesticides should flow through venturi absorber or column absorber sprinkled with circulated liquid agent e.g. the water solution of sodium hydroxide. The sewages from column or Venturi absorber together with the other ordinary sewages should be conditioned in the basin-container by alcalisation and then by oxidation e.g. with the water solution of hypochloride. The sewages treated in such a way will be filtered from sediment and then directed to sewage system. The laboratory and pilot plant should be equipped with the explosion proof electrical installations.

2.15 **The simplified easily understandable operational instructions about all the laboratory instruments and apparatus should be elaborated and placed close by.** The personnel operating the instruments should have full understanding of the operational instructions.

2.16 **Taking into account that some of the already purchased analytical instruments such as Thermal Analyser, Freeze Dryer, Electroforeses equipment, Aerosol Generator, Colloid Mill, Alpine, will be used rather very seldom, it is proposed to settle the possible scope of their utilisation (not necessary for pesticide work) and eventually to use them also on commission for other interested institution.** Especially for the first two, very expensive instruments such an action is recommended.

2.17 **The procedure of getting opinion about the research plan prepared by PDPI, as well as about the results of particular projects, made by Indian experts from outside of PDPI, should be formulated.**

2.18 **In the progrmmes of training of research workers abroad, as well as in the progrmmes of consultancy of UN experts, more attention should be given to methods of planning experiments and to specific methods of conducting of experiments as well as testing of materials.**

The same recommendations concerns the training course organised by PDPI for representatives of Small Scale Formulators.

2.19 It is recommended to one of PDPI research worker to participate in training in HICO company how to test surface active agents. During his training he should also try to get full information about two instruments used in this laboratory.

- Preparative Liquid Chromotograph 5000 assigned for preparation of highly pure compounds upto 150 grams. This instrument could be eventually used for preparation of analytical standards of pesticides.
- HP/TLC scanner for quantitative Thin Layer Chromotography.This instrument, if not too expensive. could be purchased by PDPI and later on eventually recommended for Small SCale Formulators.

2.20 Taking into account the important, leading position which in relatively short time the R&D Centre in Gurgaon should attain in India, it is recommended to send regularly the research workers of Centre on international symposia and conferences concerning pesticides, organised by such associations or organisations as CIPAC, FAO, WHO and the like.

2.21 The R&D Centre in Gurgaon should enter in scientific and technical collaboration with some of related institutes from abroad. Such collaboration would be especially fruitfull in the beginning period of work. Author is convinced that such collaboration could be possible e.g. with Polish Institute. For Organic Industry in Warsaw, which from 35 years is working on pesticides and have considerable achievements on this field of research and development.

(see also p. ix on page 38)

3. ACTION

3.1 RESEARCH PROGRAMME

Together with my counterpart Dr. Ramdas, the research programme for the forthcoming period of time had been prepared. Within its limit the following investigations are proposed:

i) Testing of the following physical, physico-chemical and chemical properties of components of PF-s.

Mineral carriers

- particle size distribution;
- sorptive capacity;
- flowability;
- compressibility;
- pH of water suspension;
- acidity (pKa) of surface;
- content of heavy metals;
- wettability;
- suspensibility;
- compatibility with pesticides.

Solvents

- ignition temperature;
- acidity;
- moisture content;
- refractive index;
- density;
- water numbers;
- solubility of pesticides;
- compatibility with pesticides;
- emulsification ability;

Emulsifiers

- HLB (Hydrophylic Liophylic Balance) by different methods;
- temperature and point of inversion of emulsions (TIE and PIE)
- surface tensions of water solutions of emulsifiers;
- critical molecule concentration (CMC) in water and solvent solutions;
- moisture content.

Dispersing and wetting agents

- surface tensions of water solutions;
- CMC in water solutions;
- absorptibility on mineral carriers and pesticide;
- dispersibility, suspensibility and wettability of mineral carriers and their mixtures with pesticides.

Thickening agents

- dynamic viscosity of water solutions;
- compatibility with pesticides.

i) METHODS OF PREPARINGOF SOME NEW PF-s

Suspension concentrate(SC) of Carboxin

- Selection of dispersing and wetting agents;
- finding of optimal parameters of milling process;
- selection of thickening agents;
- testing of flocculants;
- testing of viscosity and stability of ready product;

iii) DETAILED RANGE OF INVESTIGATIONS

Detailed range of investigations have been prepared for the following projects:

Solvents;
Emulsifiers;
Emulsions;
Suspension Concentrates;

Each of the above elaborations contains the following headings:

- Basic definitions;
- Kinds of materials or products and their characteristics;
- Methods of preparing of products;
- Methods of testing of materials and products;
- Description of some of physico-chemical phenomena taking place in products;(see appendix A, Pages 39 - 52.

iv) COOPERATION ON SOME OF LECTURES

The consultation to some of authors about their papers had been given as well as some number of scientific papers had been afforded for reference. The list of papers furnished is presented in appendix E, pages 130 - 131.

v) PREPARATION OF LECTURES ON TRAINING COURSE

The following papers have been made by myself:

Emulsion & Emulsifiers theory & practice;

New Pesticide Formulations - flowables;

Efforts to Increase Effective and save use of Pesticide., Liquid and Dry Flowables.

In the papers the following data are comprised:

- Basic definitions;
- Theoretical fundamentals of phenomena;
- Methods of preparing of products;
- Adiuvants used and criteria of their selection;
- Advantageous and disadvantageous of particular pesticide formulations;

- Methods of testing
- The main directions of investigations.
(see appendix B, pages 53 - 118.

vi) PRELIMINARY EXPERIMENTS

Owing to the incidental supply of electrical power some of the training experiments would be possible to perform. Together with my counterpart Dr. Ramdas the following of them had been carried out:

Particle size determinacion of suspensions by employment of Micron Photo Sizer (MPS) an instrument functioning on the basis of light absorption.

Determination of moisture in some of emulsifiers and solvents by Karl Fisher method.

Determination of refractive index of organic solvents.

It was also intented to carry out some of the preliminary experiments in preparing dispersible granules by the use of Freeze Dryer. These experiments however, could not be performed, where it was discovered the lack of Dewar flasks.

As a result of testing of particle size determination by using of MPS, it had been found that the procedure is rather tedious. Moreover, during the reading of OM of MPS it had been found several mistakes, as well as not quite clear explanations of some of mathematical relationships. Due to that it was necessary to make some of corrections as well as commentary to OM. This entitled "Supplement Data For Control Particle Size Determination by using MPS" contains the following headings.

- Theoretical basis
- Applied calculations
- The relationship between particle size and rate of their sedimentation.
- The calculation of time of centrifugation
- The calculation of particle size determination.
- Supplementary determinations
- Operational Manual

vii) CONSULTATIONS CONC: SOME OF CURRENT RESEARCH AND PRODUCTION PROBLEMS

The following problems had been consulted;

a) The selection of carriers for biocide dust formulation;

b) Improvement of the quality of WP of Dosanex;

c) Decomposition of Malathion in 25% WP.

Conclusions and Proposals

Ad a. The main objective of investigations was to prepare a formulation which would be well and uniformly distributed on the surface of water, and would be not floodable.

During the consultations I proposed to use as carriers, hydrophobic ones, not wetted by water e.g. soapstone or hydrophobic synthetic silica. The formulation prepared by Dr. Ramdas, my counterpart, who used soapstone disclosed good physical properties, better than former formulation prepared by hydrophylic calcium carbonate, as well as good biological activity. I recommended to use, in the next trials, also hydrofobic synthetic silica, or eventually its mixture with soapstone. The silicas of this type are commonly used as additives of powders to improve their flowability and their dustibility.

ad.b The question was to improve the quality of Dosanex wettable powder which became lamped. Considering the nature of lamping the view was expressed that observed drawback would not be harmful if its water suspension would be properly prepared. Several experiments to determine the right way of procedure had been suggested.

ad.c To stop the possible decomposition of Malathion, the reusage of sodium salt of carboxy methyl celulose had been proposed. This component was used as a suspending agent but its usage had been given up. I focused attention on the fact that this product acted also as stabiliser against decompoisition of Malathion what was found by Tyler & Rowland. (see appendix E, p. 131, No. 20.

viii) PERIODICALS AND MONOGRAPHS ACCESSIBILITY

Shortage of essential scientific periodicals and monographs in R&D Centre can be a serious drawback in conducting effective research works. To overcome this disadvantages it will be necessary to visit regularly some of other Research Centres where appropriate periodicals and monographs are available. To get some idea which of them can be obtainable in Indian libraries, two of scientific institutes had been visited and the lists of more important periodicals and monographs as well available as recommended had been prepared(see appendix E, pages 132 - 138.

ix) DUTY TRIPS AND VISITS.

The two days duty trip to Bombay had been made. During the stay in Bombay I visited the CHEMTEC + ORT'85 exhibition as well as some companies and their representatives.

The all interlocutors showed a big interest in the PDPI.

In general, as most important direction of research in PDPI Centre they see the following:

Development works on the new and more precise analytical methods of PFs(Excel Co.).

Development works on economisation and more safe production of PFs(Excel Co.).

Development works on flowables, slow release granules and micro encapsulation technology(Excel & Gharda Co.)

Works on degradation of different pesticides, especially O-P and carbamate pesticides and the methods of their stabilisation against deterioration in light and higher temperature (Excel & Gharda Co.)

Works on utilisation of different vegetable oils for ULV formulations and to find their eventual synergetic effect on some of pesticides (collaboration with AGricultural Institute in Delhi) (Excel).

Testing of different solvents and emulsifiers for ECs.

The excel company is also interested to get training on instrumental analysis.

The interlocutors like to have more information regarding the intentional direction of research work and about the analytical facilities of PDPI. After getting these informations they will deliver the more detailed proposals for research and for scope of eventual cooperation.

During my visit in HICO Co. (the main producer of nonionic emulsifiers and surface active agents) I had the opportunity to be acquainted with the excellent equipped research laboratory where 80 scientific instruments, some of which very modern and sophisticated, are in full work. The scope of investigations conducted in this laboratory is very wide. Mr. Patil R&D Manager expressed readiness to train the people from RC-G (see appendix F, pages 139 - 144.

APPENDIX A

SOLVENTS

1. SCREENING OF SOLVENTS FOR PESTICIDES

Solvents are selected accordingly the following criteria:

a) High solubility of active ingredient(a.i)
b) No decomposition of a.i. (compatibility)
c) No phytotoxicity to plants to be protected.
d) Low volatility and inflamability
e) Enhancement activity of a.i.
f) No toxicity and irritation to eye and skin
g) Economy

2. TYPE OF SOLVENTS USED FOR FC-s

a) Aromatic and aliphatic hydrocarbons, xylene, toluene, ethylbenzene, isoparrafin, Aromax, Solvent C IX.

b) Halogenated hydrocarbons
Methyl chloride, tetrachloroethylene, o-dichlorobenezene.

c) Alcohols
Methanol, ethanol, isopropanol, n-butanol, isobutanol.

d) Polyhydric alcohols and their derivatives
Ethylene glycol, diethylene glycol, propylene glycol, Polyethylene glycol, polypropylene glycol, methyl cellosolve (methyl glycol), phenyl cellosolve, diethylene glycol esters (methyl carbitol).

e) Ketones
Methyl-ethyl ketone, methyl isobutyl ketone isophorone cyclohexanone.

f) Others compounds
Dimethylformanide (DMF), dimethyl sulfoxide (DMSO), acetonitile, dibutylphtalate.

One of the above solvents may be singly used, or especially for less soluble a.i., as the main solvent may be used in mixture with one or more co-solvents. The more often used are solvents grouped in aromatic hydrocarbons, which dissolve highest amount of a.i. and can be used non specifically with different emulsifiers.

Solvents may have effects on stability of a.i. Some of O-P compounds are easily decomposed by highly polar solvents such as alcohols, polyhydric alcohols, cellosolve and DMF which are often used as co-solvents for dissolving a.i.s less soluble in aromatic solvents.

3. CHARACTERISTIC OF SOME OF SOLVENTS USED FOR EC-s

Type	Sp.graw.*	dest.r.* °C	fl.p.* °C	Ar.C.* %
Mixed xylene(ESSO)	0.872	137,5-140,5	27	99,9
Solvesso 100 "	0.872	156 - 178	40	97.5
HAN 0.932	180 - 275	67	85,7	
SOLVENT 200 "	0,985	227 - 270	108	99
DMSO	1,1	189	95	
Isophorone	0,9229	215,2	96	

4. METHODS OF TESTING OF SOLVENTS

It is often happened, that solvents used for production of EC differ in some properties from that one which was accepted as a standard.

These differences can be caused by small variation in compositions of technical solvents which are not chemically pure and in general are a mixture of several components as in the case of commonly used aromatic solvents. Moreover solvents can be contaminated during improper storage or transportation. These small differences in solvent compositions are in majority even as meaningless

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* Sp.graw. - Specific Gravity
dest.r. - Destilation range
fl.p. - Flame point
Ar.C. - Aromatic content

but unfortunately they can have substantial effect on choice of emulsifiers for EC's.

These characteristics of solvents which are given in p.3 can be insufficient for explanation of their different emulsification ability. Moreover, some of these tests as destilation range and aromats content may be rather troublesome to carry out precisely or may be not enough accurate.

For getting more informations about the quality of solvent and for deciding if it is equivalent to that one which was accepted as a standard the following simple tests are proposed : specific gravity, refractive index and cloud numbers estimated in several different temperatures.

The methods of established the first two characteristics are commonly known but for getting the cloud numbers is the following.

> 2,50 ml of solvent is solved in 25,0 ml of absolute ethanol and titrated with destilated water or 2,0% water solution of chemically pure phenol. The titration should be carried out in 20°, 30° and 40°C.

It is proposed to perform the above test also for some mixtures of solvents as well as solution of pesticides in selected solvents. The cloud numbers of solvents and pesticide solution should be correlated with cloud temperature and eventually HLB numbers of emulsifiers used for preparing EC-s.

EMULSIFIERS

DEFINITION AND FUNCTIONS OF EMULSIFIERS

The molecules of emulsifiers are composed of two parts, one hydrophobic or liophylic and second one hydrophylic or liophobic According to the electric charge of the hydrophylic part the emulsifiers are classified as : anionic, cationic and nonionic. For the pesticide formulations mainly anionic and nonionic emulsifiers are used. Emulsifiers are used to enhance the stability of emulsions and to improve the wetting of leaf surface.

They can also act in other ways, particularly when present in relatively large amounts either initially in the spray solution, or through higher concentrations developing as spray drops dry out on leaf surfaces.

Above the critical micell concentration they can have a solvent action, destroying the structure of the wax on the leaf surface and removing fatty constituents of plant membranes.

They may act as co-solvents or solubilizers thus allowing aqueous herbicides to penetrate liophylic bariers, or to remain in a liquid state on leaf surfaces.

HLB CONCEPT

Taking into account that emulsifiers are composed of hydrophilic and liophilic part of molecule one may assume that the ability of each emulsifier to emulsify particular oil will be depended on the hydrophility and liophility of the each part of emulsifier. In the case of nonionic emulsifiers,in which hyrophilic oxyethylene or oxypropylene groups are attached to the hydrophobic aliphatic group, the emulsifying properties of emulsifier is depended on the length of alifatic chain and also the length of oxyethylene or oxypropylene chains.

The longer the aliphatic chain the more hydrophobic emulsifier is, and vice versa. The hydrophilic-lipohilic characteristics of the emulsifier molecule is a concept of so called hydrophile-lipohile balance or HLB, which quantified the properties of emulsifiers on arbitrary numerical scale. The larger the HLB numbers the more hydrophilic emulsifier is. These numbers practically are lying in a range between 5 and 50. HLB numbers may be determined experimentally by comparison with standard emulsifiers of known HLB or calculated in various ways. Their values are now quoted for a wide range of emulsifiers.

It is also assumed that the HLB numbers are additive. From two emulsifiers of different HLB numbers, the new one of any HLB number, lying between, can be prepared by their mutual mixing.

Because however, there are emulsififers which despite of the same HLB number vary considerably in their emulsifying abilities, the HLB system may be used only as a preliminary selection of emulsififers.

METHOD OF TESTING

By emulsifying the oil phase with the series of standard emulsifiers the most effective one, of known HLB number, can be found.

Emulsifying the same oil with others emulsifiers, of unknown HLB numbers, the one of similar emulsifying ability to the standard one can be found. It is then assumed that HLB number of unknown emulsifiers is the same as the HLB number of the standard one.

The unknown HLB number of emulsifier can also be found when demanded HLB number of emulsifier for emulsification of oil is known, as well as the HLB number of one emulsifier using for test.

The HLB number of unknown emulsifier is then calculated from the following relationships.

$$HLB_o = \frac{X(HLB)_a}{100} + \frac{(HLB)_b\,(100-X)}{100} \qquad (1)$$

$$(HLB)_a = \frac{(HLBo100 - (HLB)_b(100 - X)}{X} \qquad (2)$$

Where $(HLB)_o$ - the demanded HLB number of emulsifier

$(HLB)_a$ - the HLB of unknown emulsifier(a)

$(HLB)_b$ - the known HLB number of emulsifier used for testing

X percentage of emulsifier (a) in the mixture of emulsifiers

Example

if $(HLB)_o = 12{,}7$; $(HLB)_b = 8$; and $X = 32$

then $(HLB)_b = \underline{12.7 \,.\, 100 - 8.68} = \underline{22.6}$

The above procedure of finding HLB numbers of emulsifiers is troublesome and used rather sporadically.

More important is a test which can ascertain that the properties of emulsifier from the new delivery are the same or very similar to the standard one. The following tests are proposed:

1. The cloud temperature of water solution of emulsifier
2. The Tanaka cloud numbers
3. The water numbers

Description of methods

1. The cloud temperature

100 ml of 0,500 % (W/V) of water solution of tested emulsifier (or mixture of emulsifiers) is treated slowly in laboratory flask of capacity of 250 ml on water bath until appearance of opacity. Then the solution is slowly coolled and the temperature by which the opacity disappears is fixed.

For preparing the solution of emulsifiers the following liquids are used:

a. - distilated or deionized water
b. - 5% (w/v) water solution of Nacl
c. - 10% (w/v) water solution of Nacl

Method B & C for emulsifiers of high HLB numbers > 20

For measuring the cloud temperature the standard thermometers with division of 0,2°C are used.

2. The Tanaka cloud numbers

0,500g of emulsifier soluble in 5.00 ml of 98% ethanol is titrated with 2.00% water solution of phenol in temperature of 25 ± 0.2°C. The titration is carried out until appearance of opacity which does not disappear through 5 minutes.

