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PESTICIDE DEVELOPMENT PROGRAMME IN INDIA

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INDIA

Technical report: Findings and recommendations\*

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

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## **1. ACKNOWLEDGEMENT**

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

**In particular I would like to express thanks to Dr. S.P. Dima, CMD, HIL, Dr. M.A. Slam, UNDP, SIDFA, Mr. M.Lal, HIL, (GM(P), Dr. S.K. Khetan and Mr. Satpal from UNDP for their activity which allowed me to come to I.DIA and take a part in the project.**

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

**I thank also Mr. Vijay Gandhi for his patient typing of my draft report.**

## **2. SUMMARY**

During the present mission my consultancy concerned several problems which at present are worked out in PDPI project or which will be dealt with in the near future.

After the discussion with the research workers the following of problems have been consulted by myself:

- 1 METHODS OF STABILIZATION OF MALATHION FORMULATIONS AND DETOXIFICATION OF TECHNICAL MALATHION;**
- 2 METHODS OF PREPARING DIFFERENT KINDS OF SULPHUR FORMULATIONS;**
- 3 VERIFICATION AND INTRODUCTION OF THE NEW METHODS OF TESTING OF EMULSIFIERS;**
- 4 PROBLEMS ENCOUNTERED WHILE USING HLB SYSTEM FOR TESTING OF DISPERSING AGENTS:**

During the consultancy concerning to the above problems some of experiments had been done, and for some theoretical papers, patents as well as samples had also been transferred to the concerned people.

During conducting of some of experiments unexpected results were obtained. The main causes of these were lack of the proper equipment as well as necessity of using those ones which were not in laboratory possession. For that reason several proposals concerning the outfit of laboratories in additional instruments had also been given.

### 3. INTRODUCTION

Having the privilege to work as a consultant in PDPI at the initial period of the project (the year 1984) and then in successive years up to near the end of the project, I would like to express my opinion about the progress during this period. In general, one could say that "much" has been done. This "much" is composed of the following elements:

- outfit of respective laboratories in apparatus and instruments for research work;
- to train the research workers in different subject of pesticide formulations in the foreign research centers with eminent scientists;
- to organise several workshops as well for domestic participants as for foreign ones from Asian and Pacific Region; the majority of lectures had been prepared and delivered by the research workers of PDPI and R&D Centre;
- to gain the basic know-how about the methods of preparing the various modern pesticide formulations e.g. suspension and emulsion concentrates, microemulsions, water dispersible granules and biocide formulations;
- to gain know-how about the methods of testing of the emulsifiers, dispersing agents, carriers and other adjuvants and choosing the proper ones for pesticide formulations;
- to prepare and communicate several papers for publication;
- to prepare of compendium containing the main lectures delivered during the workshops and sending it to UNIDO Hq. for the purpose of publication.

The Research Centre for Pesticide Formulation which has been organised during the period of UNIDO project is now quite well prepared to take up and solve some of physicochemical and technological problems connected with pesticide formulations. This can be done exclusively by the team of the Centre or by its cooperation with other specialized Indian Research Centers.

It is evident that much has been done and no doubt that the progress has been satisfactory towards achieving the targets. However, in my view this is not all and hence, I would suggest (rather recommend) the extension of this project so that what has been done till now can be realised in true terms i.e. translated into practice. For that I present here below some of the arguments in favour of the extension.

Pesticide Formulation Research Centre in Gurgaon is at present a unique center of R&D in whole Asian & Pacific Region and for that reason should be the leading and guiding center. To get however such position the further financial support from Indian Government and from UNIDO is indispensable.

In case when the present PDPI project is extended the main tasks which I see for it would be the following:

- the supplementation of PDPI Center with additional modern instruments which are highly essential for the research work concerning the application technology, biological tests, development and standardization of botanical and microbial pesticide formulations.
- taking into account very good outfit of Research Laboratories with unique, very sophisticated and expensive research and testing instruments, the steps for their full utilisation should be undertaken. Because many of these instruments are also used in researches in other branches of industry e.g. pharmacy, cosmetics, paint and paper etc., it is proposed to widen the scope of use of the above mentioned instruments and apparatus also to solve some problems in which the mentioned various industries are interested. If such direction of research work would be carried on, it is not excluded that the present Pesticide Formulations Research Center will be changed in Multibrached Research Center specialized in physicochemical research and test methods used in highly dissipated systems as : suspensions, emulsions, powders aerosols etc.

Such R&D Center would be very important for improvement of standards and economy of production of many commercial Indian products and to help the other countries from Asian and Pacific Region in the same.

#### **4. RECOMMENDATIONS**

**Concerning the future activity in PDPI R&D Center:**

Taking into account very good outfit of PDPI Research laboratories with unique very sophisticated and highly expensive apparatus, the steps for their full utilisation should be undertaken. It is recommended to widen the scope of use of the above mentioned instruments to solve the problems in which various industries can be interested.

The present Pesticide Formulations Research Center should be after some time, be changed in Multibranch Research Center specialized in physicochemical research and test methods used in highly dispersed systems as: suspensions, emulsions, powders, aerosols etc. To get however such position the further financial support from Indian Government and from UNIDO is indispensable ( see pp 4 )

**Concerning the experiments devised during my present mission :**

- to elaborate method of selecting dispersing/wetting surfactants for WDGs of sulfur ( see pp 10-11 )
- to conduct full pilot process for getting WP of sulfur ( see pp 12-13 )
- to characterize the Indian emulsifiers by such characteristics as : phenol index, water number and cloud points ( see pp 14-16 )
- to use the PIP method for selecting a proper emulsifier for concentrated emulsion ( see pp 16-17 )
- to check the difference between the stability of EC of Malathion prepared according to presently used recipe and the one prepared with new type of emulsifiers as well as stabilizers ( see pp 7,8 )
- to check the proposed method of detoxification of technical Malathion ( see pp 7,8 )



**Concerning the improvement of apparatus installed in Pilot Plant.**

- to check and improve the compressor which is working with 8 "Micronizer ( see pp 13 )
- to cut off the smaller 4" Micronizer from the smaller compressor and connect it to the installation of 8 " Micronizer ( see pp 13 )

**Concerning the purchasing of additional instruments : The following instruments should be purchased**

- small laboratory Lodiqe Mixer, ( see p 13 )
- small laboratory mixer (to 15,000 rev/min)( see p 17 )

## **5. PROBLEMS CONSULTED**

### **5.1. MALATHION.**

#### **5.1.1. Stabilization of E.C. of Malathion.**

As it is commonly known, pure Malathion is an insecticide of relatively low mammalian toxicity (LD<sub>50</sub> rats) 12.500mg/kg. It is the reason why it has found the broad usage in crop protection all over the world.

The detailed examination however, which had been undertaken after the tragedy in Pakistan in 1976, disclosed in Malathion WP some very toxic compounds created from Malathion by its decomposition or isomerization. The one of them of high toxicity, (LD<sub>50</sub> rats) =120mg/kg, is isomalathion. Some other impurities, also very toxic, occur in general in much smaller amount than isomalathion.

In Malathion formulations the decomposition and isomerization is accelerated by some carriers (in WP-s) or by polar solvents (in EC-s) which induce hydrolyzation of Malathion.

The most stable EC formulations are the ones which do not contain polar solvents. For that reason the one of the emulsifier components—calcium salt of DBSA solution—should be used in hydrophobic xylene and not hydrophylic butanol. (The last one is commonly used for EC-s of other pesticides.) The other condition, to get stable EC of Malathion is as small as possible amount of water in EC. The main origin of it are nonionic emulsifiers. The quantity of water in nonionic emulsifiers should not be higher than 0.5% (w/w) and in mixed nonionic/anionic emulsifiers not higher than 0.3% (w/w). Unfortunately, very often however the amount of water is higher. For that reason to improve the stability of EC of Malathion some stabilizer binding this water must be used. One of them is epoxidized soja oil, popular plasticizer.

#### **Detoxification of technical Malathion.**

The other problem, which, sometimes can require the solution is the problem of detoxification of technical Malathion by removal from it the toxic impurities, eg by hydrolysis of isomalathion. In this procedure, the decomposition parameters should be so selected that the rate of hydrolysis of isomalathion should be faster than isomerization of Malathion.