3. The water numbers

1,000 g of emulsifier is soluble in 30.0 ml of mixture of benzene and isopropanol (weight ratio 25 ± 0,2°C. The water number is that amount of water in ml which caused the appearance of opacity not disappearing through 5 minutes.

METHOD OF PREPARING AND TESTING OF CONCENTRATED EMULSIONS (CE) OF PESTICIDE

1. CLASSIFICATION OF EMULSIONS

Emulsions, which are defined as continuous liquid phase in which a second immiscible liquid is dispersed, may be classified on the basis of:

i) Nature of the external (continuous) or internal (dispersed) phase:

According to this classification there are two groups of emulsions, usually called O/W and W/O type of emulsions. The letter "W" symbolized water and letter "O" oil. Any hydrophobic (or liophylic) non-polar liquid falls in the "Oil" category.

ii) Concentration of the internal phase i.e. based on the internal/external phase ratio (I.P.R)

In low concentrated emulsions the I.P.R's <30%, in medium concentrated 30-70% and in high concentrated >70%.

iii) Structure of the system

According to the droplets of dispersed phase the following types of emulsions are distinguished, **macroemulsions, microemulsions (or transparent) and mixed emulsions.**

2. SOME OF PHYSICAL CHARACTERISTICS OF EMULSIONS

a) Viscosity

i) Emulsions of low I.P.R(<30%)

This type of emulsion shows newtonian reological properties i.e. the viscosity of the system does not depend upon the rate of shear by the applied stress.

ii) Emulsions of medium (30-70%) and high (>70%) I.P.R.

These types of emulsions are characterized by high and very high viscosity and non-newtonian reheological properties. The viscosity of the system depends upon the rate of shear by the applied stress.

b) Physical instability of emulsions

Emulsions of type i and ii are thermodynamically metastable what means that after some period of time separation of phase takes place. Drops of dispersed phase settle out (sedimentation) or rise to the top (creaming). As a result there is a separation of the system into two emulsions of different I.P.R. One richer and one poorer in the disperse phase than the original emulsion. Because of **aggregation** or **floculation** of drops the phenomenon of their **coalesence** can take place. The creaming or sedimentation process is primery governed by **Stokes law.** It is clear from this equation that the creaming may be reduced by adjustment of the specific gravity of one or both phases, by lowering the particles size and by increasing the viscosity of the continuous phase.

Decisive influence on the stability of emulsion has emulsifier which protect the droplet of oil against coalesence. It also facilitate the dissipation of oil phase by lowering the interfacial tension between oil and water.

3. EMULSIONS AS THE FORMULATIONS OF PESTICIDES

The most popular emulsions used in chemical protection of crops are the diluted **O/W** emulsions prepared from emulsifiable concentrates (EC-s). These emulsions are used as carrier of pesticides. The same emulsions may however be prepared not only from EC-s but also from the **CONCENTRATED EMULSIONS (CE)** of "mayonnaise type". These formulations are less eye and skin irritating, lower fine hazardous and for that reasons more safe in usage. In some cases they also can be more economic, because of solvent which is used in the production of EC-s, is suibstituted by water. It is worth to mention that concentrated emulsions of "mayonnaise" type were already used before the EC-s had been introduced on the market. But that time the preparing of stable concentrated emulsions was more different than today when we have to dispose a much larger number of various effective emulsifiers. Besides, the requirements of safe usage of pesticides were not in those days so critical as are today. The another emulsion type formulations of pesticides on which some research are now-a-days carried out are **MICROEMULSIONS (ME-s)**.

As their name pointed out they are composed of very small droplets. They particle size may vary in the range of 100-600A°, a distinct from ordinary or macroemulsions in which the lower limit of particle size is probably 0.1µ. The microemulsions represent a class of thermadynamically stable dispersions. The mechanics of forming them differ from that used in the preparation of macroemulsion. The most important is optimum composition of oil, emulsifiers and water. If it is reached the microemulsification occurs spontaneously and no mechanical work is required.

4. METHODS OF PREPARING CE-s

The combination of the emulsifiers hydrocarbon solvent and pesticide are slowly added in several portions to the water or water solution of some adjuvants (ethylene glycol, glycerol thickener. Such procedure is necessary to avoid the formulation of **W/O** emulsion which could be formed if high amount of oil would be added at once to the low amount of water. Following that procedure a very coarse particle size of emulsion is formulated. Afterwards a very intensive stirrer with high shear has to be used. The relation of "oil" to water can attain as 8:2 and it will depend on the nature of "oil phase" Ethylene glycol or glycerol act as antifreezing agent and as adjuvants which facilitate "blooming" during pouring CE to water. The water used to prepare CE is deionized:

Before starting to prepare CE it is proposed to find the best pair of nonionic emulsifiers in the selection procedure commonly used for EC-s.

These emulsifiers should be then used in different concentration to prepare CE. It is also suggested to try to use one of selected emulsifier(more hydrophylic) in water solution, and the second one in the hydrocarbon/pesticide solution.

5. SUGESTED EVALUATION TECHNIQUE OF CE-s

i) Visual inspection of stability of CEs

The emulsion is observed for change which have occured after storage at different temperature for longer period (two weeks or one month). Changes in temperature may range from freezing to high temperature but should be applied very cautiously.

ii) Cycling tests

Freeze-thow stability. Samples are cooled to 10°C for 8 hours and then thowed for 16 hours at room temperature to check if the CE fluidises spontaneously. After each cycle a suspensibility test should be carried out - Freez thow elevated temperature test.

Ist period	8hr.	40°C	-10°C	50°C	-10°C	40°C	-10°C
	16 hrs	RT	RT	RT	RT	RT	RT
2nd period	16hrs	-10°C	50°C	-10°C	40°C	-10°C	50°C
	8hrs	RT	RT	RT	RT	RT	RT

RT - Room Temperature

iii) Centrifugation of emulsions

In this case the amount of oil separation after centrifugation is used to predict shelf life. The results obtained for CE-s aged for some periods of time at various temperatures are compared with the results obtained for accepted standards.

iv) Flowability

The CE should be easily poured from its container to the spray tank filled with water. The flowability is visually inspected and compared with that one of standard sample.

v) Spontaneous dispersibility in water

The above property defined also as "bloom" is visually estimated and rated qualitatively on a three point scale very good, good , fair and poor. If the CE does not disperse spontaneously then the number of inversion of cylinder for full dispersion is fixed.

vi) Viscosity

Some of the properties of CE-s can correlate with their **dynamic viscosity**. For that reason this measurement should be also performed. For this measurement the rotational viscosimeter e.g. Brookfield LVT viscorimeter is used using the cylinderical spindle 2 at low speed (6 RPM).

vii) Stability of diluted emulsion prepared from CE.

This test is performed analogical as that one for EC.

vii) Other techniques

Other techniques to predict shelf life of CE-s include **electroconductivity** and **zeta potential.**

ACUEOUS OR AQUEOUS/OIL BASE SUSPENSION CONCENTRATES(SC-s)

Plan of work

Collection of the following adjuvants or their equivalents:

(a) **Dispersing agents**

Atlox 4862
Atlox 1096
Atlox 4868B

(b) **Wetting agents**

Atlox 3002
Atlox 4991
Renex 36
Atlox 4875
Atlox 4853B

Any others wetting agents may be suitable. Particularly successful are allkylnapthalene sulfonates, dodecyl benzene sulfonates.

c) **Thickening agents for aqueous based SC.**

i) Rhodopol 23 of Rhone boulenc. This product is an anionic polysacharide with weak sensitivity to temperature and has also shear thinning properties.

(ii) Bentone EW (A) montmorillonite clay NL Industries USA.

(iii)Actigum CS 6-CFCA, France.

(iv)Kelzan-Kelco, USA.

(v) Attagel 40 - Engelhard Minerals & Chemical Co,- USA.

(d) **Biocide.**

It use is necessary if the thickener used is susceptible to microbial attack.

(f) **Antifoaming agents.**

(g) **Floculants (Organic).**

(h) **For oil-based flowables**
Emulsifiers and Wetters

Atlox 1045A, Atlox 3386B, Atlox 4856B, Atlox 4885, Renex 702, Atlox 4884, Atplus 300.

Sulfated oils, short chain ethoxyloated alcohols or nonyl phenols and sulfosuccinates.

Remarks

Dispersing agents are generally short chain polymers with charged groups. Typical of these are alkayl naphtalene sulfanate / formaldehyde condensates and lignosulphnauotes.

The choice of a dispersing agent is more critical and specific than the choice of wetting agents. Some wetting agents themselves may have some dispersing property, particularly if they create electrical charges.

1. Viscosity modifying surfactants

Some of surfactants have good viscosity increment effect and allow to produce stable flowables without using an extra thickening agent. The following surfactants can be used:

Atlox 1096 - Atlox 1086 - Atlox 4868B Atlox 3387B, Brij 76, Brij 78.

2. Parameters which should be found out in preparation of SC of Vitavax

(i) Parameters of pregrinding of Vitavax Tech. grade in different type of mills.

(ii) Preliminary testing of different combinations of dispersing/ (wetting agent on wet milling and on suspensibility of particles of Vitavax (tests in small glass grinder).

(iii) Influence of thickening agents and polyol on the stability of suspension.

(iv) Using the selected adiuvants, find the following parameters of milling and mixing of mixtures in Dyno-mill.

- The speed of revolutions
- the fine of milling

The process will be monitoring by Sediment Balance or MPSA.

3. EVALUATION OF PRODUCT

(i) Viscosity

Measuring with Brookfield LVF type Viscometer, using a cylindrical spindle 1 and 2 at low speed (6 or 12 rpm)

(ii) Storage stability

Bleeding
Thickening (gelling)
Sedimentation
Redispersibility
Bloom
Freez-thaw stability

4. IMPROVEMENT OF PRODUCT

If the product, after some time of storage, will create the hard "cake" then try to solve the problem by adding floculants. The added floculants should create loose sediment, very easily dispersed after weak mixing.

EMULSIONS AND EMULSIFIERS

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DEFINITIONS AND CLASSIFICATIONS OF EMULSIONS

Having no idea about your scope of knowledge about emulsions and emulsifiers I think it would be advisable to remind some basic definitions and then to throw light on these problems of emulsions and emulsifiers which apper - in pesticide formulations.

The classical definition of an emulsion as a dispersion of one liquid in a second immiscible liquid is far from complete. For getting more knowledge about emulsions some of additional definitions have to be introduced. They are the following:

Disperse phase - the liquid which is dispersed in continuous phase in the form of fine droplets;

Continuous phase - the liquid in which one of two liquids is dispersed;

Since the majority of emulsions contain water as one of the phases, it is customary to classify emulsion in two types : the oil-in-water or O/W type, consisting of droplets of oil dispersed in water and the water in oil or W/O type in which the phases are reversed. The term "oil" is used to any hydrophobic or nonpolar liquid not soluble in water.

Presented during the training course on Pesticide Formulation Development conducted by Pesticide Development Programme in India at the Management Development Institute, Gurgaon Haryana, India, from 18 to 22, February 1985

Both types of emulsions in which water is used as continuous or dispersed phase are used in crop protection as carriers of pesticide, however, the O/W type of emulsion is used more commonly. In this type of emulsion "o l" is a solution of pesticide in some of hydrophobic solvent e.g. xylene, Solvent-naphta or some similar others.

Besides the O/W and W/O classification of emulsions they can be divided on the basis of concentration of the internal phase i.e. on the internal/external phase ratio (IPR). The classification is as under:

Low IPR-the amount of dispersed phase is <30%;
Medium IPR-the amount of dispersed phase is 30-70%;
High IPR-the amount of dispersed phase is >70%

The first type of emulsion is prepared from emulsifiable concentrate (EC) and the second may be prepared in the form of concentrated emulsion which similarly to EC is used for preparing diluted emulsion. The basis for the third way of classification of emulsions is according to their structure. The following of them are distinguished :

Micro-emulsions, Macro-emulsions and
Mixed emulsions

PHYSICAL INSTABILITY OF EMULSIONS

Emulsions belong to a system which is thermodynamically unstable. This results from the high surface area of finely dispersed liquid, created during the preparation of emulsion and accompanied by a large surface free energy. With time, the system tends to reduce this energy through a number of break-down processes such as:

- gravitional separation
  (creaming or sedimentation)
- flocculation or aggregation
- coalescence.

The creaming or sedimentation takes place when droplets of dispersed phase rise to the top or settle down to form layer of droplets. The system is then separated into two emulsions, one richer and one poorer in the disperse phase than the original one. The both processes, creaming and sedimentation, are primarily governed by the Stokes' law which states that :

$$V = \frac{2gr^2 (d1-d2)}{9\eta}$$

where V - the rate of sedimentation of spherical particles;
r - radius of particles
d_1 - density of disperse phase
d_2 - density of continuous phase
η - viscosity of continuous phase

It is clear from the above equation that the creaming or sedimentation can be reduced by changing specific gravity of one or both phases, increasing viscosity of continuous phase or lowering the droplets size of dispersed phase.

The flocculation is a phenomenon in which the dispersed droplets of emulsion stick together to form clumps or chains. Such floccules are easily redispersed upon shaking.

The third undesirable phenomenon, for stability of emulsions, is coalescence. It occurs when the "interface" between the droplets and the continuous phase is "clean" and the droplets will then join together, resulting in a continuous increase in droplet size and reduction in the number of droplets.

Coalescence is in general irreversible process and a case of instability of emulsion.

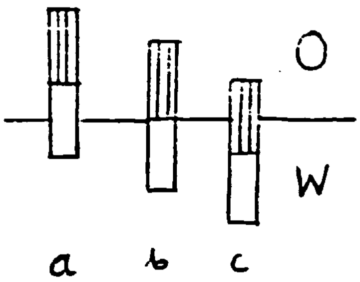
All of the above mentioned unfavourable phenomena may be considerably reduced if the third component - specific emulsifier in proper concentration is introduced to the system.

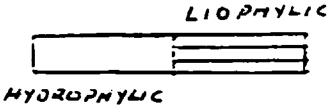
STRUCTURE OF EMULSIFIERS

As already have been said the practically stable emulsions can be obtained only when an adequate emulsifier in proper concentration is used.

The number of different emulsifiers is very large but nearly all of them have similar structure. They are composed of two parts. One hydrophylic, which shows a tendency to penetrate to water and the second one liophilic or hydrophobic having affinity to oil. It can be said that the molecule of emulsifier is composed of hydrophilic and hydrofobic part. When the oil is mixed with water in the presence of emulsifier then latter is arranged in the interphase between oil and water. One part of emulsifier will be joined with oil and the second one with water. Such orientation of emulsifier reduces the interfacial tension between oil and water, favour dispersibility of oil phase and moreover protect the dispersed droplets against flocculation and coalescene. The more uniform orientation of emulsifier in the interface the best emulsification and more stable emulsion.

The type of orientation of emulsifiers in the interphase can be illustrated as follows :





On drawing a, the emulsifier is strongly pulled into oil phase whereas on drawing c, inversly the emulsifier appears to have a stronger affinity to water. The balanced orientation is pictured on the drawing b.

The type of hydrofobic and hydrophylic groups are different in particular groups of emulsifiers. In water soluble soaps e.g. the hydrofobic is parafinic chain whereas the hydrophylic - a neutralized acid radical. In this case, the parafinic chains of the soap molecules are concentrated in the oil droplets and their polar hydrophilic groups are directed towards the continuous water medium. The additional effect which takes place in the case of using soaps as emulsifiers is dissociation of their polar groups and formation of charges at the interface which prevent coalescence of oil droplets.

The most commonly used emulsifiers are however, nonionic emulsifiers. Some of them are obtained by condensation of ethylene oxide - the component of hydrophylic group - with other hydrophobic component containing active hydrogen.

The general formula of these type of nonionic emulsifiers is the following :

$$R - (CH_2CH_2O)_xOH$$

The process by which this group of emulsifiers is obtained is called the process of ethoxylation. According to the component which is ethoxylated and according to the amount of oxyethylene groups in molecule, different types of emulsifiers can be obtained.

The following groups, among the others can be distinguished:

ethoxylated monohydric alcohols;
" polyhydric alcohols;
" alkyl/phenols;
" fatty acids;
" esters of phosphoric acids;
" alkano amines

The term nonionic emulsifiers refers chiefly to polyoxyethylene or polyoxypropylene derivatives but other emulsifiers are also included to this category e.g.:

anhydrohexitol derivatives (SPANS)
or sugar esters

The other group of nonionic emulsifiers is formed by the sequential addition of one alkylene oxide to an initiator, followed by the sequential addition of another alkylene oxide. This type of surfactants are called block ionic copolymers.

The most known products are PLURONIC POLYOLS (trade mark of Wyandotte Chem. Corp.) made from ethylene oxide, propylene oxide and low molecular weight reactive hydrogen compound (propylene glycol).

Depending on the average number of oxyethylene groups(x) in molecule of emulsifier the various will be its affinity to water and to oil. More hydrophilic will be that emulsifier in which the number (x) will be bigger.

CRITERIA OF SELECTION OF EMULSIFIERS (HLB)

Over the years, numerous empirical and semi-empirical methods have been evolved to assist in the selection process of emulsifiers. One of the most popular of these is the concept of hydrophile-lipophile balance (HLB). This quantifies the balance of hydrophilic - lipophilic characteristic of the emulsifier molecule on an arbitrary numeric scale. The HLB numbers may be determined experimentally by comparison with standard emulsifier of known HLB number or may be calculated in various ways. The HLB numbers are now quoted for a wide range of emulsifiers.

The smaller the (x) number in nonionic emulsifiers the smaller is the HLB number. For ethoxylated nonylophenol e.g. with two oxyethylene groups in molecule the HLB = 5.7 and for that one with 50 oxyethylene groups the HLB = 18.2. HLB can be calculated if the structure of emulsifier is known or if not, it can be estimated experimentally.

For polyhydric fatty acid esters - $\text{HLB} = 20(1-\frac{S}{A})$

where: S - saponification number of esters
A - acid number of acid
e.g. glycol monostearate with S=161 and
A=198 will have HLB = 3.8

If the emulsifier contains only poly (ethylene oxide) as the only hydrophilic group the HLB can be simply calculated from the relation : $HLB = \frac{E}{5}$. If other hydrophylic groups are also comprised e.g. polyhydric alcohols then the following relation may be used:

$$HLB = \frac{P+E}{5}$$

where : P - weight percentage of polyhydric alcohol groups
E - weight percentage of Eto-groups

Davies has devised a method for calculation of HLB directly from chemical formulas using empirically determined group numbers. HLB is getting from the following empirical relation :

$$HLB = 7 + \sum \text{hydrophilic group numbers} - \sum \text{liophilic group numbers}$$

or

$$HLB = 0.36 \ln \frac{CW}{Co} + 7$$

C_o and Cw are respectively, the equilibrium emulsifier concentrations in the oil and water phase.