### 3.1.3. Experiments

1. It has been proposed to prepare three samples of EC formulation of Malathion. One according to HIL recipe currently used in production and the two other ones according to the following recipe:

	% (w/w)	
	<u>A</u>	<u>B</u>
Malathion tech (95%)	52.6	52.6
CaDBSA	3	3
Rokafenol N-14	2	2
Epoxidized Soja Oil	0.5	1.0
Xylene	41.9	41.4
	<hr/>	<hr/>
	100.00	100.00
	<hr/>	<hr/>

All three samples has been kept in temperature 55°C for 14 days and after the quantity of isomalathion will be determined.

2. Some suggestions concerning the experiment aiming to detoxify the technical Malathion have also be given.

## 5.2. FUNGICIDE FORMULATIONS OF SULPHUR

### 5.2.1. DISCERNMENT OF THE PROBLEM

Because HIL has been interested in different fungicide formulations of sulphur the discernment (insight) as well as some of the experiments had been carried out.

The discernment had been devoted to the types of technical sulphur which are available on Indian market and which could eventually be used for production of some of fungicide formulations. We were interested in the following types of sulphur:

1. The "colloidal" sulphur of very fine particles occurring in the form of water paste, recovered in the process of desulfurization of different gases such as ; natural gas, refinery gas or coal gas;
2. The finely ground natural sulphur, of particles size smaller than 100  $\mu\text{m}$  (and better if it is smaller than 60  $\mu\text{m}$ ) which is generally used in rubber industry for compounding and vulcanization processes.

The first type - "colloidal" sulphur is obtained in the process used for recovering of hydrogen sulfide or sulphur from coke or producer gases, including the Thylox, sodium phenolate and related systems.

The Thylox process utilizes an arsenical solution to absorb sulfide from the gases. The impregnated solution is oxidized to release elemental sulphur in very fine particles (1  $\mu\text{m}$ ) as a froth which is removed and washed. the concentration of sulphur in paste is about 50%-60% (w/w).

This "colloidal sulphur" can be used without the process of milling to production of;

- Suspension concentrate, by mixing with other ingredients and adjuvants.
- Wettable powders of a about 80% of sulphur, by mixing the water paste of sulphur with dispersing and wetting agents and then spray drying of the suspension. If for spray drying the fountain spray dryer is used, the granular form of WPs can be obtained. However to get such granules the choice of proper dispersing and wetting agents as well as appropriate temperature of spray drying must be applied.

Unfortunately according to the accessible information this type of "colloidal" sulphur is not available in the Indian market. There is only that one which is obtained from refinery gases. In this processes, different from the previous one, the hydrogen sulfide is absorbed in an alkylamine. On being heated the pregnant amine solution gives up its hydrogen sulfide in concentrated form, which is then fired in combustion chamber and burned in such a manner that one third of the volume is converted to sulphur oxide. After cooling, the products of combustion are passed through a converter packed with catalyst, in which the hydrogen sulfide and sulphur dioxide react to produce sulphur vapor and water vapor. Sulphur is condensed by washing with liquid sulphur. The end product is liquid sulphur or solid sulphur in the form of bigger pieces or lumps.

The second type of sulphur, which can be used for the production of fungicide formulation is that one which is primary ground. Such as sulphur can be prepared from natural sulphur obtained from its deposits by various methods as well as from sulphur recovered from refinery gases.

The primary ground sulphur can be used for all type of fungicide formulations but the most economical process is one which is used for production of WP-s. Such a sulphur formulation is called. **m i c r o n i z e d w e t t a b l e s u l p h u r**. This type of sulphur can also be used for the production of suspension concentrate and for the WP-s or granulated WP-s, but in the last two cases the process will not be economically favourable because it is necessary to grind sulphur in water and then to evaporate the water from the slurry.

In case of using "dry" process for preparation of micronized WP-s of sulphur the degree of finess of primary ground sulphur is very important. In cases where rigid top particle specifications are set up e.g. below 15  $\mu\text{m}$  for micronized product (as for WP sulphur), pregrinding to the range of 200-325 (74-44  $\mu\text{m}$ ) results in more economical operation and improved quality. The sulphur of same finess which is used in rubber industry would be the best.