HLB can be determined also by GLC method using emulsifier as the substrate and passing mobile phase (50:50 ethanol and hexan) down the column. HLB is then calculated from the relation :

$$HLB = 8.55 R_t - 6.36$$

Taking into account the discovered proportionality between the HLB numbers and some of the characteristics of emulsifiers, the HLB number of emulsifier of known structure can be found from this relationship. The following characteristics of emulsifiers can be utilized :

- cloud points
- water numbers

It is assumed that HLB numbers are additive what means that from two emulsifiers of different HLB numbers, the new emulsifiers of intermediate HLB numbers, can be, by their mutual mixing, prepared. For calculation of the HLB number of mixed emulsifier the following equation are used :

$$(HLB)_m = \frac{(HLB)aX}{100} + \frac{(HLB)b\ (100-X)}{100}$$

e.g.

$$(HLB)_m = 10.5; \quad (HLB)a=5 \quad \text{and} \quad (HLB)b = 20$$

$$10,5 = \frac{5X}{100} + \frac{20\ (100-X)}{100}$$

$$x = 63,33\ ; \quad 100-x = 26,67$$

From the same relation the unknown HLB of emulsifier can be calculated. In that case the demanded HLB of emulsifier for particular oil phase must be known as well as HLB number of one of emulsifier

While HLB numbers help to make preliminary selection from the wide range of emulsifiers the further more detailed testing is necessary before arriving at a final formulation.

The selection of emulsifiers on the basis of HBL numbers is mainly recommended in preparing of emulsions of medium or high IPR, such as cosmetic emulsions where nonionic emulsifiers are used. The HLB system is less however helpful for selection of emulsifiers for EC-s of pesticides from which emulsion of low TPR are prepared. The best effect is obtained by using the mixed emulsifiers - anionic and nonionic. The idea of using mixture of different type of emulsifiers is old one. In 1940 Schullman and Cockbain increased markedly stability of O/W emulsion of parafin oil by using amphiphilic compounds (e.g. cetyl alcohol, cholestrol, etc) in combination with ionic surfactant such as cetyl sulphate. The enhanced stability was attributed to the formation of interfacial complexes at the O/W surface. This "complex" formation was assumed to be associated with the formation of "densely packed" interfacial layers. The maximum effect is probably obtained when a water soluble and oil soluble surfactant capable of interacting together at the oil/water interface are used in combination.

Using the same idea,Saribaan and Koot were the first to use the mixed emulsifiers for EC-s of pesticides. As an anionic the calcium salt of dodaecylobenzenesulphonic acid (CaDBSA) was used as nonionic some of already mentioned emulsifiers.

The more effective relation of anionic emulsifier to nonionic one is dependent on the property of oil phase, it means on the property of pesticide solution in oil solvent, and on the HLB number of nonionic emulsifier.

The higher the HLB number, the more anionic component in mixture and vice versa the lower HLB number, the less anionic component. It is in accordance with the principle of additivity of HLB numbers of emulsifiers. However, the best effect of emulsification as well as the spontanity of creation of emulsion and its stability is obtained when instead of one nonionic emulsifier a two, three or more in combination with CaDBSA are used. Moreover the good O/W emulsions can be obtained in such a case for several proportion of anionic and nonionic emulsifiers, whereas in the case of using a single nonionic emulsifier only one combination is giving satisfactory result. This is contrary to additiveness of HLB. Moreover, such a multicomponent mixture of emulsifiers is less susceptible into small differences in physico-chemical properties of solvent or pesticide what is common in technical product.

SELECTION OF SOLVENTS

In the selection of solvents the following properties are taken into account :

- solubility of pesticide
- stability of pesticide and emulsifier
- lack of phytotoxicity
- volatility and inflaminability
- solubility in water
- toxicity and irritation to eye and skin

The following solvents are used for preparation of EC-s :
Aromatic and aliphatic hydrocarbons such as : ethylene, toluene, ethylbenzene, methylnaphtalene, alkylbenzenes, naphta, isoparafins.

Halogenated hydrocarbons such as mythylene chloride, tetrachloroethylene, o-dichlorobenzene.

Alcohols: methanol, ethanol. isopropanol n-butnanol, isobutnanol.

Polyhydric alcohols and their derivatives such as : ethylene glycol, diethylene glycol, Cellosolve, carbitol, etc

Ketones like methyl ethyl ketone, isophorone, cyclohexanone.

Other compounds : dimethyl formamide, dimethylsulphoxide, acetonitrile.

According to the solubility of pesticide a single solvent or mixture of two or three may be used. The most popular solvents which dissolve highest amounts of active ingredients are : xylene and that ones, which are rich in aromatic hydrocarbons as Solvent-naphta, Aromasol and the like.

The highly polar solvents such as alcohols, polyhydric alcohols and Cellosolve can be used as cosolvent, but not in all cases. For some of organophosphorous compounds e.g. they can not be used because O-P pesticides can be easily decomposed by such solvents. Decomposition of some of O-P pesticides can also be caused by isobutanol which is used as a solvent for CaDBSA or also for its mixture with nonionic emulsifiers. Therefore, for EC-s of these O-P insecticides xylene instead of isobutanol as a solvent of CaDBSA is commonly used.

The other aspects which should be taken into account during the selection of solvents are their solubility in water and volatility. As it is commonly known the emulsions prepared from EC-s are often very diluted ones e.g. around 0.2 or even 0.05%. In the case of some degree of solubility of solvent in water it can happen that part of solvent can be soluble in water what cause the reduction in volume of solvent and loss of total solvent capacity. As a result some amount of solid pesticide may come out of dispersed phase in crystal form.

Such a crystallisation can transform the active ingredient into less biologically active form and it may lead to filter blockage or even sedimentation and under dose.

Such e.g. solvents like methylisobutyl ketone and cyclohexanone are both better solvents for many pesticides than aromatic hydrocarbons, but both are around 2% soluble in water and at the dilution used for preparing sprays both would lose their solvent power almost completely. Chloroform which also is good solvent is about 1% soluble in water. Solubility of benzene is about 0.2% and methylonaphtalenes around 0.001% similar to hexane.

SPRAY MODIFYING ADJUVANTS

These criteria which have been discussed concern only the stability of emulsions.

But beside good stability of emulsion several other factors must be taken into account in order to obtain the biological effectiveness of sprays applied to foliage. The impact of droplets, spreading of emulsion and retention of oil phase, wetting of the leaf surface should receive considerable attention.

Because, however, the above phenomena are depended not only on the properties of emulsion but on the characteristics of surfaces which can differ from plant to plant, it is easier to adjust the properties of sprays by adding to them some Spray Modifying Adjuvants than to prepare for each of protected crop different composition of EC-s.

This Spray Modifier Adjuvant may improve the activity of pesticides by :

- sticking of P-F upon target's surface;
- spreading of P-F upon targets surface;
- increasing penetration into target surface;
- increasing viscosity of spray to reduce drift;
- reducing evaporation of pesticide;
- reducing moisture loss through plant surface;
- promoting foaming of spray to reduce drift.

Discussion of all these problems would require separate lecture.

CONCENTRATED EMULSIONS AND MICRO EMULSIONS

Before ending my lectures some words about the concentrated emulsion as well as microemulsion.

The both formulations of pesticide are yet not in common usage but more and more work on them is conducted.

The principle of concentrated emulsion formulations or emulsion flowables is fairly simple. The oil solution of pesticide is emulsified in such a way that concentrated emulsion of medium IPR is prepared. To get such emulsion however specially balanced emulsifiers combination must be used and special procedure of preparing.

The advantages of this formulations lie in the fact that concentrated emulsions are :

not flammable
less dermal toxic
less costly becuase of lower concentration of solvent

However, it is rather difficult to get such emulsion of suitable properties. The main problem is to get the long term stability.

It is hoped that this problem will be not so important if oil solution of pesticide will be prepared in the microemulsion formulations. As their name implies the size of the droplet in this type of emulsion is very small. Indeed their droplet size may vary in the range of 100-600 Å as distinct from ordinary or macroemulsions in which the lower limit of particle size is probably 0.1 micron or 1000 Å. Some other terms are also used for this type of emulsion like transparent or translucent emulsion as well as swollen micellar solution or solubilized solution.

This type of emulsion represent a class of thermodynamically stable dispersions.

In spite of the advances made in recent years on the theoretical basis of explaining physics and chemistry of microemulsion formation the formulation of microemulsions is still an art. The mechanics of forming a microemulsion differ somewhat from that used in the preparation of macroemulsion.

In the macroemulsion the more work put to its formation and higher concentration of emulsifier, the better its stability. In the case of microemulsion this parameter is not important. Microemulsion will be formed spontaneously if the specific interaction between oil molecules emulsifier and water will be realisable which depends mainly on the type of used emulsifier.

The O/W microemulsions are prepared in four-step process which involves selection of a surfactant which is just barely soluble in the oil phase, adding this to the oil, and then adding this mixture to the water phase to produce an emulsion. A second surfactant which is more water soluble than the first surfactant is finally added to produce the clear microemulsion of oil in water.

The crucial part in formulating a microemulsion lies in choice of emulsifiers. However, because of the lack of understanding of the complex interacting that takes place between emulsifier, oil and water there are yet not definite guide rules which combination of emulsifiers should be used. In any case however the knowledge of basic characteristics of used emulsifiers as e.g. HLB, CMC their chemical structure and method of testing will facilitate the better understanding of creation of microemulsions as well as their structure.

Formulating the bioactive materials in O/W microemulsions has many advantages. The much finer droplet size of microemulsions will lead to a higher penetration ability, a much larger contact area of the active substance to treated surface, and a much more even distribution during application. The higher concentration of surfactants generally needed to formulate a microemulsion can also be an advantage. It had been indicated that a definite relationship exists between herbicide and surfactant structures and its concentration for maximum herbicide penetration. Increased efficacy of the insecticices by applying "microemulsions" instead of macroemulsions has also been demonstrated. Microemulsions have already found very wide scope of usage in many fields e.g.

Tertiary oil recovery;
Drilling fluids;
Microemulsion of gasoline with water
Textile lubricants

Also for that reason yet it seems profitable to conduct the research on this type of pesticide formulations because the gained results may be utilized also as mentioned above as well as other fields.

RECOMMENDED PAPERS

Virendra V. Chavan	"Physical Principles in Suspension and Emulsion Processing" Advances in Transport Processes, 3(1984)1-34
Th.F.Tadros & B Vincent	"Emulsion Stability" Encyclopedia of Emulsion Technology Vol. 1. Basic Theory, Ed. P. Becher, & M. Dokker (1983)
Gilberg, Gunilla	"Practical use of microemulsions" Surfactant Scie. Ser. 1984 - p.1-43
D. Ramban A.K. Dorle	"Flocculated Emulsions" Indian I. Pharm. Sci, 1983, 45([illegible]) 172-5.
E.W. Kaler & others	"Toward Understanding Microemulsion" J. Chem. Phys. 1983, 79 (11)
G.S. Hartley	"Elumsions as Carriers of Pesticides" Chemistry & Industry, April 8, 1967

FLOWABLE FORMULATIONS

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INTRODUCTION

Flowable formulations are comparatively new ones and therefore it seems advisable to give some basic definitions and general information about them. Then, on the example, of most popular flowable - suspension concentrates, (SC), the following problems will be discussed:

- The desired properties of SC-s
- The adjuvants and their function
- The production technique
- The quality requirements for pesticide and some of adjuvants
- The methods of testing of SC-s

I think that it will also be proper to present some of the phenomena characteristic for SC-s.

Presented during the training course on Pesticide Formulation Development conducted by Pesticide Development Programme in India at the Management Development Institute, Gurgaon, Haryana from 18-22, February 1985.

1. GENERAL

Flowable liquid formulations of different kinds have common appearance of a fairly liquid paste. A suspension concentrate is a dispersion of a micronised active ingredient in a liquid dispersing medium. This medium is usually water, however, if pesticide is sensitive to water, oil (organic solvent) can also be used.

Based therefore on the composition of dispersing medium, one speaks about aqueous or oil flowables. In flowable emulsions or concentrated emulsions the oil solution of pesticide is finely dispersed in water.

Suspenso-emulsion, as its name indicates contains dispersion of micronised particles of pesticide and finely dispersed oil in water. Compared to conventional formulation types, flowables offer the following advantages:

- more safe in handling (freedom of dusting);
- ease of measuring by volume, which is more convenient in the field;
- low packing volume;
- usually solvent free (no flash point problem);
- excellent suspension properties giving homogeneous distribution of the active ingredients in the spray;
- possible improvement of biological activity (mainly fungicide) due to smaller particle size of pesticide.

While many wettable powder formulations (WP-s) are today reformulated into flowables, it should be pointed out that WP-s still have the following advantages:

- in general, higher concentrations of active ingredient (a.i.) are possible;
- unlimited cold stability;
- lighter packaging is possible for toxicant with low toxicity to humans;
- problems with the chemical storage stability rarely occur.

2. DESIRED PROPERTIES OF SC-s

Similarly as WP-s and EC-s, the SC-s are used to prepare diluted water suspensions or emulsions. Therefore some of their properties should correspond to that of former ones. They should be as EC-s easily measured by volume and easily poured into the spray tank. To fulfilll these requirements the viscosity of SC-s must not be too high at the time of application. After pouring into water they must, similarly to WP-s or EC-s, disperse spontaneously and ensure very evenly distribution of fine particles in the spray, as well as, good stability of suspension. Equally important, but most difficult to obtain, is storage stability of SC-s. Ideally SC should be stable under severe conditions of storage and have a normal shelf life of two years. Their particles must not settle or if some slight settlement takes place it is essential that the sediment will be readily re-disperse and form easily homogeneous suspension. The last requirement is not only the most important but also most difficult to obtain.

It is obvious that chemical stability must also be accomplished.

3. ADJUVANTS AND THEIR FUNCTION

In order to get SC of demanded properties the following two requirements must be fulfilled --

- The particles of pesticide must be very small,much smaller than in the case of WP-s
- The SC formulation must contain several specific adjuvants.

Some parameters which are responsible for desired properties of SC-s are noticeable from Stokes' equation -

$$V = \frac{2r^2 (d-d^\circ)g}{9\eta}$$

While the above equation is valid only for very diluted suspension and is more complex for concentrated suspension, the basic proportionality between V and d, d_o, e^2, g and η are also valid for concentrated suspension.

It is seen from the above equation that kinetic stability of concentrated suspension, which means that it will not create hard sediment (caking) for some periods of time, is dependent on particle diameters (r), densities of solid (d) and liquid medium (d_o), GRAVITY (g) and viscosity of liquid media (η).

From all of these properties only the density of solid is fixed, while the others may be changed such as 'r' by milling process and the others by introducing to formulations some of the specific adjuvants. Some of them are also used for good dispersibility and wettability of SC-s as well as freeze thaw stability during storage.

The type of commonly used adjuvants and the function which they perform are the following:

Dispersing agents (DA)

These surfactants are used to facilitate the communition process as well as to stabilize the micronized particles in the dispersing medium against irreversible flocculation. The ionic or nonionic dispersing agents can be used as well as some of macromolecules or polyelectrolytes. With ionic surfactants irreversible flocculation is prevented by the repulsive force generated by electrical double layer.

With nonionic surfactants and macromolecules repulsion between the particles is ensured by the "steric" interaction of the adsorbed molecules on the particle surface. With polyelectrolytes both electrostatic and steric repulsion exist. Dispersing agents are generally shortchain polymers with charged groups. Typical of them are:

Sodium salt of alkil naphtalene sufphonic acid; (Atlox 4862)
Sodium salt of naphtalene formaldehyde sulphonic acid condensate;
Sugar free sodium-based lignine sulphonates (POLYFONS, UFOXANES).

Wetting agents (WA)

The WA-s are used to facilitate the communition of solid pesticide during wet milling process, as to make efficient milling the solid particles must be wet and the air must be displaced from their surface. The most widely used WA-s are ethoxylated alcohols and ethoxylated nonyl or octylphenols which should have very low foaming properties. The mostly used are that ones in which the numbers of oxythylene groups (ETO) ranging from 6-12. The mixtures of the nonionic surfactans with some of the anionic ones can also be used. The recommended Atlas products are the following:
Renex 30, Renex 36, Atlox 4991, Atlox 4853, EL 1026.

Thickening agents (TA)

As it is seen from the Stock's equation the kinetic stability of suspensions can be considerably improved if the viscosity of dispersing medium (DM) will be increased. One common way to do this is addition of thickeners - high molecular weigh polymer natural or synthetic, soluble in water. Another way is to use of inorganic swelling clays. Mixture of polymers and clays are sometimes most effective. The mainly used thickeners are:

- polyanionic - polyhetero - sacharide (Xanthangum) (XA)
- magnesium Silicat (MAS) and their mixture.

The following commercial products are recommended as TA-s:

Rhodopol (Rhone-Poulenc, France) (XG)
Bentone EW - (NL Industries, USA) (MAS)
Actigum CS6 - (CECA, France) (XG)
Attagel 40 - (Engelhard Minerals & Chemicals Co USA)(MAS)
Weegum (Vanderbilt Co Inc) (XG/MAS)

Some of nonionic surfactans have also a good viscosity increment effect and allow us to produce stable SC-s without using an extra thickening agent.

From Atlax products the following are recommended :
Atlox 1096, Atlox 1086, Atlox 4868B, Atlox 33878

Antifreez agents (AA-s)

To make a good cold stability of SC (freez-thow stability) what is often desired, it is necessary to include into the liquid phase of SC an polyol which may be e.g. ethylene glycol, gliceryne, propylene, glycol, sorbitol.

The polyol has also the other following functions:

- act as a humectant to stop drying and skinning. These features are usually noticed at elevated temperature.
- assist the wetting process before and during milling.

Anitfoam agents.

These adjuvants are sometimes necessary to reduce foaming during the production process and end use. Silicon emulsion types are commonl used (nonanol, silcolapse).

Biocide or preservatives (if necessary).

It has been found that worsening of stability and other properties of SC-s after some period of storage can be caused by deterioration activity of some kind of bacteria on some of SC components e.g. polysacharides.

These deteriorations can be prevented e.g. by Proxel range of biocide produced by ICI.

4. PRODUCTION TECHNIQUES

Apparatus

An easy method of preparing a SC would be to stir WP in water. However, simple experiments show that SC made this way do not satisfy requirements made for this formulation.

The reason for this lies in the relatively coarse and broad particle size spectrum produced by the mechanical and air mills.

The most suitable method in predominant numbers of cases is wet grinding method and the most efficient milling by use of stirred bead mill. These are the sand mill type very widely used for the processing of printing paints. In these mills a mixture of grinding elements (Ottawa sand or specially prepared ceramic pearls) and product to be milled (grinding stock) is rotated by an agitator on which grinding discs are mounted. This technique allows to obtain most particles below 5 microns mean diameter. The mill be vertical or horizontal batch or continuous. The vertical types of mill are exemplified by the MOLINEX PE 075 and the horizontal mills are examplified by the DYNO-MILL. These both mills are the closed type and therefore such disadvantages of milling process like air entrainment and foaming are eliminated.

Conditions of milling

The premixture containing all ingredients is prepared. The typical order of addition of ingredients during preparing the premixture is the following:

water + antifreeze agent -
dispersing agent -
- wetting agent - active ingredient -
thickening agent
- antifoam agent - biocide - dye.

However, in some cases it is advisable to prepare premix without thickening agent, dye and biocid which are added to the mixture after the milling process.

The initial particle size of the grinding stock should be below 50 microns. If it be coarser it is desirable to carry out pre-grinding by means of an air or mechanical mill. Sometimes two wet grinding mills are placed in series to allow the formulator to start often with coarse grinding stock.

As the energy of milling is dissipated in the form of heat, cooling by water is necessary. The aim of the milling process is always to produce a fine and narrow particle spectrum below 6 microns and if for biological reasons necessary also below 2 microns. Care however, must be taken not to overmill by too long milling or milling at too circumferential speed. In the case of overmill to much surface may not be wetted and particicles not dispersed rapidly enough and re-aggregation or flocculation of suspension particles may occure.

5. THE QUALITY REQUIREMENTS FOR PESTICIDES AND SOME OF ADJUVANTS

In principle, all toxicants which are crystalline at room temperature can be formulated into SC. However, due to the necessary storage stability at elevated temperatures, the melting point of the a.i. should be above 60°c. It is obvious that only compounds which are chemically stable in the water can be formulated into water flowables.

The solubility of the toxicants is very important. If it is too high then crystal growth occurs particularly when there are any fluctuations on temperature of storage. For that reason the solubility of 40°c should not exceed 100 ppm.

The solid pesticide should be as pure as possible. The impurities adsorbed on the surface may cause wetting problems and eventually flocculation. Practically all commonly used surfactants may be used as dispersing and wetting agents. The choice of a proper one naturally depends upon the pesticide. The choice of a dispersing agent is more critical and specific than the choice of wetting agent. The wetting agent must not be too firmly adsorbed - otherwise the dispersing agent will be not enough firmly attached to the surface and thus the repulsive forces between particles will be weekened. If the nonionic dispersing agents are used they should have a sufficient high cloud point (c.p.) usually above 10°c above the milling temperature and maximum required storage temperature. If the c.p. is to low the desorption of the surfactants from the particles may take place. Disadvantageous effect on some properties of SC-s may be caused by too high electrolyte concentration as well as wrong pH of dispersing medium. Therefore, the deionized water is recommended for their production.

6. METHODS OF TESTING

1. Viscosity

The viscosity in relation to the shearing is measured using rotary piskometer. It is measured in one day, one week and one month intervals. A minimum rise in viscosity is tolerated. The required property is low viscosity at high sheering stress.

2. Storage stability

In this test the physical changes of SC stored at 50°C, 40°C and room temperature are observed. The following changes can take place:

- bleeding - separation of liquid on top of SC
- thickening or gelling or skinning: normally seen on the container walls.
- sedimentation or caking.

3. Suspensibility

Evaluation is carried out according to the CIPAC handbook.

4. Spontaneous dispersibility (bloom)

Assessment criteria

good - practically no lumps
fair - few lumps
poor - many lumps

After the SC is added to the tube, the number of inversions necessary to disperse the portion of the flowables, which do not disperse spontaneously, are recorded.

From what has been said up to now it would be possible to conclude that preparation of SC should be relatively simple. Such conclusion could be however correct only, when the following conditions prevail:

- The formulator has full knowledge about these physico-chemical phenomena taking place in SCs which can cause some disadvantageous changes of these formulations.

- The formulator has at his disposal indispensable assortment of surface active agents and other adjuvants needed for these kinds of formulations.

- The formulator has at his disposal appropriate research and testing apparatus and has good experience in research methods essential for carrying out the assessment and interpretation of observed phenomena.

Because the time assigned for me for lecture is limited it is not possible to discuss in detail all of the above conditions. For that reason only some of the phenomena will be briefly discussed.

The first one is the increase of small particles of SCs during the storage of suspension. The increase of particles may be caused by excessive solubility of pesticide in water. In such a case, when the surroundings temperature is lowered, the solubility of pesticides diminished and some part of it give off. The evolved pesticide bind the particles of suspension and increased them. Therefore, only the pesticides whose solubility in water at t.40° C is $\leq$100 ppm can be used. Disadvantageous increase of particle size of suspension can also be caused by phenomen known as Oswald ripening which occurs as a result of the difference in solubility between small and large particles as given by the following Gibbs - Thomson (also known as the Gibbs - Kelvin or Ostwald-Freundlich) relationship :

$$\frac{RT}{M} \ln \left(\frac{S_1}{S_2} \right) = \frac{2\gamma}{\rho} \left(\frac{1}{r_1} - \frac{1}{r_2} \right)$$

If the solubility of large particles with flat surfaces ($r \to \infty$) is denoted by Sc the solubility Sr of particles of radium r can be expressed by : $\ln \frac{Sr}{Sc} = \frac{2M\gamma}{RT\rho r}$

Significant increase in solubility occurs when $r < 1$ micron.

If the particles suspended in a solvent are small enough, concentration greater than that one represented by "normal" solubility can temporarily be obtained. If mass transport is possible between poly dispersed particles, the larger will grow at the expense of the smaller ones.

Crystal growth can be controlled by proper choice of the dispersing agent or by rise of crystal growth inhibitors which will be adsorbed on the "active sites" on the crystal faces which prevents further deposition.

However, it should be noted that if the phenomena of Oswald ripening is theoretically well elaborated the choice ot an inhibitor still remains an art rather than a science.

Control of settling

The most common way to control settling of particles in SCs and hence to avoid the formation of hard sediments ("cake") is by using thickeners which increase the viscosity of dispersing medium. Such a solution to the problem is however not always the best one. If the viscosity is not high enough the creation of "cakes" can take place in too short a time and if viscosity is high enough to stop settling, the product can be too thick for the user to pour.

There can be other drawbacks of using organic thickeners such as lack of dispersion spontaneity or the algeing of the polymer solution due to the degradation of the polymer with time. The better solution of settling problem is by use of mixture of some of clays in inorganic oxides with polymers.

The polymer chains act as "bridges" or "links" between small inorganic particles forming by this way a "three dimensional structure" which entrap all the particles and stop settling. This system which today is commonly used by formulators is usually referred as bridging flocculation. They are studied by measuring their rheological values. The rheology of these mixed systems is complex and the network structures not well understood. The most promising solution of the settling problem seems to be controlled flocculation. This system can be used where the stabilising mechanism, electrostatic in nature, is caused by ionic surfactants which create electrostatic double layer around each particle of suspension. These electrical charge of double layer counteract the always present van der Waals forces which by themselves lead to flocculation and phase separation. Only when the repulsion between particles is strong enough, they do not flocculate and the dispersion is considered stable in kinetic sense.

If the repulsive force between particles of suspension is not too strong the weak flocculation occur and the formation of weakly structured particles throughout the system will take place. Such weakly flocculated suspension will show thixotropic behaviour. On shaking the container the floc structure can be easily broken down and a fluid system results. On standing the flocs reform, preventing settling.

Weak flocculation can be caused by aluminium chloride or by synthetic organic flocculants. The use of the former one suffers from the complication of the likelihood of hydrolysis of Al$^+$ions. While such hydrolysis may play a significant role in reducing settling by some mechanism other than weak flocculation, this could make the system less easily controllable under manufacturing conditions.

RHEOLOGICAL MEASUREMENTS

The viscosity is that parameter which is used to characterise the rheological properties of concentrated suspensions or emulsions.

Before entering on the practical problems the basic principles of rheology are shortly summarised.

Viscocity (η) is defined as the ratio of shearing stress (τ) over rate of shear(D) $= \frac{\tau}{D}$

The two types of liquids are distinguished:

- the ideal viscosous or Newtonian liquids
- the non-Newtonian liquids, (to which concentrated suspensions and conc. emulsions belong.)

For Newtonian liquids the η is constant and for non-Newtonian it is variable. The different relations between shearing stress (τ) and rate of shear (D) as well as between viscosity (η) and shear (D) are shown on the figure A and B.

curve N: represents NEWTONIAN flow, where the rate of shear is proportional to the applied shearing stress i.e. viscosity is a constant for a wide range of D.

curve PP: pseudoplastic flow of liquid

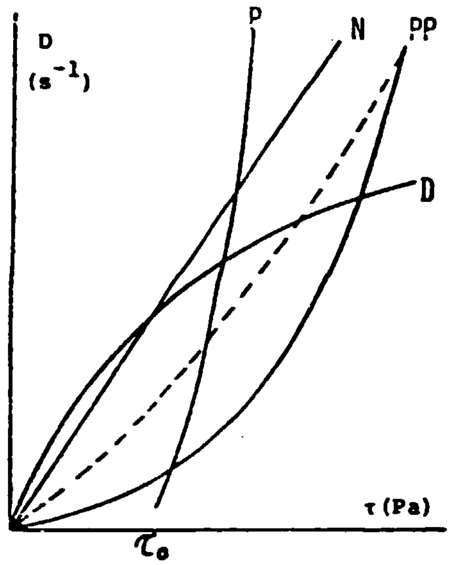
Curve P is characterised for plastic flow. The relation for this flow shows a certain value of shearing stress which must be exceeded before flow starts. The value of τ_0 is called yield value.

Curve D shows dilatant flow, where an increase in viscosity is observed with increasing share rate. (shear thickening). Since the viscosities of non-Newtonian liquids vary with the rate of shear it is essential to know the viscosity, or better expressed it as apparent viscosity, over a wide range of the rate of shear, D.

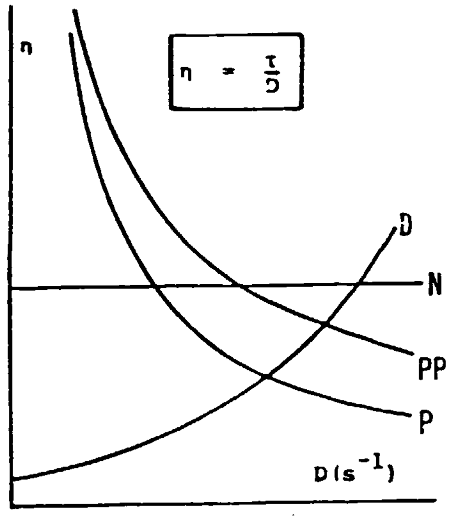
It has been found that the stability of concentrated suspensions over a period of time of storage depends on the yield value, the magnitude which gives an indication of the strength of interaction between particles in structured system. Therefore it is useful to follow the change of this value with time for stored systems. As it is seen from the showed curves for plastic flow the magnitude of yield value can be measured in low share range. For these measurements some type of viscosimeters which are also called rheometers, are used.. One of the most common is Brookfield LVF. viscosimeter.

During the testing of some of SCs it has been observed that type of curve, plastic or pseudoplastic, it was dependent of the type of used dispersing agent. When anionic one had been used, the curve was characteristic for pseudo plastic flow whereas for non-ionicplastic flow. – It has been found also that while yield value increases stability, it decreases spontaneitv of dispersion of SC in water. The optimal yield value is between 0,3 (minimal stability) and 1.5 pa (still good spontaneity).

MEASURING OF VISCOSITY



A. Different types of flow



B. Viscosity n(nPa.s) depending on the share rate D(s^{-1})

VISCOSITY $= \frac{\tau}{D} = \eta$

Newtonian liquids

non-New tonian liquids

PP-pseudoplastic flow] apparent viscosity
P-plastic flow]

YIEL VALUE (0,3 - 1,5 Pa)

Brookfield LVF Viscosimeter

RECOMMENDED PAPERS

Th. F. Tradros	"Physical Stability of Suspension Concentrates" Adv. Colloid Interface Sci, 1980, 12, 141
Th. F. Tadros	"Control and assessment of the physical stability of pesticidal suspension concentrates" chemistry & Industry, 15 March 1980
B Vincent	"The stability of particulate suspensions" Chemistry & Industry, 15 March 1980
Chavau Virendra	"Physical principles in suspension and emulsion processing", Advan. Transport Processes 1984, 3, 1-34
Th. F. Tadros	"Dispersion Science and Technology in Pesticidal Formulations" Advances in Pesticide Science, (1983) 245-246

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ABOUT SOME EFFORTS TO INCREASE EFFECTIVE AND SAFE USE OF PESTICIDE

In a supplement of Dr. Pillai's lecture I would like to take up several problems concerning efforts aiming to more effective and safe use of pesticide.

As it is commonly known the ultimate activity of pesticide depends primarily upon its chemical constitution and its capability of entering into a suitable biological reaction. Realization of this ultimate capability depends upon proper formulation and application, which primarily answers the problems of handling toxicant so that it can be distributed adequately to reach a specific part in a specific area.

It is obvious, taking into account high potency of modern pesticides, that the particle size of pesticides must be quite small in order to be dispensed adequately.

Assuming that the exposed foliage surface area of crops is in general four to five times of the soil surface it can be calculated that spraying 10 gallons of liquid per acre and getting droplets of 50 microns, we approximate 300 drops per square centimeter. But the covering of treated surface will not be complete even if we assume perfect distribution and no loss of drift. The degree of covering which will be obtained is shown on Fig. 1.

If water, which is mainly used as carrier of pesticides will contain a wetting agent, the droplets will spread to approximately three times their original diameter whereas in the case of oil sprays the droplets spread over fifteen times their original diameter and thus compensate for incomplete coverage.

In the case of some number of dry particles, there is disconcerting portion of uncovered surface even under these assumed perfect conditions because these particles do not spread over surface. Distribution of 10 microns particles would increase the number 125 times and theoretically would solve the coverage problem. But particles of these sizes are not good enough for deposit and adherence to plant surface. They should be > 30 microns. Mathematical calculation and field experience have established that the old inorganic toxicant such as calcium arsenate require an average particle diameter of 40-50 microns in order to obtain effective distribution at dosages of 20-30 pounds per acre in full foliage. This is also an optimum average particle size for carriers. Where more potential modern organic insecticides are used their dosage will of course be much lower. But to get good coverage using such amount of insecticides we must produce at least the same number of particles from the smaller quantity. This would be attained if their particles would be 13 microns. Preparing however and using dust having such particles would be not economical and very dangerous. Most of the particles would be drifted out of the protected area. The better solution would be to prepare a powder of very small particles of pesticides and to stick them on bigger particle of carriers. To get however, even coverage of carrier with pesticide the particles of the latter one should be about 4 microns. The degree of covering of particles of carrier of diameter of 40 microns by insecticide particles of different size are illustrated on fig. 2. The dusts of such characteristics can be prepared by mixing carriers with concentrated dust containing high concentration of very small particles of pesticide mixed with a second carrier of similar size of particles or by mixing the carriers with solution of insecticide and after mixing evaporate the solvent. It is obvious that such procedure is very costly and this is the main reason why the dust formulations which were used widely yet before World War II have been displayed by that formulations which are used for spraying. But unfortunately these formulations, however the best to achieve even distribution of very small quantity of the active ingredient over a large area, are also not devoid of several possible drawbacks.

The physical and chemical properties of active ingredients may prevent their being easily dissolved in common solvents at any rate, not without expensive formulation. Several problems appear in aerial application what is related with the evaporation of solvents and drifting problems.

From the safety point of view, preparing liquid pesticide mixtures increases the possibility of exposure to concentrated, very often, very toxic materials to workers. The alternative to liquid sprays besides dusts formulation are many and varied. Such can be mentioned like granular formulations,more popular for soil treatments because they poor retained on foliage. The granules used for soil application can be prepared as slow or quick release pesticide. The first one offer one way of extending the biological half-life of pesticide which as such is rapidly degraded. Pheromones or repellent chemicals may best be applied in formulations which slowly release the active ingredient over a long time. Quick-released devices are available which consist of water-soluble capsules containing an insecticide which is itself formulated to spread over the water surface when the capsules disolves and releases it. Slow release formulations on the other side can be prepared if the foamed plastic is used. It may float on the surface of water and release the insecticide at a controlled rate over a long time. The rate of release depends upon toxicant and surfactant concentration as well as polymerization conditions of the plastic matrix.

The mentioned examples of various non-liquids specific formulations are not so widely used as formulations for dusting or spraying. For that reason the efforts are also taken to improve as well effectiveness of these formulations as their safe usage.

Taking into account social presures now-a-days to prevent environmental pollution and to eliminate the danger of inflicting injury on those who handle pesticides even at the sacrifice of some degree of effectiveness research and experiments have been aimed at finding a suitable distribution of particle size with respect to effectiveness and drift. From the same reasons cost of production of new pesticide formulations is less critical.

The efforts aimed to improve dust formulations are twofold:

by improving their deposition and distribution on protected plants and
by reduction of their drift

Unfortunately these two phenomena are interdependend. The smaller particle size of dust the better distribution but at the same time the more drift.

The first problem is trying to be solved by a method named as 'ELECTROSTATIC DUSTING'. Observations showed that there was an enormous difference between the behaviour of one dust and another in the field. Close study showed, as was expected, that this could be ascribed to the nature of the filler used. It was further found that this efficiency could be tied down to electrostatic charges imparted to the filler by friction while being passed through the machine outlet. Various fillers behave in different ways. Some charged negatively, some positively and others carry mixed charge. Others do not acquire any charge at all. It has been found also that different types of outlet varied in their ability to charge the particles and that some were much more effective than others.

On the basis of these observation the next step was to try to apply a charge electrically.

The basic principles underlying electrostatic dusting are contained in the two axioms that "like forces repel, unlike forces attract" and that, an electrical force induces an equal and opposite charge at the other side of conducting surface. When a charge is placed upon a cloud of particles, if that charge is all in one direction, then the cloud will be prevented from agglomerating by the mutual repellency exhibitied.