## 5.2.2. EXPERIMENTS.

### 1. Preparation of water dispersible granulated sulphur by fluidized drying method.

The concentrated water suspensions of sulphur which were prepared in Dyno-Mill had been dried and granulated in AEOROMATIC LABORATORY UNIT. AS a dispersing agent Local Tamol were used or ICI product Athlox.....and as a wetting agent Arkopon T of Hoechst Co. However, in order to counteract the excessive

foam of suspension the process of milling was operated without wetting agent. It was added to suspension after the process of milling. Using different amount of dispersing and wetting agent several samples had been prepared.

The temperature of drying and granulation was about 75-80°C and as a seeds fine particles of sulphur or lactose had been used. The suspension of sulphur, prepared from Russian water dispersible granules of sulphur (80% in small cylindrical shapes), was used as a comparative sample.

From all of the tested samples only the comparative one gave granules spontaneously dispersed in water and creating stable suspension. It is necessary to stress here that the main difficulty to get WDG of sulphur is caused by the high hydrophobicity of sulphur surface. The proper types of dispersing and wetting agents and their proper weight ratio must be chosen. It must be remembered that the main condition to get the good WDG-s in process of spray or fluidized granulation is to counteract the individual particles to join together through their "clean" surfaces. This will be reached if each particles will be covered by protective layer of dispersing and wetting agents, strongly adsorbed to the surfaces of particles.

The proper ways of finding the efficient dispersing and wetting agents are by testing of their adsorptivity on particles of pesticides (3) as well as by testing of their spreading characteristic (4,5).

In the next experiments which will be carried out it is proposed to prepare small (10-20 grams sulphur) samples of concentrated water pastes, using different combination of dispersing and wetting agents and some of humectants and dry them in three different temperature : 70,80,105°C. After drying the pastes, the dried cakes will be crushed and the particles of about 200-500 µm separated and then their dispersibility in water tested.

It would be of course very desirable to conduct parallely the tests of adsorption and wettability.

Remarks : The purpose of the above proposed tests is not only to find the right recipe and parameters for getting WDG-s of sulphur but also (and this is probably more important) to get experience how to solve the problems in cases when hydrophobic, not easily wetted, pesticides will be used for preparation of WDG-s by spray drying method.

## 2. Milling of sulfur by using of Micromizers

To find the right composition of WP- of sulfur the best procedure is to prepare "blank" finely milled sulfur or the sulfur mixed with some amount of mineral carrier, and to test different dispersing and wetting agents to get the best suspensibility. To get such blanks the following procedure has been planned:

- to mix 100-200 g of sulfur (after primary grind, having particles of less than 80  $\mu$ m) with synthetic silica and kaolin (10% w/w)
- to mill premixes in small (4") Micromizer.

The planned experiments could not be performed in the desired manner because of :

- lack of small size efficient mixer (the best Lötige type) which could be used for homogenisation of powdered mixtures. The one in pilot plant has a bigger capacity and much more product must be used;
- the efficient pressure which should be used to get the good milling is about 7 atm. (105 psig), but by using the small Micromizer, the pressure fluctuated between 7 and 5 atm. Undesirable fluctuation of pressure was caused by the lack of surge pressure tank which should be installed between the compressor and Micromizer.

From the above mentioned disturbances the bigger Lötige mixer and bigger Micromizer as well as bigger amount of sulfur had been used for experiments.

But again, because of some faults of compressor of too low pressure (5.5atm instead of 7.5atm) the efficient milling could not be obtained. Good effect of milling was obtained only by two-fold milling.

The particle size of comminuted blanks had been checked by microscope. They were same as that one of Excell WP sulfur.

The both blanks, one with silica and the second one with kaolin were then used for testing of various combination of dispersing/wetting surfactants, by the commonly used method and to select the most efficient ones. As a standard the Excell product was used.

The further planned experiments are the following:

- 1 -to mix carriers (silica and kaolin) with surface active agents in Lötige mixer;
- 2 -to mix sulfur with premixes, prepared acc. to point 1.in Lötige mixer;

3 -to mill premixes prepared acc. to p.2. in 8" Micronizer, using the pressure of air of 7.5 at and dosing the premix at a uniform rate to the mill;

4 -to homogenize the products after milling in Lodige mixer.

Remarks: The very important condition for getting micronized sulfur of good self-dispersibility and suspensibility is to use, as much as possible, of good carriers which will protect the particles of sulfur, against agglomeration. Much better results are obtained when synthetic silica carrier is used instead of kaolin. The second condition to get good product is to use surface active agents in dry powder form.

The following recommendations are given for further experiments of mixing powders and fine milling of products:

1 -the compressor which is working with 8" Micronizer must be checked and improved;

2 -the smaller (laboratory) 4" Micronizer should be cut off from the compressor and connected to the pressure air pipe going out from the pressure vessel installed with 8" Micronizer;

3 -to get a uniform feeding to Micronizers the vibratory feeder must be installed;

4 -the small laboratory Lodige Mixer for homogenizing the mixtures of comminuted materials should be purchased.



## 6. ADDITIONAL CRITERIA OF CHOOSING EMULSIFIERS

### 6.1. Relation between HLB numbers and some of characteristics of emulsifiers.

The well known and commonly used criteria for choosing emulsifiers are the ones based on HLB system.

In case of EC formulations the efficiency of emulsifiers is tested by observation of physical stability of emulsion as well as spontaneity of its creation. It is assumed that the best effect in emulsifying a particular oil phase can be obtained only when emulsifier or mixtures of emulsifiers of definite HLB number are used. In other words, every oil phase requires emulsifiers of one HLB number which is known as "required" HLB number. The nonionic emulsifiers of known HLB number (which can be calculated from the known structure of emulsifiers) are characterized by various parameters, relatively easy to check such as: cloud point, water numbers or phenol indexes. For some of the emulsifiers there is a rectilinear dependence between HLB and the above characteristics, at least in some range of their HLB numbers.

The cloud point characteristics of emulsifiers can be checked in the whole range of HLB numbers if three test solutions are used.

1- for lower HLB numbers eg for polyethoxynonylphenols (PENF) up to HLB 12.5 the solution of 5g emulsifier in 25 ml of aqueous butylglycol (25%);

2- for medium HLB number (HLB,12.5-15.0) eg for PENF-s, the solution of 1g of emulsifier is made up with distilled water to 100ml, in graduated flask;

3- for higher HLB numbers (HLB 15.0) eg in case of PENF-s, the solution of 1g of emulsifier dissolved in 100 ml aqueous common salt solution (10%).

The cloud points for several types of nonionic emulsifiers of Hoechst Co. are given in tables 1-3

Very useful characteristic of nonionic emulsifiers, which can also be used, in wide range of HLB numbers, is their phenol index. For some of nonionics there are also rectilinear dependence between their HLB numbers and phenol indexes.

The phenol index characteristic can also be used for checking of quality of mixed emulsifiers-nonionic and anionic which are commonly used in preparation of EC-a.

Another characteristic "water number", is obtained by titration of solution of emulsifiers in the mixture of organic solvents with water. The water number characteristic can also be used for characterisation of hydrophobicity of oils. (e.g. solution of pesticide in organic solvent.)

All of the above described characteristics can be used for checking the quality standards of various emulsifiers of different HLB number. It is proposed to use these characteristics (cloud points, phenol indexes and water numbers) to test the quality of emulsifiers used in India for production of different pesticide formulations and to supplement the studies written already in the form of a paper entitled:

**"EVALUATION OF SOME EMULSIFIERS SYSTEMS FOR USE IN PESTICIDE FORMULATION" AUTHORS: P.K. RANDAS & S.K. KHÉTAN.**

**6.2. Phase inversion temperature (PIT) and phase inversion point (PIP) as an additional characteristic of emulsifiers.**

The PIT and PIP characteristics are also recommended as additional criteria as a guide of choosing or testing of nonionic emulsifiers. In both cases, the inversion temperature on inversion point of emulsion from W/O to O/W type or vice versa, can be fixed by measuring the conductivity of emulsion. The W/O emulsion show very small conductivity while the O/W much higher. When nversion takes place the change in conductivity follows.