Normal uncharged dusts rely upon the velocity of discharge and the force of gravity, to deposit on a plant surface. In normal dusting there is enormous waste of material since not only does the speed of the dust overcome the force of gravity, but the existence of a barrier layer of a thermal nature of the plant surface directly prevents deposition of much dust that might otherwise be deposited.

When however an individual particle is charged, it creates its own attraction to the plant surface in proportion to its proximity to the surface, and when sufficiently close those force is sufficient to overcome the speed of particle and the resistante of the barier layer. Owing to lines of electrostatic force, which resemble lines of magnetic force the dust particles precipitated on both the surfaces.

The method of electrostatic dusting is not very complicated. A probe at the outlet of duster is charged with a very high potential, in this case a positive one. By passing dust particles through the electric field they are charged in one direction only. It has been found that by using electroduster the overal increase of deposition of dust was over four and half times. The second direction of improving dusting aimed to reduce droft.

These can be realized by using dust of closely range of particle size and without small particles easily drifted. Several need of such type of dusts called corse dust has been already registered in Japan. They are insecticide as well as fungicide dusts. Their range of particle size is narrower than normal dusts. They contain a little fine particles under 10 microns. A little flocculating agent is also added to this formulation for flocculating fine particles on the large particles.

Similarly as in the case of dusts the new techniques are also introduced to improve the efficiency and safeness of using of sprays. The two directions of solving these problems are :

by using special deviced spryers giving controlled Droplet Application (CDA) and electrostatic charged ULV.

The first technique where spinning disc device is used will spray both oil and aqueous formulations while the second technik by using device known as Electrodyne sprayer requires special oil based formulations.

Research into the relationship between droplet size and biological efficiency suggests that different droplet size are required for different types of target. CDA machines are designed to produce a restricted range of droplets suited to the pest target, thereby eleminating westage and reducing the volume of liquid applied and in some circumstnces the quantity of chemical. The both machines enable chemicals to be applied at 0.5-1.0 litres per hectar compared to 2,5-5,0 litres with conventional ULV application. In the case of Electrodyn sprayer the better deposition of droplets is achieved by the use of high voltage 25,000 volts to atomise and propel the oil-based pesticide formulation. Electrodyn-sprayer is powered by four 1.5 volt batteries which give 60 hours operation before they need changing.

At the end of my lecture I think it would well to give a little more information about a new type of formulations DRY FLOWABLES. These formulations are also called, more properly, as DISPERSIBLE GRANULES(DG-s). These are non-dusty pesticide granules, easily dispersed in water and similarly to WP-s used to prepare diluted water suspensions. The main reason of producing this type of formulation is mainly safety, for a farmer as well as environment, and of their more convenient usage in comparison to WP-s. In particular cases, better activity in comparison to WP-s can also be obtained. This formulation has advantages of liquid flowable or suspension concentrate as well as those ones of wettable powders -

DG-s may be produced by two methods:

i) by spray drying of water suspension of fine particles of pesticide and

ii) by agglomeration of solid fine powders of pesticide

The choice of method depends on economical factors of production process.

The spray drying method is preferable in the cases when water suspension of pesticide in last step of synthesis is obtained or when smaller particles which can be obtained by wet milling, are demanded (e.g. for fungicides).

For spray drying method special construction spray dryer must be used. It is installation in which suspension is splashed as droplets by hydraulic system and not by spinning disc commonly used in more common spray dryers in which the solution or suspension is atomized.

For agglomeration the fluidized method often is used.

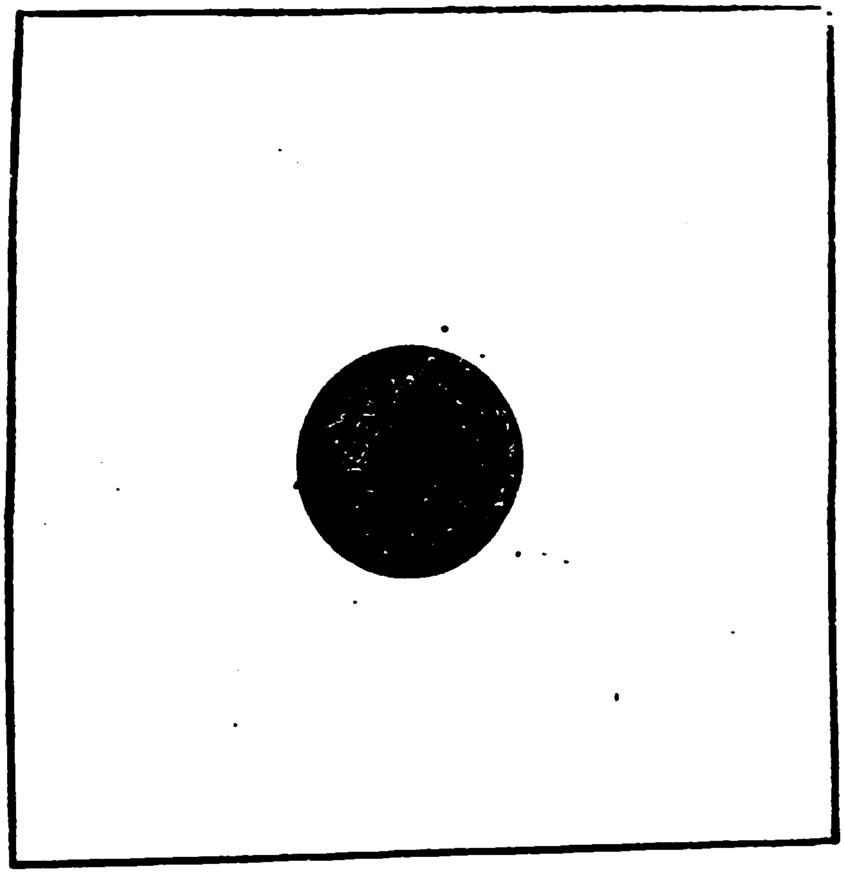
It is obvious that in both methods special surface active agents and binding agents must be used.

Surface active agents are added to the system to overcome the resistance of solids to wetting and to ensure ease of dispersibility in water and good stability of suspension. The binding agent must be easily and quickly dissolved in water. Optimization of the system bindergum-wetting agent-dispersing agent should result in disperible granule integrity, reduced dust, good disintegration and dispersion of end formulation.

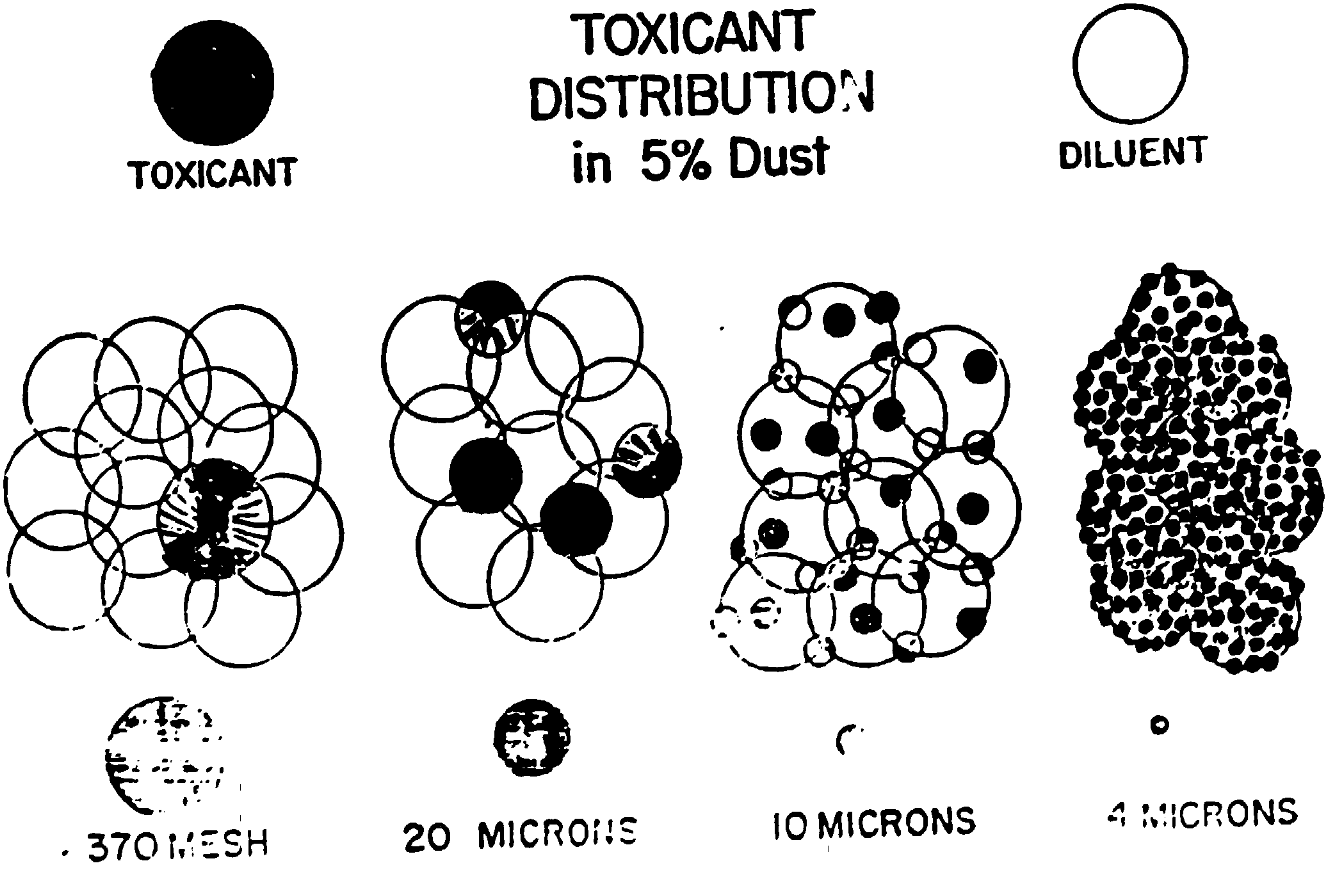
Beside the surface active agents and other adjuvants the parameters of processes are also critical for quality of products. In the case of spraying temperature of drying, size of droplets, type of nozzles and speed of drying and in the case of fluidised bed granulation. Such parameters as fluidising air flow rate, fl. air temperature, fl. air humidity, nozzle type, spray angle, liquid flow rate, atomising air pressure droplet size.

The DG-s are today yet produced only by several companies but it is sure that this formulation will very soon be a dominant one as very safe, very convenient and, in many cases, very effective.

Fig.1



Comparative area. 10 gallons in 50 micron drops on 5 acres foliage surface



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LIQUID AND DRY FLOWABLE
(New Formulations of Pesticides)

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DEFINITION OF TERM - THE NEW FORMULATION

In my lecture I will discuss the problems concerning the two new pesticide formulations viz. suspension concentrate (SC), which belong to the group of liquid flowable formulations (LF) and dispersible granule (DG) called also dry flowable. Prior to, however, it would be well to clarify what kind of products can be considered as the new formulations. I think that for further discussion the following definition will be useful.

If a specification of a product is different from that ones, which alreadyare commonly known and used then we have to do with a new formulation.

Accepting such definition we can ask : are we to do with a new formulation of dust if a new product is produced in such a way that very small particles, had been blown away and consequently a new product is more safe and even more effective than other ones. We can answer yes, it is a new formulation because specification for this product is different than the specifications for other commonly used dusts. But if because of a change of composition of dust formulation, or change of some of the parameters of their production process a cheaper

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Presented during the training course on Pesticide Formulation Manufacture conducted by Pesticide Development Programme in India at the Management Development Institute, Gurgaon, Haryana, India from March 18-22, 1985 product, or that one of better quality is obtained then we can say that it is an improved dust formulation but not a new dust formulation. The quality parameters for the new product can be different but specification will be the same as for others dusts. If e.g. distribution of such insecticides as DDT or BHC among carriers in 5% dust will be better than in other similar dusts than the first one can not be considered a new formulation but only as an improved one or better one.

The difference in distribution of DDT in four dust formulations are shown on fig. 1.

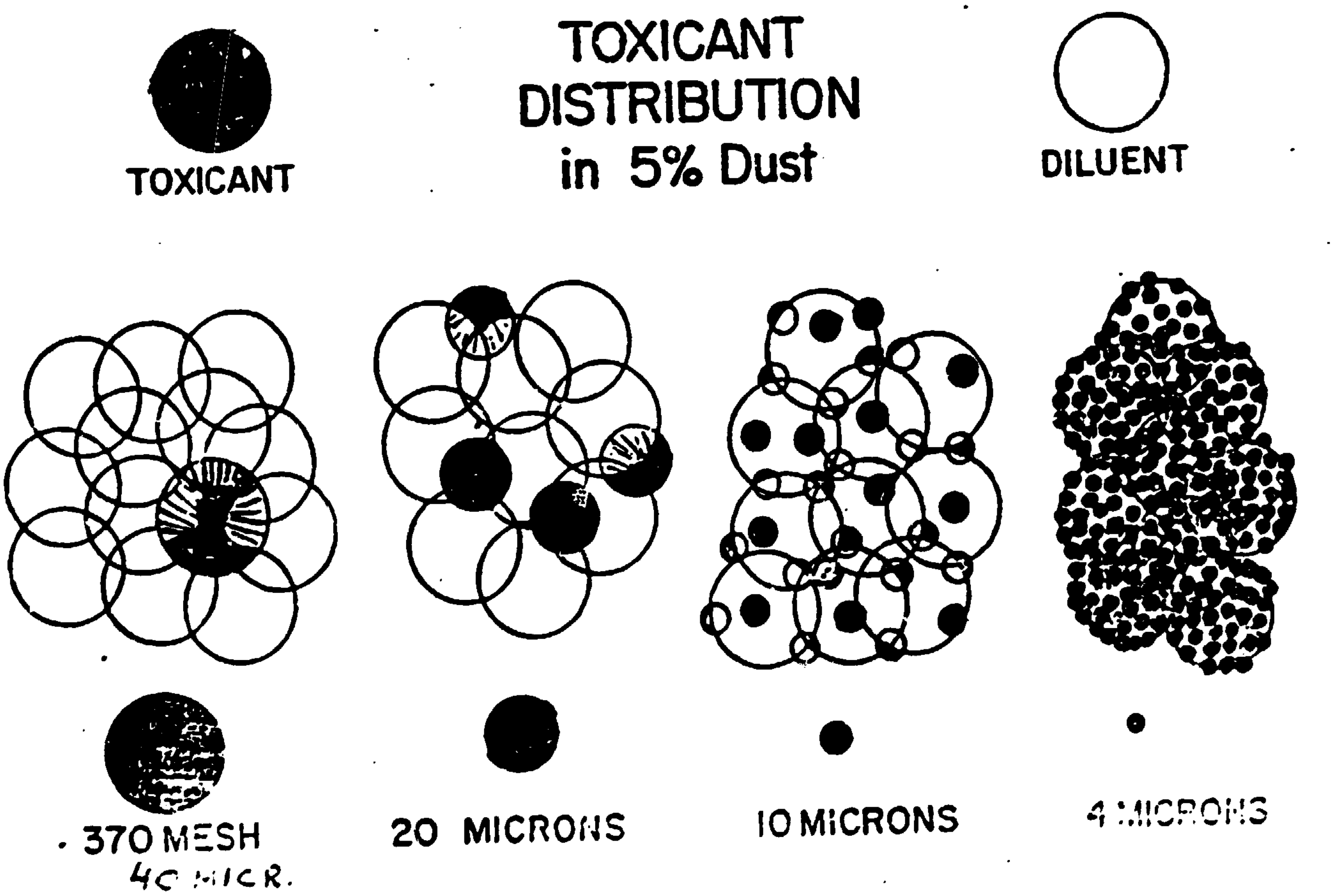

Fig.1

These differences between the products can cause the different activity but if all of them fulfiled the same approved specification none can be considered as a new formulation.

And yet the last example:

If one of EC formulation is giving better distribution of pesticide on leave surface and better its tenacity to it, than other EC of the same pesticide as the first one can not be considered as a new formulation, because in specifications for EC such properties as distribution of pesticide on leaves surface and its tenacity to leaves are not specified.

If, however, such EC formulation will be introduced, on the market which, in contrary to previously ones used is characterised by quick separation of emulsion, and this characteristic will be specified in new specification, then this EC formulation will be considered as a new formulation.

LIQUID FLOWABLES - GENERAL CHARACTERISTIC

The new type of pesticide formulations which are characterized by different specification than others PF-s are liquid flowables.

There are three different types of them:

SUSPENSION CONCENTRATE
EMULSION CONCENTRATE
SUSPENSIO-EMULSION CONCENTRATE

Because many characteristics are similar for all of LF-s formulations only that ones which characterised SC will be discussed in more detail.

What is SC, how it looks, what are its properties and what are its advantages in comparison with other formulations of pesticides commonly used? The SC is a mixture of fine particles of solid pesticide with water, surface active agents and some other adjuvants.

It can be said that SC is a mixture of pesticide in which instead of mineral carrier as in WP, or organic solvent as in EC the water is used. SC is a water paste of pesticide easily to flow and the same easily pour to water and for that reason is called, "flowable".

The main difference in composition between EC-s, WP-s, and SC-s are shown on table 1.

Table 1 **THE DIFFERENCE BETWEEN COMPOSITIONS OF EC-s,WP-s AND SC-s(% w/w)**

Components	**Formulations**		
	EC	**WP**	**SC**
Pesticide	45	45	45
Solvent	50	-	-
Mineral Carrier	-	50	-
Emulsifiers	5	-	-
Dispersing & Wetting Agents	-	5	6
Water	-	-	30
Other Adiuvants	-	-	19
	100	100	100

The concentration of pesticide in SC calculated on the weight basis is about 45-50%, but it is higher if the calculation is made on the weight volume basis what is caused by higher density of pesticides in comparision with the density of water.

These differences in concentration are ilustrated for sulfur and copper oxychloride in table 2.

Table 2

COMPOSITION AND CONCENTRATION OF PESTICIDE OF TWO SC-s, SULFUR (1) AND COPPER OXYCHLORIDE (2)

	1		2
Sulfur	60	Copp.Ox	45
Adiuv	20	Adiuv.	20
Water	20	Water	30
	100		100
%(w/w)	45	%(w/w)	45
%(w/v)	85	%(w/v)	67
d_s = 2,0		d_c = 3,7	

SPECIFICATIONS FOR LF-s

Similarly as WP-s and EC-s the LF-s are used to prepare diluted water suspensions or emulsions. Therefore, some of their properties should correspond to that of former ones. They should be as EC-s easily measured by volume and easily poured into the spray tank. To fulfil these requirements their viscosity must not be too high at the time of application. After pouring into water they must, similarly to WP-s or EC-s, disperse spontaneously and ensure very even distribution of fine particles or droplets in the spray, as well as, good stability of dispersion. Equally important, but most difficult to obtain, is storage stability. Ideal LF should be stable under severe conditions of storage and shelf life should be at least two years. Their phases must not separate in this time or if some slight separation takes place it is essential that the separated phase will be readily re-dispersed and form easily homogenous dispersion. The last requirement is not only the most important but also most difficult to obtain. It is obvious that chemical stability must also be accomplished.