There is relation between HLB numbers of some of nonionic emulsifiers and PIP. It is depicted in fig. 1. A general tendency for the PIP value is their decreasing with an increasing of HLB of emulsifiers. In required HLB value for an O/W emulsion PIP reaches a minimum (1).

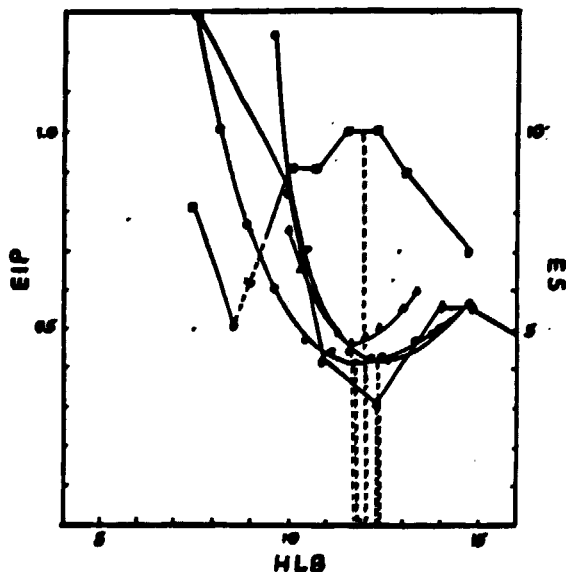


Figure 1. A plot of PIP against HLB for blends of Span 80 - NPE<sub>20</sub> (●), NPE<sub>10</sub> - Cremaphor EL (Δ), NPE<sub>10</sub> - NPE<sub>20</sub> (○) and single NPE<sub>10</sub> (◊) initially placed in paraffin oil phase (2% w/v). Emulsion stability (ES) as a function of HLB for mixture of NPE<sub>10</sub> - NPE<sub>20</sub> in paraffin oil-in-

HLB Values of Commercial Nonionic Surfactants

Surfactant	Abbr.	HLB Value
Polyoxyethylene (3) nonyl phenol (a)	NPE <sub>3</sub>	7.5
Polyoxyethylene (5) nonyl phenol (a)	NPE <sub>5</sub>	10.0
Polyoxyethylene (6) nonyl phenol (b)	NPE <sub>6</sub>	10.9
Polyoxyethylene (8) nonyl phenol (a)	NPE <sub>8</sub>	12.3
Polyoxyethylene (12) nonyl phenol (b)	NPE <sub>12</sub>	10.0
Polyoxyethylene (14) nonyl phenol (a)	NPE <sub>14</sub>	10.7
Polyoxyethylene (20) nonyl phenol (a)	NPE <sub>20</sub>	16.7
Span 80 (c)		9.3
Cremaphor EL (d)		13.3

(a) marketed as Stebapole (Leva, Steina, Germany)  
 (b) marketed as Rebalonole (Rehita, Poland)  
 (c) Atlas Chemie GmbH, Essen, Germany  
 (d) BASF, Ludwigshafen, Germany

The selection of suitable emulsifier by the PIP or PIT systems is similar to their selection on the basis of HLB system. As, however, PIT and PIP are experimental variables they have the advantage of reflecting all experimental variables. A peculiar utility of PIP system seems to be in choosing emulsifiers for concentrated stable emulsions. For such emulsions selection of emulsifiers on the basis of their stability ( as in the case of EC-s ) would be very trouble-some. The choosing of proper emulsifier for concentrated emulsion by using PIP measurements, can be combined with microscopic observation of the sizes of emulsion globules.

In table 1 the values of HLB at which the minima of PIP occur and required HLB for studied oil, calculated by Griffin procedure are give (1).

Table 1

Emulsified oils	Griffins required HLB	Required HLB from PIP
Paraffin oil	11,5	11,8
Rape oil	9,0	9,8
Methyl silicon oil	11,0	11,5
Olive oil	13,0	12,5
Soya bean oil	12,0	12,5
Oleic acid	17,0	16,3

The cited above results were obtained according to the following method:

The emulsion inversion point was determined with an electrical device by adding increments (1 ml) of water to a measured amount (50 ml) of oil. Emulsifiers, or their mixtures of various HLB, were dissolved or dispersed in the oil phase (2 or 4% w/v). After adding each portion of water the emulsion was mixed for 15 sec.....in mixer of 6000 per/min. After mixing the conductivity of emulsion was measured. The sharp increase in emulsion conductivity was due to phase inversion from water - in - oil (W/O) to oil - in - water type (O/W) emulsion.