All pesticide formulators know from their experience that the rate of sedimentation of suspension prepared from WP depends upon their particle sizes. The smaller the particle sizes the better stability of suspension and less amount of sediment after some period of time. It is also commonly known that "hard" sediment or "cake" created by settling down of suspension is often very difficult to redisperse, especially when suspension is standing for the longer time.

If a similar phenomena - the creating of "hard" cake, could have taken place in the case of SC, then the following serious troubles may appear:

If part of "hard cake" will not redisperse after mixing the SC, then the concentration of liquid spray prepared from partly sedimented SC, will not be high enough and the protection effect can be much worse from that one expected. If, after all, the redispersion of "hard cake" is obtained, it can happen that this redispersion is not complete and some amount of bigger aggregates have been introduced to the liquid spray. They can clog the nozzles of spraying machine.

From the practice of work on WP-s it is known how it is sometimes difficult to get good stability of suspension of WP-s in spite of the fact that demanded stability is not too high, viz. 50-80% suspension stability after 30 minutes.

But in the case of SC the required stability is much, much higher. The SC should be stable during at least 2 years and in this period the creating of "hard cake" is not accessible.

BASIC FACTORS AFFECTING THE PHYSICAL STABILITY OF SC-s

Now the following question should be clarify : What are the basic factors affecting the physical stability of SC-s. They can be easily noticeable from the basic equation of sedimentation of suspension i.e. from the Stokes equation, which is as follows:

$$v = \frac{2\,(\Delta d)\,g\,r^2}{9\,\eta} \qquad (1)$$

While the above equation is valid only for very diluted suspension, and is more complex for concentrated suspension, the basic proportionality between V, d, r^2, g and n are also valid for concentrated suspension.

It is seen from the above equation that the stability of suspension is directly proportional to the square of radius and to difference between density of solid particles and liquid and inversly proporticnal to the viscosity of liquid.

Then the rate of sedimentation may be reduced by decrease the particles of suspension or by increase the viscosity of dispersion medium or by changing both of these quantities.

The rate of sedimentation of suspension of sulfur and copper oxychloride of different particle size are given in table 3.

Table 3

RELATIVE RATE OF SETTLING WITH REFERENCE TO PARTICLE SIZE AND DENSITY

(HEAD HEIGHT = 40 Cm.)

Particle size in µm (radius)	Sulfur (density = 2.0)	Copper oxychloride (density = 3.7)
0.1	210 days	78 days
1.0	2 days	18 hrs
10.0	30 minutes	11 minutes

It is seen from the table 3 that even the particle size of 0,1 µm, is not enough small to assure the needed specification for SC. This specification however, would be satisfy if as the same time the viscosity of dispersing medium would be increased.

PRODUCTION TECHNIQUE OF SC-s

In greater number of cases the milling process is necessary in production of SC-s. The choice of method of grinding depends on the physical properties of pesticide (its hardness and melting point). Some times however, it can happen that process of milling is not necessary. This will be the case when enough small particles of pesticide are obtained in the process of its synthesis. (What have taken place e.g in the production of copper oxychloride, atrazine or pyramine). In such a case, the process of production of SC consist of mixing of such fine particles of pesticide with water, dispersing and wetting agents and other adjuvants. The process of mixing is performed in such mixers which are commonly used for mixing of flowable pastes e.g. flowable oil paints or enamels.

If however, the pesticide particles are not fine enough,are not too hard and have not too low melting point, the dry grinding, by using one of the commonly used mill can be used.

The choice of equipment for grinding will depends on grinding capabilities of pesticide, on economy of grinding and what is most important on the particle size range that is required in the final product for assuring the shelf life stability. Good result of milling may be obtained already by the use of hammer or pin mill whereas for others materials even the using of jet -o- mill may appear to be insufficient.

From up to date experience it is known that the best fine milling is obtained by the wett process and that the best device for this type of milling is bead or pearl mill.

These are the sand mill type very widely used for the processing of printing paints. In these mills a mixture of grinding elements (Ottawa sand or specially prepared hard ceramic pearls) and product to be milled (grinding stock) is rotated by an agitator on which grinding discs are mounted. The mill be vertical or horizontal, batch or continuous.

The vertical types of mill are exemplified by the MOLINEX PE 075 and the horizontal mills by DYNO-MILL. Both are the closed type mills and therefore such disadvantages of milling process like air entrainment and foaming are eliminated.

As the energy of milling is dissipated in the form of heat, cooling by water is necessary. The aim of the milling process is always to produce a fine and narrow particle spectrum below 6 microns and if for biological reasons necessary also below 2 microns. Care however, must be taken not to overmill by too long milling at too circum speed. In the case of overmill too much surface may not be wetted and particles not dispersed rapidly enough and re-aggregation or flocculation of suspension particles may occure. Besides the efficient milling, the wett process in bead mills assure quick and good mixing of all components as well as good dispersion of solid particles.

SPECIFICATION FOR PESTICIDES USED FOR SC-s.

In principle, all toxicants which are crystalline at room temperature can be formulated as

SC. However, due to the necessary storage stability at elevated temperature, the melting point of the active ingredient should be above 80°C.

It is obvious that only compounds which are chemically stable in the water be formulated into water flowables The initial particle size of the grinding stock should be below 50 microns. If it is coarser, it is desirable to carry out pre-grinding, if possible by using dry milling. Some times however two wet grinding mills are placed in series to allow the formulator to start often with coarse grinding stock.

The solid particles should be as pure as possible. The impurities adsorbed on the surface of particles may cause their wetting problems and the same efficient milling. For the same reason it is necessary to use for wet milling deionized pure water.

The degree of solubility of pesticide in water is very important. If it is too high then crystal growth occurs, particularly where there are any fluctuations on temperature of storage. In such a case

some amount of pesticide soluble in water in higher temperature can percipitate after lowering of temperature and small particle of precipitate will be able to combine the particles of suspension and create the biger agregates. For that reason the solubility of pesticide in water in 40°C should not exceed 200 ppm.

ADJUVANTS AND THEIR FUNCTIONS

The type of commonly used adjuvants and the functions which they perform are as follows:

Dispersing agents.(DA). These surfactants are used to facilitate the communition process as well as to stabilize the micronized particles in the dispersing medium against irreversible flocculation. The ionic or nonionic dispersing agents can be used as well as some of macromolecules or polyelectrolytes. With ionic surfactants irreversible flocculation is prevented by the repulsive force generated by electrical double layer around each particle.

With nonionic surfactants and macromolecules repulsion between the particles is ensured by the steric" interaction of the adsorbed molecules on the particle surface. The attaching compounds to the particles prevent from coliding them by the "tail" of the dispersing agent, which interferes in the collision. With polyelectrolytes both electrostatic and steric repulsion exist. Dispersing agents are generally short chain polymers with charged groups. Typical of them are: Sodium salt of alkil naphtalene sulphonic acid; (Atlox 4862) Sodium salt of naphtalene formaldehyde sulphonic acid condensate; sugar free sodium-based lignine sulphonates (POLYFONS, UFOXANES).

Wetting agents (WA)

The WA-s are used to facilitate the communition of solid pesticide during wet milling process. They displace the air from the surface of solid particles and make the

the milling process more efficient. The most widely used WA-s are ethoxylated alcohols and ethoxylated nonyl or octylphenols which should have very low foaming properties. The mostly used are that ones in which the numbers of oxythylene groups (ETO) ranging from 6-12. The mixtures of the nonionic surfactants with some of the anionic ones can also be used. The recommended Atlas products are the following:

Renex 30, Renex 36, Atlox 4991, Atlox 4853, EL 1026.

The type of surface active agents depends upon the type of pesticide. The choice of dispersing agents is more critical and specific than the choice of wetting agents. The wetting agent must not be too firmly adsorbed on surface of pesticide particles - otherwise the film of WA will prevent the firm attache of dispersing agent to particle surface.

The repulsive forces between particles will be then weakened and stability of suspension worsening. For the same reason the concentration of wetting agents should be not too high. If nonionic dispersing agents are used, their cloud points should be about 10°C higher than the temperature of grinding stock during the process of milling and above the maximum storage temperature. The cloud or temperature point of nonionic dispersing agent is a temperature of their water solutions by which their solubility is smaller and part of emulsifier is emited from solution. For non-ionic surface active agents the higher temperature the lower its solubility. The cloud temperature depends upon the amount of oxyethylene group in molecule or upon the HLB of surface active agent. If the cloud temperature of non-ionic dispersing agent is not higher than the temperature of stock during milling or temperature of storage of SC, then during the milling or during the storage the dispersing agent will evolve from solution and the flocculation of SC will have taken place.

Thickening agents(TA)

As it is seen from the Stokes' equation the kinetic stability of suspensions can be considerably improved if the viscosity of dispersing medium will be increased. One common way to do this is addition of thickeners -high molecular weigh polymers, natural or synthetic, soluble in water. Another way is to use of inorganic swelling clays. Mixture of polymers and clays are sometimes most effective. By using these type of thickeners the viscosity of dispersing medium can be easily increased many thousand times. Using e.g. a concentration of 0,3-0.5% of some thickners, the viscosity can be increased from 1 cp to 11,000-16,000 cps. As a result the rate of sedimentation of particles will be considerably reduced. The mainly used thickners are:

- polyanionic-polyhetero sacharide(Xanthan gum)(Xg)
- Magnesium Silicat(MAS)
- Mixtures of XG and MAS

The following commercial products are recommended as TA-s:

Rhodopol (Rhone-Poulenc, France) (XG)
Bentone EW - (NL Industries, USA) (MAS)
Actigum CS6 - (CECA, France) (XG)
Attagel 40 - (Engelhard Minerals & Chemicals Co USA)(MAS)

Weegum (Vanderbilt Co Inc) (XG/MAS)

Some of nonionic surfactants have also a good viscosity increment effect and allow us to produce stable SC-s without using an extra thickening agent.

From Atlas products the following are recommended: Atlox 1096, Atlox 1986, Atlox 4868B, Atlox 33878

Antifreez agents (AA-s)

To make a good cold stability of SC (freez-thaw stability) what is often desired, it is necessary to include into the liquid phase of SC an polyol which may be e.g. ethylene glycol, gliceryne, propylene, glycol, sorbitol.

The polyol has also the other following functions:

- act as a humectant to stop drying and skinning. These features are usually noticed at elevated temperature.
- assist the wetting process before and during milling.

Because some pesticide can be more soluble in water solution of polyols what is disadvantageous phenomena for stability of suspension(Ostwald ripening) as an alternative of antifreeze agent urea might be used.

Anitfoam agents.

These adjuvants are sometimes necessary to reduce foaming during the production process and end use. Silicon emulsion types are commonly used (Nonanol, Silcolapse).

Biocide or preservatives (if necessary). It has been found that worsening of stability and other properties of SC-s after some period of storage can be caused by deterioration activity of some kind of bacteria on some of SC components e.g. polyscharides.

These deteriorations can be prevented e.g. by Proxel range of biocide produced by ICI.

METHODS OF TESTING

Viscosity

Because SC belong to non-Newtonian liquid in which viscosity depends upon shearing stress, the viscosity in relation to the shearing is measured, using rotary wiskometer. It is measured in one day, one week and one month intervals. A minimum rise in viscosity is tolerated. The required property is low viscosity at high shearing stress. Very important characteristic of SC is YIELD VALUE. It is a minimum shear stress which breaks a hydrogen binden structure of SC and cause its flow.

PARTICLE SIZE ANALYSIS OF SUSPENSION CONCENTRATES

Coulter counter

The principle of the instrument is as follows. The suspension concentrate is diluted with an electrolyte solution and suspended particles are passed through a small orifice, on either side of which is an electrode. As each particle passes through the aperture and displaces its own volume of electrolyte, the resistance in the path of the current changes. These changes in resistance generate voltage pulses whose amplitudes are proportional to the volume of the particles. The resulting series of pulses are amplified, counted and classified in upto 16 channels, i.e. 16 size groups. The results are plotted directly as a histogram or a cumulative distribution by volume. The median can therefore be read directly off the plot.

Centrifugal photosedimentator

The suspension in sedimentation chamber can be rotated at speeds between 600-6000 rev/min. This sedimentation process is monitored by measuring intensity of beam of white light of known initial intensity and this intensity is detected by appropriate resistor and recalculated on particle sizes.

Optical microscopic size determination

DRY FLOWABLES or WATER DISPERSIBLE GRANULES (WDG-s)

If some number of particles of wettable powder would be stick together to form agregates in such a way that dust free, small granules are formed, which after pouring to water will spontaneously, as WP, create water suspension, then such a new product can be called DISPERSIBLE GRANULES

The process of sticking of small particles to form big granules is in general relatively simple and is commonly applied in pharmaceutical industry since a long time. Also in pesticide industry some type of granules used for combat pest in soil are prepared from fine particles of pesticide mixed with mineral carrier.

But in the case of DG-s the process is more complex, because it is necessary to prepare not only dust free granules but also easily dispersed in water. Such granules can be obtained if appropriate surface active agents and sticking agents will be used as well as well-chosen parameters of the process

DG-s may be produced by two methods:

i) by spray drying of water suspension of fine particles of pesticide and

ii) by agglomeration of solid fine powders of pesticide

The choice of method depends upon economical factors of production process.

The spray drying method is preferable in the cases when water suspension of pesticide is obtaining in last step of synthesis or when very small particles of active ingredients, obtained by wett milling, are demanded.

For spray drying method special construction of spray dryer must be used. It is installation in which suspension is splashed on droplets by hydraulic system and not atomized by spinning disc as in more common spray dryers

For agglomeration of solid fine particles several granulation techniques are known, but the most appropriate for WDG is the pan or disc granulator. In this method dust is fed to a rotating shallow pan inclined to cause the dust to spread over the flat bottom as it rotates. A fin mist of water or solution is sprayed on the dust, causing aglomerates to form during rotation . These fall to the bottom edge and spill over to collector. Depending on the composition of the mixture, a drying step may be required.

More commonly the fluidized method is also used. It is obvious that in both method special surface active and binding agents must be used. Wetting agents are added to system to overcome the resistance of solid to wetting and to ensure good covering of particles by dispersing agent as well as to stick them by binding agent. Bindergum-wetting agent-dispersing agent should result in dispersible granule integrity, reduced dust and good disintegration and dispersion in water.

The wetting and dispersing agents are the same which are used in production of WP-s. As a binding agent most commonly POLYVINYL PYROLIDONE is used.

Besides the appropriate adjuvants, the parameters of process are also critical for quality of products. In the case of drying method the following parameters are critical.

Size of droplets of spray temperature of drying, speed of drying and degree of drying of product, and in the case of fluidize bead granulation method such parameters as :

fluidising air flow rate, fluidising air temperature, fluidising air humidity, nozzle type, spray angle, liquid flow rate, atomising air pressure, droplet size of sprays.

The DG-s are today yet produced only by several companies but it is sure that this formulation will be very soon a dominant one as very safe, very convenient and in many case very effective.

LIST OF LF-s FORMULATIONS

Acc. to Pesticides Mannual 6th 1979/80
and Pharmaceuticals Jan. 1984

HERBICIDE FLOWABLE

GESPAN 500 FW (CIBA GEIGY)	contains ametrine
MODOWN (Mobil Chem. Co.)	contains bifenox
FENERON Multi 500 FW(CIBA-GEIGY)	contains bromofenoxim
FENERON COMBI 500 FW (CIBA-GEIGY)	-do-
FENERON GB 500 FW (CIBA GEIGY)	-do-
DIPOFENE 600 FW	contains chlormethiuron
DICURAN 500 FW	contains chlortoluron
GARDOPRIN	contains terbuthylazine
IGRAN 500 FW	contains terbutrine

FUNGICIDE FLOWABLES

BINAPACRYL (HOECHST)	
DACONIL (Diamond-Schemrock)	
Mil-Col (ICI)	contains drozoxolon
Milsten (ICI)	contains ethirimol
THIRAM (RHOME & HAAS)	
ZINEB "	
BANISTIN FL (BASF)	contains Karbedazim
DEROSAL - Lig (Chafer)	contains Karbendazim

INSECTICIDE FLOWABLES

CARBARYL (Union Carbide)	
CARBOFURAN (FMC)	
COL 400/L (ICI)	contains o-p insec. menazon
GARDONA (SHELL)	

RECOMMENDED PAPERS

Th. F. Tradros	"Physical Stability of Suspension Concentrates" Adv. Colloid Interface Sci, 1980, 12, 141
Th. F. Tadros	"Control and assessment of the physical stability of pesticidal suspension concentrates" chemistry & Industry, 15 March 1980
B Vincent	"The stability of particulate suspensions" Chemistry & Industry, 15 March 1980
Chavau Virendra	"Physical principles in suspension and emulsion processing", Advan. Transport Processes 1984, 3, 1-34
Th. F. Tadros	"Dispersion Science and Technology in Pesticidal Formulations" Advances in Pesticide Science, (1983) 245-246
M.E. Aulton M. Banks	"The factors affecting fluidised bed granulation" Manufacturing Chemist & Aerosol News, December,1978, 50-56
M.E. Aulton M. Banks	"Fludised Bed Granulation - Factors Influencing the Quality of the Product" Int.J.Pharm. & Prod.Mfr.2(4),24-29(1981)

A Training Programme on
PESTICIDE FORMULATION DEVELOPMENT

18-22 February 1985

MONDAY, 18 FEBRUARY 1985

09.00-09.30	Registration of Participants
09.30-10.30	PESTICIDE FORMULATION DESIGN - SOME ASPECTS Dr. S. K. Khetan
10.45-11.45	EMULSIFIABLE CONCENTRATES AND THEIR DEVELOPMENT Dr. E. P. Yesodharan
11.45-12.45	EMULSIFIERS AND EMULSIFICATION Dr. S. Mosinski
12.45-13.15	Discussion
14.30-16.00	- WELCOME BY CMD,HIL - REMARKS BY UNDP REPRESENTATIVE - INAUGURAL SPEECH BY SECRETARY MINISTRY OF CHEM. & FERTILIZERS - VOTE OF THANKS BY GM(P),HIL