### 6.3. Experiments

The following runs of experiments have been carried out:

Emulsification with tap water of the following solutions.

- 1- solutions of Span/Tween mixtures of different HLB in xylene;
- 2- solutions of PENF-s of different HLB in xylene;
- 3- solutions of mixture of Span/Renex 650 of different HLB in paraffine oil;
- 4- solutions of mixture of Span/Rokafenol 8 and Rokafenol 8 and Rokafenol 14. (polyoxynonylphenols of HLB 12,3 and 14.7) in paraffinic oil.

The PIP took place only in experiment 2-4 and results, similar to that given in literature (1), had been gained. Some difficulties in carrying out the PIP experiments were caused by nonavailability of proper mixer. There were only two types in R&D Laboratory. One of them (the part of Metler titrator DL 40 RC) appeared to be too weak for PIP experiments and the other one, the Silverson Mixer, which was too big. Using the last mixer the sample of volume at least 100ml must be used. For that reason it is recommended to supply the laboratory in more adequate and versatile mixers equipped with different type of stirrers and with regulated speeds up to 15000 rpm.

The important problem in the case of concentrated emulsions is the method of testing their stability. Since such emulsions are usually opaque, the study of creaming in such systems can be tested by determination of droplet-size distributions in samples taken regularly from the same level of region of emulsions stored over some period.

Droplet-size distributions can be determined using Malvern -Laser particle sizer e.g. 2600 HSD type. Other method which lastly also had been used for testing stability of concentrated emulsion depends on measurements of creaming profiles by using technique of propagation of ultrasounds through an emulsion (2)

7. **Problems encountered while trying to elaborate of system (similar to HLB) for testing dispersing agents.**

During my previous, as well as present mission, I had been asked of the possibility of elaboration and using of system similar to HLB system by which the dispersing agents could be classified and on the basis of which the proper one could be selected.

Taking into account simplicity and utility of the HLB system, but only useful for emulsifiers, such a question is entirely understandable. In case of suspensions however the mechanism of their stabilization by dispersing agents is different than that one of stabilization of emulsion by emulsifiers.

As it is known the different emulsifiers used for preparing water emulsions are mostly nonionic, composed of two parts, a hydrophobic and a hydrophilic. Depending upon the weight ratio of both parts the emulsifier will be less or more hydrophilic or hydrophobic. For known hydrophobic group the degree of hydrophilicity can be easily modified by extension or shortening of the change of Eto groups.

Such various nonionic emulsifiers when added to the mixture of water and oil will show various affinity to these two phases. Those of more hydrophilicity will be "pulling" to the water and those of more hydrophobic character to the oil phase. Some of them will have the emulsifying effect. But the best one will be shown by the emulsifier which is characterised by the optimum affinity to water and oil and which will be, well orientated on the interface.

It has also to be found that if nonionic emulsifiers are used to disperse some pigments in water the best effect is obtained for the one of specified HLB numbers (6,7)

In case however of anionic dispersing agent the mechanism of their functioning is different though they also are composed of two parts; one contains less water attracting groups and the other more attracting toward water. The particles of suspension thus become coated with a sheath of water-attracting groups. On close approach of two particles, due to random kinetic motion, the energy of translation can be opposed by the energy with which the water attracting groups tend to draw water into the small element of volume between particles. In such a case the suspensions are "stabilized by solvations". The other stabilization is by "electrostatic repulsion" between like charges. In most cases both stabilizing mechanisms are present, however, one of them may be more dominant.

Contrary to the nonionic emulsifiers, which belong to the exactly defined chemical groups, the anionic dispersing agents belong the many various chemical groups. The affinity (adsorption) of hydrophobic groups of individual dispersing agents to various solids is much more differentiated than the affinity of hydrophobic groups of emulsifiers to different oils.