TUESDAY, 19 FEBRUARY 1985

09.30-11.00	DUST AND WETTABLE POWDER FORMULATIONS AND THEIR DEVELOPMENT Dr. N. K. Pillai & Dr. Stefan Mosinski
11.15-12.45	SIZE REDUCTION AND BLENDING TECHNIQUES Mr. S. Kumar & Mr. V. N. Dutta
14.00-17.00	EXPERIMENTAL DEMONSTRATIONS

WEDNESDAY, 20 FEBRUARY 1985

09.30-10.30	ROLE OF SURFACTANTS IN PESTICIDE FORMULATIONS Mr. B. B. Bagalkote
10.30-11.45	DEVELOPMENT OF GRANULAR FORMULATIONS D. P. K. Ramdas
11.45-12.45	DEVELOPMENT OF FLOWABLE FORMULATIONS Dr. S. Mosinski
14.00-17.00	EXPERIMENTAL DEMONSTRATIONS

THURSDAY, 21 FEBRUARY 1985

09.30-10.45	PROCESS SCALING UP OF PESTICIDE FORMULATIONS Mr. V. N. Dutta M. S. Kumar
11.00-12.15	BIO-ASSAY AND FIELD TRIALS OF PESTICIDE FORMULATIONS Dr. Y. P. Ramdev
12.15-12.45	INTERACTION OF THE PARTICIPANTS WITH THE COURSE FACULTY
14.00-17.00	EXPERIMENTAL DEMONSTRATIONS

FRIDAY, 22 FEBRUARY 1985

09.30-10.45	QUALITY OF PESTICIDE FORMULATIONS AND QUALITY ASSURANCE Er. V. C. Bhargava
11.00-12.30	VISIT TO INSTRUMENTATION AND ENTOMOLOGY LABORATORIES
13.30-14.45	DISCUSSIONS AND FEED BACK FROM THE PARTICIPANTS
15.00-16.00	CONCLUDING REMARKS, PRESENTATION OF CERTIFICATES

A Training Programme on
PESTICIDE FORMULATION MANUFACTURE

18-22 March 1985

MONDAY, 18 MARCH 1985

09.00-09.30	Registration of Participants
09.30-10.30	- WELCOME BY CMD, HIL - INAUGURAL ADDRESS BY DR. M. KAMAL HUSSEIN, SIDFA, UNDP - VOTE OF THANKS BY HEAD, PDPI
11.00-12.00	PESTICIDE FORMULATIONS - A SURVEY Dr. S. K. Khetan
12.00-13.00	PESTICIDE FORMULATION MANUFACTURE IN INDIA - A Status Report Dr. N. K. Pillai
14.00-15.15	STATUTORY REQUIREMENTS OF PESTICIDE FORMULATIONS Dr. K. D. Paharia
15.30-16.45	PRE-REQUISITES FOR PESTICIDE FORMULATION MANUFACTURE Mr. P. N. Khanna

TUESDAY, 19 MARCH 1985

09.30-10.45	CARRIERS AND DILUENTS FOR SOLID FORMULATIONS Dr. R. K. Khandal
11.00-12.00	SIZE REDUCTION PRINCIPLES AND SELECTION OF PROCESS EQUIPMENTS Prof. S. Ramanujam
12.00-13.00	POWDER TECHNOLOGY/GROUP DISCUSSION
14.15-17.00	EXPERIMENTAL DEMONSTRATIONS

WEDNESDAY, 20 MARCH 1985

09.30-10.45	LIQUID FORMULATIONS Dr. E. P. Yesodharan
11.00-12.00	GRANULAR FORMULATIONS Dr. P. K. Ramdas
12.00-13.00	PACKAGING AND HANDLING Mr. V. N. Dutta
14.15-17.00	EXPERIMENTAL DEMONSTRATIONS

THURSDAY, 21 MARCH 1985

09.30-11.00	- SPECIALTY FORMULATIONS - FLOWABLES AND WATER DISPERSIBLE GRANULES - Dr. S. Mosinski - CONTROLLED RELEASE GRANULES Dr. P. K. Ramdas - MICROEMULSIONS Dr. E. P. Yesodharan
11.15-12.30	QUALITY ASSURANCE OF PESTICIDE FORMULATIONS
13.45-17.00	EXPERIMENTAL DEMONSTRATIONS

FRIDAY, 22 MARCH 1985

09.30-10.45	PESTICIDE FORMULATION MANUFACTURING PLANT DESIGN Mr. M. D. Mulay
11.00-12.00	COSTING OF PESTICIDE FORMULATIONS Dr. S. Kumar
12.00-13.00	SAFETY AND HYGIENE IN FORMULATION MANUFACTURE - Ms. V. N. Dutta
14.00-15.00	DISCUSSION AND FEED BACK FROM THE PARTICIPANTS DISTRIBUTION OF CERTIFICATES

A Training Programme on
QUALITY CONTROL OF PESTICIDE FORMULATION

15-19 April 1985

MONDAY 15 APRIL 1985

10.00-10.30	Registration of participants
	FACTORS RESPONSIBLE FOR QUALITY OF PESTICIDE FORMULATIONS
10.30-11.15	QUALITY OF RAW MATERIALS Dr. S.K. Khetan/Dr. N.K. Pillai
11.30-12.15	PRODUCTION PROCESS AND EQUIPMENT Mr. V. N. Dutta
12.15-13.00	PACKAGING, STORAGE & TRANSPORTATION Er. V. C. Bhargava
14.00-14.45	TRAINING OF THE PRODUCTION AND QUALITY CONTROL PERSONNEL Mr. R. L. Bakshi
	INAUGURAL FUNCTION
16.00-16.05	WELCOME by Dr. S. P. Dhua, CMD Hindustan Insecticides Ltd.
16.05-16.20	INAUGURAL ADDRESS by Dr. P.V. Shenoy, Addl. Secy., Min. of Agriculture
16.20-17.15	KEY NOTE ADDRESS by Dr. S.K.Mukherjee, Prof. of Eminence, IARI
17.15-17.20	VOTE OF THANKS Mr. Munni Lal, GM(P), HIL

TUESDAY, 16 APRIL 1985

	PESTICIDE FORMULATION SPECIFICATIONS
09.30-10.10	INDIAN STANDARD SPECIFICATIONS Mr. E. N. Sunder
10.10-10.50	INTERNATIONAL SPECIFICATIONS Ms. Thelma Antazo
11.00-12.00	SAMPLING AND METHODS OF TESTING FOR PHYSICAL CHARACTERISTICS OF FORMULATIONS Mr. D. R. Sharma
12.00-12.30	SHELF LIFE OF PESTICIDE FORMULATIONS AND STATUTORY REQUIREMENTS Dr. K. D. Paharia
14.15-17.00	PRACTICAL DEMONSTRATIONS

WEDNESDAY, 17 APRIL 1985

	METHODS OF ANALYSIS
09.30-10.30	CHEMICAL METHODS Dr. D. Sengupta
	CHROMATOGRAPHIC METHODS
10.45-12.00	GAS LIQUID CHROMATOGRAPHY Dr. D. Sengupta/Ms. Thelma Antazo
12.00-13.00	COURSE FACULTY-PARTICIPANTS INTERACTION
14.15-17.00	DEMONSTRATION

THURSDAY, 18 APRIL 1985

09.30-11.00	HIGH PERFORMANCE LIQUID CHROMATOGRAPHY Dr. S. Mohan/Ms. Thelma Antazo
11.15-12.45	SPECTROSCOPIC METHODS Dr. A. S. N. Murthy/Dr. [illegible]. K. Ramdas
14.00-17.00	PRACTICAL DEMONSTRATIONS

FRIDAY, 19 APRIL 1985

09.30-10.45	BIOLOGICAL METHODS OF QUALITY CONTROL OF PESTICIDES Dr. B. P. Shrivastava
11.00-12.00	REQUIREMENT OF A QUALITY CONTROL LABORATORY FOR PESTICIDE FORMULATIONS Mr. M. L. Kumar/Ms. Thelma Antazo/ Dr. S. Mosinski
12.00-13.00	Discussions and Feedback from the participants
14.00	DISTRIBUTION OF CERTIFICATES

SUPPLEMENTED DATA FOR CONTROL PARTICLES SIZE DETERMINATION BY USING MICRON PHOTO SIZER(MPS)

elaborated by

Dr. S. Mosinski

Remark

This elaboration should be read together with:
OM - OPERATIONAL MANUAL OF MPS
MPS - MICRON PHOTOSIZER BOCKLET
CST - Compiled Sheets of Tables

CONTENTS

1. THEORETICAL BASIS

The measurements of particle size distribution by the use of Micron Photosizer apparatus (MPSA) are based on the two following equations:

a. The Stokes' equation of relationship between the rate of sedimentation of particles in suspension and the sizes of suspended particles and;

b. The Lambert-Beer equation of relationship between the intensity of beam light passing through suspension and the concentration of suspended particles in suspension.

Ad.a. The tokes' equation is the following:

$$V = \frac{2g\,(d'-d)r^2}{9n} \quad (1)$$

Where- rate of sedimentation;

d - true density of the particles;
d - true density of the liquid;
n - viscosity of the liquid;
r^2 Stokes, radius of the particle.

the equation (1) can be written also as follows:

$$V = \frac{A\,(d'-d)}{n}\,r^2 \quad (2)$$

Where A is a factor of value, which depends of the used units.

For these used in MPSA method A=0.03267 and the rate of sedimentation is given by the Eq.(3)

$$V=0.03267\left(\frac{d'd}{n}\right) r^2 \quad (3)$$

Where V in mm/min.
d in g/ ml^3
d in g/ ml^3
n in c.p.
r in microns.

Ad.b. The Lambert-Beer equation, which along with Stokes' equation is used to convert attenuation readings to particles size distributions. The Lamber-Beer equation can be written in the form:

$$I = I_o \exp \frac{-KCL}{d} \quad (4)$$

Where I - intensity of beam of light after passing through suspension;

I_o- intensity of beam of light in the absence of obscuring particles.

c - mass concentration of particles per unit volume.

l - length of light path in the suspension;

d - particle diameter

k - a constant

Equation (4) demands that for given powder, log (I_0/I) should be directly proportional to the concentration of suspension and to the length of the light path.

A modified form of equation usually used is:

$$I = I_o \exp \ (-Acl) \ (5)$$

and in the form (6)

$$\log e \frac{I_o}{I} = AcL \ (6)$$

Where A is projected area per gram of particles and Ac is projected area per unit volume.

For a given sedimenting suspension, the ratio of Ac at a given level of time to the value of Ac in the oryginal homogenous suspension is given by the expression:

$$\frac{\log_e\left(\frac{I_o}{I_t}\right)}{\log_e\left(\frac{I_o}{I_o}\right)} \quad (7)$$

Where I_t - is the intensity of the transmitted light at time.t.

The plot of these ratios against the values of the diameters calculated from Stokes' equation gives the cumulative undersize distribution area which can also be calculated as in MPSH booklet(on page 7) by equation(8).

$$(\log I_n - \log I_m)\frac{n+m}{2} \quad (8)$$

Where:

$\log I_n$ - the value for particle of size n
$\log I_m$ - " " " m

and $n>m$

The equation (8) is giving rigorous results only for bigger particles (e.g. in MPSA for particles >22,5 microns)

*To get the rigorous results also for smaller particles a correction factor must be introduced. These factors are given in table 2 on page 6 of OPERATIONAL MANUAL (OM).

2. APPLIED CALCULATIONS.

a. The relationship between particle sizes and rate of their sedimentation in suspension.

From the equation (3) the following equation can be derived:

$h = 0.03267\ (d' - d)\ \gamma^2 t$ (9)

Because $V = \frac{h}{t}$;

Designating the expression $(d' - d)$ by Y

we get the following equation:

$h = 0.03267.Y.\gamma^2.t$ (10)

and $t = \frac{h}{0.03267.Y.X^2}$ (11)

For calculation of the relationship between t and X, the path of falling of particles should be fixed. Because of the dimension of measuring cell in MPSA it must take a value IO<h<0.7cm.

The value of h is also depended of the maximum particles size in tested suspension.

Taking however, into account that first reading of light intensity (I_t) will have to be taken at 30 seconds after setting the measuring cell in MPSA, th value of h shouldbe such that the particles of maximum sizes will not settle down before 30 seconds.

The value of h is calculated from the equation (12)

$h = A.Y$ (12)

and the value of A for different particles sizes from the equation (13)

$A = 0.03267.0.5 \times \gamma^2$ (13)

Where 0.5 is a time in minute after which the measurement has been started (see also the equation (10). The values of A for some of particle sizes are given on page 5 of MPSA booklet, in table 1 on page 6 of OM and in table A of CST.

b. RAPID MEASUREMENTS WITH THE CENTRIFUGE

See p.10 of OM.

The rate of sedimentation of particles in centrifuge is inversly proportional to the number of revolution per minute. The following relation can be written.

$$\frac{\text{Centrifuge force}}{\text{Gravity}} = \frac{\text{the time under gravity}}{\text{the time under centrifugal force}}$$

$$= \frac{T}{T_N} = f \quad (14)$$

Where:

N - number of revolutions per minute.

f - multiplying time factor.

Knowing the multiplying factor f and sedimentation time under gravity (from t-x chart on page 6 OM or on graph on page 12 of MPSA) the time under centrifugal force can be calculated. The factor f for known numbers of revolutions of centrifuge (N) and known path of sedimentation (h) can be found from N-f chart (see page 7 of OM as well as page 13 of MPSA and inner cover of CST)

b.1 The calculation of time of centrifugation.

If gravital sedimentation (for h=29.4 and Y=2) for particles $\geq$ 6u is finished after 12'30" (see page 9 of MPSA) than the calculation of time for centrifugal sedimentation of particles size <6u and >3u will be

$$T_N = \frac{\Delta t}{f}$$

Where Δt - the time difference between the time of gravital sedimentation of particles of 3u and the time of gravital sedimentation of particles of 6u.

N - number of revolutions per minute

Knowing the multiplying factor f and sedimentation time under gravity (from t-x chart) the time under centrifugal force can be calculated. The factor f for known numbers of revolutions of centrifuge (N) and known path of sedimentation (h) can also be readed from N-f chart on page 7 of OM as well as on page 13 of MPSA and inner cover of CST.

b.2 The calculation of particles size distribution

Knowning the values of log I_n and log I_m and the average value of n and m $= \frac{n+m}{2}$ the calculation is performed as eqzample given on p.7 of MPSA booklet. For more precise calculation the factors for particle size smaller than 22.5 microns should be used (see remark under * on page)

3. SUPPLEMENTARY DETERMINATIONS

3.1 Maximum particle size of powders

By wet sieving method.

3.2 Density of tested powders

a. Individual powdered substances(e.g)

Kaolin, soapstone, inorganic or organic pigments and the like not soluble in dispersing medium)

By picnometric method or can be find in specialistic guide book.

b. Powdered pesticide formulations or concentrated suspensions ("flowables") (CS-s)

By picnometric method but simultaneously the medium density must be determined and in the case of CS-s also the concentration of solid particles.

Both determinations can be performed after separation of solid particles from liquid medium by centrifugation.

3.3 Liquid density

By aerometers or can be find in guidebooks

3.4 Viscosity

The viscosity of some liquids in different temperature can be find in specialistic guidebooks and also in viscosity TABLE attached to OM.

For small amount of liquids e.g. that one which will be obtained after centrifugation of supensions of WP-s or CSs the small glass viscosimeters e.g. Ubbelhode should be used.

4. OPERATIONAL MANUAL

Knowing the number h(orH) proceed according to points 7-10 of Operational Manual.

APPENDIX E

LIST OF PAPERS GIVEN TO PDPI SCIENTISTS FOR REFERENCE

S. No.	Author(s)	Title	Where Published
1.	H. E. Kingston	"The Fluid Energy Mill"	British Chemical Engg. 1956, Moly
	F. E. Albus	"The Modern Fluid Energy Mill"	Chem. Engg. Progr. V.60, No. 6, 1964
2.	R. Nied	"The Fluidized BEd Counter Jet Mill - Recent Findings & New Applications	Aufberaitunsk-Technik Nr. 5, 1982
3.	J. Peate	"Grinding-Improving on an Ancient Art"	Process Engg. May 1983
4.	Clive Taylor	"Size Reduction: This is Classified Information"	Process Engg. May 1984
5.	Stefan Mosinski	"Some Data Concerning Grinding"	Not published
6.	G. Scheuber Chr. Alt. R. Lucke	"Investigation the Mixture Process in Solids Mixers of Varying Size"	Aufberaitungs-Technik Nr. 2, 1980
7.	Max S. Peters Klaus D. Timmerhaus	"Scale up in Design"	Plan Design and Economics for Chem. Engrs. McGraw-Hill Book Comp., New York, 1968
8.	Andreas G. Kanellopoulus Richard J. Wood	"Particle Size Analysis Techniques for Suspension Cone"	Pesticide Science, 7, 1976
9.	Coulter Electronics Ltd.	"Prinzip des Coulter Counter"	Leaflet
10.	F. M. Fowkes & others	"Cly-Catalyzed Decomposition of Insecticides"	Agricultural & Food Chemistry V.8, No. 3, 1960
11.	Gotharol Synnatschke & Walter Guckel	"The Influence of the pK-Values of Carriers on the Storage Stability of Different Pesticides"	Not published
12.	G. J. Marrs & M. R. Middleton	"The Formulation of Pesticide for Convenience and Safety"	Outlook Agri. 1973

13.	C.G.L. Furmidge T-Shenton	"Formulation: Some factors affecting pesticide performance"	Span 16, 2, 1973
14.	C.G.L. Furmidge	"Pesticides: Trends in Formulation Design"	Span 23, 1, 1980
15.	Y. F. Yost & J. B. Frederick	"Formulation of Malathion Dusts & Concentrates"	Farm Chemicals Oct. 1959
16.	Marshall A. Malina	"Flowability of Dust Formulations"	Agricultural Chemical 1960, Nr. 9
17.	W. F. Entney D. C. Blue H. A. Stansbury Sr.	"Techniques used in Formulating Sevin"	Farm Chemicals, June 6
18.	P. M. Heerties W. C. Witvoet	Some Aspects of the Wetting of Powder"	Powder Technology 3(1969)70.
19.	Max Sobelman	"Patterns & Problems of DDT Formulating"	Workshop on Pesticides Vienna, 28 May - 1 June
20.	P. S. Tyler D. A. Rowland	"Sodium Carboxymethyl Cellulose as a Stabilizer for Malathion Formulation"	J. Stored Prod. Res. 1967, V.3. pp 109-115

LIST OF SOME SCIENTIFIC PERIODICALS AVAILABLE IN NEW DELHI

Nr.	Title	Library
1.	Advances in Analytical Chemistry & Instrumentation (US)	ADIALA/ADIMAI/ADIPIS
2.	Advances in Chemistry Series (US)	ADISNA
3.	Advances in Chromatography (US)	ADIAIA/ADIEIT/ADISDS/ADISNS
4.	Advances in Colloid & Interface Science (NE)	ADIMAI/ADISNS/ADIUDU
5.	Advances in Pest Control Research (US)	ADIAIA/ADISNS
6.	Chemical Abstract (US)	ADIAIA/ADIEIT/ADISDS
7.	Chemical Abstract-Physical & Analytical Chemistry (US)	ADIMCC
8.	Chemical Engineering (US)	ADIECT/ADIEEI/ADIEIT
9.	Chemical Engg. Journal (UK)	ADIEEI/ADIEIT
10.	Chemical Engg. Progress (US)	ADIAFA/ADIAIA/ADIEEI
11.	Chemistry & Industry	ADIAIA/ADIECR/ADIEEI
12.	Chemtech	ADIAIA/ADIEEI/ADIEIT
13.	Colloid & Polymer Science	ADIEIT
14.	FAO Plant Protection Bull	ADIAIA/ADIAIC/ADISIS
15.	Indian Drugs & Pharmaceutical Industry	ADIMCC
16.	Indian Journal of Agricultural Chemistry	ADIAIA/ADIAIC/ADISNS
17.	Indian Journal of Pharmaceutical Science	AIAIA/ADIMCC/ADIMNA
18.	Indian Journal of Plant Protection	ADIAIA/ADISNS
19.	International Pest Control (UK)	ADIAIA
20.	Journal of Agricultural and Food Chemistry (US)	ADIAFA/ADIAIA/ADIAIC
21.	Journal of Chemical Physics	ADIAIA/ADIEIT/ADISOS
22.	Journal of Colloidal & Interface Science (US)	ADIAIA/ADIEIT
23.	Journal of Physical Che, (US)	ADIAMA/ADIEIT/ADIECR

24.	Journal of Scientific and Industrial Research (II)	ADIAIA/ADIAIC/ADIECR
25.	Journal of Scientific Instruments (UK)	ADIAIA/ADIECR
26.	Journal of the Society of Cosmetic Chemists (New York)	ADIMNA/ADISNS
27.	Journal of Testing and Evaluation (US)	ADIECR/ADIEEI/ADIEIT
28.	Journal of Thermal Analysis (US)	ADIEIT
29.	Pest Control (US)	ADIAIA/ADIEEI
30.	Pesticide Science (UK)	ADIAIA
31.	Pesticides (II	ADIAIA/ADIAIC/ADIEEI
32.	Pesticide Information	ADIAIA/ADIAIC/ADIAIS
33.	Pflanzenschuteberichte (AU)	ADIAIA
34.	Progress in Colloid and Polymer Science	ADIEIT
35.	Progress in Surface & Membr. Science	ADISNS
36.	The Chemical Engineer	ADIEEI

CODES EXPLANATION

CODE	Institution
ADIAFA	Fertilizer Association of India Jear Jawaharlal Nehru University New Delhi - 110 067
ADIAIA	Indian Agricultural Research Institute New Delhi 110 012, Tel. 587438
ADAIC	Indian Council of Agricultural Research, Krishi Bhavan, Dr. Rajendra Pradas Road, New Delhi 110 001, Tel: 338891
ADIECR	Central Road Research Institute, P. O. C.R.D.I., Delhi-Mathura Road, New Delhi 110 020, Tel: 632 173
ADIECT	Research & Development Directorate, Technical Centre, Opposite Safdarjung Airport, New Delhi 110 003, Tel: 618 274
ADIEEI	Egnineers India Ltd., PTI Building (4th Floor) 4, Parliament Street, New Delhi 110 001, Tel: 386171
ADIEIT	Indian Institute of Technology, Hauz Khas, New Delhi 110 016, Tel: 666979/209
ADIMAI	All India Institute of Medical Science Ansari Nagar, New Delhi 110 016, Tel: 661123/312
ADIMCC	Central Council for Research in Ayurveda and Siddna Documentation Centre, D-5, Green Park, New Delhi 110 016, Tel: 665759
ADIMNA	National Medical Library, Ansari Nagar, Ring Road, New Delhi: 110 016 Tel: 661085
ADIPIS	Indian Statistical Institute 7-SJS Samsarival Marg, New Delhi 110 089 Tel: 220021
ADISIS	Indian Standard Institution 9, Bahadur Shah Zafar Marg, Manak Bhavan, New Delhi 110 002 Tel: 272 166, 270131/223
ADISNS	National Science Library, JNU Campus, New Mehrauli Road, New Delhi 110 067, Tel: 650 431

LIST OF SOME OF PERIODICALS AND MONOGRAPHS AVAILABLE IN INDIA BUT OUT OF NEW DELHI

S. No.	Title	Library
1	Analytical Methods for Pesticides and Plant Growth Regulators (US)	1. Birla Institute of Technology & Science, Pilani-333031 Tel: 92
		2. Kerala Forest Research Institute, Peecht-680653, Tel: 22375
2.	Pesticide Abstract	1. Industrial Toxic Res. Centre Mahatma Gandhi Marg, PB No. 80, Lucknow-226001, Tel: 48227
		2. University of Madras, Autonomus Post Graduate Centre, Coimbatore-641 041, Tel: 34235-38
3.	Advances in Colloid & Interface Science	1. Bhabha Atomic Research Centre Trombay, Bombay-400 085, Tel: 52331, Telex: BARC 011-2817
		2. Calcutta Univ. Dept. of Zoology, 35, Ballygone Circular Road, Calcutta-700 019
4.	ACS Sympozium Series	1. National Chemical Laboratory Pune-41108, Tel: 56451-3 Telex: 0145-266
5.	Surfactant Science Series	1. Patent Office Technical Lib. 214, Acharia Jagdish Chandra Bose Road, Calcutta-700 017, Tel: 444401
6.	Powder Technology	1. Indian Institute of Technology Powai, Bombay-400 076, Tel: 58414/1, 581421 Telex: 011-2385
		2. National Chemical Laboratory Pune-411008, Tel: 56451-3 Telex: 0145-266
7.	Wissentshaftliche Zeitschrift Der Martin Luther Universitet Halle-Wittenberg Math-Naturwiss-Reiche	1. University of Bombay Jawaharlal Nehru Library.
		2. National Library, Belvedere Road, Calcutta 700027, Tel: 455381, Telex: ca 7935
8.	Chemical Technology Review	Patent Office Technical Library (See p. 5 App. 4)

SOME OF THE RECOMMENDED PAPERS

S. No.	Author(s)	Title	Where Published
1.	Salager, J. L. Anton, R. E.	"Physicochemical Characteristics of a Surfactant. A quick and precise method"	J. Dispersion Sci. Technology 1983, 3(3) 253-293 (Not available in India)
2.	Kaler, Eric W. & others	"Toward Understanding Microemulsion"	J. Chem. Phys., 1983, 79(11) 5673-84, 5685-92 (AIAIA/ADIEIT/ADISNS)
3.	Ramban, D. Dorle, A. K.	Flocculated Emulsions	Indian J. Pharm. Sci. 1983. 45(4), 172-5 (ADIAI/ADIMCC/ADIMNA)
4.	Friberg, S. E.	Microemulsions	Prog. Colloid, Polym. Sci. 1983, 68, 41-7 (ADISNS)
5.	Tadros, T. F.	Influence of structure & Chain Length of Surfactants on the Nature and Structure of Emulsions.	ACS Sym. Ser. 1984 253, 153-173 (ADIPIS)
6.	Chavan, Virendra	"Physical Principles in Suspension and Emulsion Processing"	Adv. Transport Process. 1984, 3, 1-34 (Not available in India)
7.	Gilberg, Gunilla	Practical use of Microemulsions	Surfactant Sci. Ser. 1984 (Emulsions & Emulsions Tech. Pt. 3) 1-43 (see p.5 appx 4)
8.	Doerfler, Hans Dieter Kruger, Helmut	Microemulsions Colloid Chemical Principles and Industries Application Properties	Wiss Z. Martin Luther Univ. Halle. Math-Natur. R. 1984 (33) (3) 51-68. (see p. 7 appx. [illegible]
9.	Belloog, A. M. & others	Microemulsions	Adv. Coll. Int[illegible]. [illegible]i. 1984, 20(3-4)1[illegible] (ADINAI/ADISNS/ADI[illegible])
10.	Tadros, T. F.	Physical Stability of Suspension Concentrates	Adv. Colloid. Interface Sci. 1980, 12, 141. (ADINAI/ADISNS/ADIUDU)
11.	Tadros, T. F.	Control and Assessment of the Physical Stability of Pesticidal Suspension Concentrates.	Chemistry & Industry 15 March 1980
12.	Brian Vincent	The Stability of Particulate Suspensions	Chemistry & Industry 15 March 1980 (ADIAI/ADIECR/ADIEEI)

13.	C. G. Halliday	Flowable Pesticide Formulations	A.S.T.M. 1983, 45-52
14.	Peter Ciullo, R. T.	Rheological Properties of Magnesium Alluminium Silicate x Anthangum Dispersions	J. Soc. Cosm. Chem., 32, 277-285 (Sept/Oct. 1981) (ADIMNA/ADISNS)
15.	J. Th. G. Overbeek	Interparticle Forces in Colloid Science	Powder Technology 37 (1984)195-208 (see p. 6 Appx. 4)
16.	Norman Harnby	Trend in Powder Mixing	The Chemical Engineer 1984, July No. v405 (ADIEEI)
17.	Douglas, N. Moir	Size Reduction	Chemical Engineering April 16, 1984 (See p.8 Appx. 2)
18.	Rosoff Morton	The Nature of Microemulsions	Prog. Surf. Mem. Sci. 1978.12 (see p. 35, Appx. 2)

SOME OF THE RECOMMENDED MONOGRAPHS

No.	Author(s)	Title	Where Available
1.	Editor P. Becher M. Dokker	Encyclopedia of Emulsions Technology	EDIEIT
2.	Prince Leon	Microemulsions Theory & Practice (1974)	ADIEIT
3.	Lissant, Kemeth H.	Emulsification: Industrial Application	EDIEIT
4.	Rosen Milton	Surfactants and Interfacial Phenomena (1978)	EDIEIT
5.	F. W. Mullin	Crystalization (1972)	EDIEIT
6.	Voitech Vanecek Miroseav Markvart Radek Debohlav	Fluidized Bed Drying (1966)	EDIEIT
7.	Karoly Remenyi	Theory of Grindability and the Communition of Binaxry Mixtures (1974)	EDIEIT
8.	Editors Torrey S.	Emulsions & Emulsifier Applications Recent Developments	See p.8, Appx.4
9.	I. T. Davies E. K. Rideal	Interfacial Phenomena	EDIEIT
10.	Kozoshinoda & others	Colloidal Surfactants	EDIEIT

APPENDIX F

LIST OF INSTRUMENTS AVAILABLE IN HICO RESEARCH LABORATORY

No.	Name of Instrument	Make	Uses
1.	I.R. Spectrophotometer	Perkin-Elmer Model No. 257	For qualitative analysis & structural studies of organic compounds through absorption measurements.
2.	DU - 2 Spectrophotometer	Beckmann	
3.	Auto Burette Titrameter	Beckmann	For potentiometric titration
4.	Synchro Electric Viscometer	Brookfield Model RVT & LVT	For measurements of viscosity of liquids
5.	Chloride Titrator	American Instruments Co.	For estimation of Chloride content of any compound
6.	Auto Aqua Titrator	Precision Scientific Co., USA	Determination of water
7.	Lovobond Tintometer	Tintometer Limited	To measure colour of oils, textiles, etc.
8.	Nitrogen Analyser	Coleman Instruments	For estimation of Nitrogen content of compounds
9.	Carbon hydrogen Analyser	Coleman Instruments	For estimation of carbon & hydrogen content of compounds
10.	Digital Densitometer - with thermostatic control bath	PARR	For determination of density of liquids @ different temperatures
11.	Spectronic 20	Baush & Lomb Co.	For visible range absorption measurements.
12.	Electronic Oil & Fat Tester	Steinlite 300 Los.	For estimation of oil content of oil bearing materials
13.	Centrifuge	Damon/IEC Division	For separation

No.	Name of Instrument	Make	Uses
14.	Atomic Oxidiser	Plasmatics	For ash determination
15.	Flask type combustion Apparatus	Heareus	Estimation of chlorine, Bromine, Iodine, Fluorine, Sulphur, Phosporous in compounds
16.	Bath & Circulator	Forma Scientific Model 2160	For constant temperatures from - 30°C to 100°C
17.	Liquid (Gas) Chromatograph with integrater & recorder	Perkin-Elmer Model No 910	For quantitative analysis of mixtures
18.	UV-Vis Spectrophotometer	Varian Series 634	For radiation (UV & Visible) absorption measurements
19.	Atomic Absorption Spectrophotometer	Varian AA 575	For elemental analysis
20.	Mass Spectrophotometer coupled with GC	Varian MAT 112	To determine mol. wt. and stru ure of the compound
21.	Molecular Weight Apparatus	Wescan	For determination of molecular weight from 100 to 50,000
22.	Aquatest	Photovolt Corpn.	For estimation of moisture content of samples
23.	Mecury Analyser	Perkin-Elmer MA-5	For estimation of mercury
24.	Lead Sulphur Analyser	Tenelec Inc.	For estimation of lead & sulphur in hydrocarbons
25.	Sulphur Analyser	L E C O	For estimation of sulphur in compounds
26.	Particle Size Analyser	C.Z. Instruments	For determination of particle size of emulsions
27.	Microscope with photomicrograph arrangement	Biovar	

No.	Name of Instrument	Make	Uses
28.	High Performance Liquid Chromatograph with Data a 10 system	Perkin Elmer Series 3	For quantitative analysis of mixtures
29.	Spinning band distillation col.	Perkin-Elmer	For preparative GLC
30.	Hydrogen Generator	General Electric	For generation of H_2 gas
31.	Tensiometer	KRUSS	To determine interfacial tension, surface tension.
32.	Mettler FP5	Mettler	To determine melting pt., boiling, softening point.
33.	Tensile strength tester	W. Germany	To find out tensile strength of the cloth.
34.	Zeno Test Instrument	Hanau, W. Germany	Testing the textile, plastic, paper, etc. for finding colour
35.	Statometer	Herfurth GmbH	For finding out static charges
36.	Erma microscope	WARSZAWA, Poland	
37.	Erma Refractometer	WARSZAWA, Poland	To find out refractive index.

No.	Name of the Instrument	Make	Uses
38.	Cloud Point Apparatus	Wescan	For determination of cloud point.
39.	Newport Analyzer	Newport Instruments	For determination of fatty matters oil contents of the material.
40.	Millipore Water System	Millipore	For high purity distilled water.
41.	Sigma 3 G.C.	Perkin-Elmer	For quantitative analysis of mixtures.
42.	Sigma 1 G.C.	Perkin-Elmer	For quantitative analysis of mixtures.
43.	M-1 Computing Integrator	Perkin-Elmer	For chromatographic data.
44.	Rub. Fastness Tester	WERNER KUENY, Germany	Testing of rubbing fastness of leather finish.
45.	Penetrometer	Bally (Swiss)	Testing of penetration resistance of finish leather.
46.	Permeometer - 7017	Bally (Swiss)	Testing of permeability of leather.
47.	Flexometer	Bally (Swiss)	Testing of flexing strength of leather.
48.	Tensometer	Bally (Swiss)	Testing of tensile strength of leather.
49.	Tanning Drum	Otto Specht, Germany	For tanning of leather in laborato
50.	Adhesion of Finish Leather (Std.112)	Satra (U.K.)	Testing of finish on leather.
51.	Leather Shrinkage Apparatus (Std. 114)	Satra (U.K.)	Testing of leather shrinkage test.
52.	Wrinkleometer (Std. 119)	Satra (U.K.)	Testing of wrinkle formation on leather.

No.	Name of the Instrument	Make	Uses
53.	Lastometer (Std. 104)	Satra U.K.	Testing of lasting strength on leather.
54.	Atlas Fabric Streak Analyser	Atlas Electric Device, USA	For fabric fault determination.
55.	Atlas Radom Tuble Pilling Tester	Atlas Electric Device, USA	For pilling testing on fabric.
56.	Scorch Tester	"	For scorch testing on fabric.
57.	Accelerator	"	For acceleration testing on fabric.
58.	Crease recover unit	Mettin, Hungary	For crease recovery of fabric.
59.	Bursting strength tester	Hans Dieter Hummer, Germany	For bursting strength of the fabric.
60.	Friction meter	Rothchild-Zurich, Switzerland	For fibre friction tester.
61.	Static Volt Meter	"	For static charge measurement.
62.	Bundesmann	Goodbrand & Co. Ltd., Britain	For water repellancy tester.
63.	Water percolating tester	Metefem, Budapaste	For water repellancy tester.
64.	Water repellancy tester	Metefem, Budapaste	For water repellancy tester.
65.	Direct reading Conductivity Meter 303	Systronics	For measurement of conductivity.
66.	Microbalance	Mettler	For weighing upto 1 microgramme.
67.	Electronic top pan balances	Mettler	For weighing upto 30 kgs.

No.	Name of the Instrument	Make	Uses
68.	F T NMR Spectroscopy Computer controlled	Varian	For structural studies of organic compounds.
69.	Vista 6000 Gas Chromatograph	Varian)	For quantitative analysis of mixtures.
70.	Vista 401 data station	Varian)	
71.	683 Infrared Spectrophotometer with 3600 data station	Perkin Elmer	For quantitative as well as qualitative study - structure determination by using library.
72.	Melt spinning Tester type C with winder	Fujifilter	For preparation of synthetic yarn.
73.	Preparative Liquid Chromatograph 5000	Waters	For preparation of highly pure compounds upto 150 gms.
74.	Hydroshear Equipment	Holland	For emulsion preparation
75.	Modular Liquid chromatograph	Waters)	For determination of molecular wt. upto 20,00000 g/mole.
76.	CMX Ligh scattering spectrophotometer	Chromatyx)	
77.	Petroleum Distillation	Fisher	ASTM distillation equipment
78.	HP/TLC scanner	Camos	Quantitative thin layer chromatography using scanner,
79.	Fan Viscometer	-	Viscosity determination