It seems that for elaboration of some of numerical system for characterization of dispersing agents, many physico-chemical phenomena have to be taken into consideration eg mainly: wettability of solid surface by water solution of dispersing agent; their adsorption on the solid surface; the electro-kinetic potential quantity.

I think that easier task would be to collect and order the literature and patented data concerning the efficiency of different dispersing agents and put them in order according to the chosen system.

It is however not excluded that system similar to the HLB one would be possible to elaborate to the new class of dispersing agents invented and introduced on the market by ICI company and which belong to the block-craft-polymeric dispersing agents (8). They are steric stabilizer of dispersions and are composed of two parts a homopolymer that is nominally insoluble in the dispersion medium whereas the other polymer is soluble in the dispersion medium.

Typical stabilizing moieties and anchor polymers for these type of steric stabilizers are given below (9):

Typical stabilizing moieties and anchor polymers for sterically stabilized dispersions

Aqueous dispersions	
Anchor polymer	Stabilizing moieties
polystyrene	poly(oxyethylene)
poly(vinyl acetate)	poly(vinyl alcohol)
poly(methyl methacrylate)	poly(acrylic acid)
poly(acrylonitrile)	poly(methacrylic acid)
poly(dimethylsiloxane)	poly(acrylamide)
poly(vinyl chloride)	poly(vinyl pyrrolidone)
poly(ethylene)	poly(ethylene imine)
poly(propylene)	poly(vinyl methyl ether)
poly(lauryl methacrylate)	poly(4-vinylpyridine)
Nonaqueous dispersions	
Anchor polymer	Stabilizing moieties
poly(acrylonitrile)	polystyrene
poly(oxyethylene)	poly(lauryl methacrylate)
poly(ethylene)	poly(12-hydroxystearic acid)
poly(propylene)	poly(dimethylsiloxane)
poly(vinyl chloride)	poly(isobutylene)
poly(methyl methacrylate)	cis-1:4-poly(isoprene)
poly(acrylamide)	poly(vinyl acetate)
	poly(methyl methacrylate)
	poly(vinyl methyl ether)

**Genapol O Products**  
Oleyl alcohol polyglycol ether



Name	Nature	Solubility					Reaction 10 g/l	Specific Weight@20°C (g/cm <sup>3</sup> )	Viscosity@20°C (mPa·s)	Infrared Index@20°C (refractive index)	Softening Point@°C (DM 21 102)	Flow Point@°C (refractive index)	Flash Point@°C (Reactivity)	Turbidity Point			Lime Soap Dispersion Power % (DM 23 102)	24 Hour Tension 20°C, 1 g/l. Solution (Tensile)	Emulsion Stability Power (DM 23 102) at 100 rev./min. @20°C
		1:10												H <sub>2</sub> O	CaCl <sub>2</sub>	NaCl			
		Water	Mineral Oil	Benzene	Toluene	Glycol													
Genapol O-020	liquid, clear	turbid	clear	clear	clear	insol.	neutr.	0.894	12.4	1.4510	2	—	186	—	35.4	—	—	—	
Genapol O-050	liquid, turbid	turbid	turbid	clear	clear	insol.	neutr.	0.936	18.4	1.4530	1	—	225	—	68.1	—	4	54	3
Genapol O-080	liquid, turbid	clear	turbid	clear	clear	clear	neutr.	0.960	25.1	1.4538	17	—	246	46.1	80.2	—	3	44	1.3
Genapol O-100	paste	clear	turbid	clear	clear	clear	neutr.	0.989	33.0	1.4558	19	—	260	77.5	87.4	90.0	2	41	1
Genapol O-120	paste	clear	turbid	clear	clear	clear	neutr.	1.000	42.5	1.4560	—	30	265	92.2	89.6	88.2	2	42	1.5
Genapol O-150	wax	clear	turbid	clear	clear	turbid	neutr.	1.020	49.1	1.4570	—	39	271	—	93.2	72.3	2	43	> 10
Genapol O-200	wax	clear	turbid	clear	clear	turbid	neutr.	1.037	65.9	1.4580	—	43	278	—	95.3	75.2	2	47	> 10
Genapol O-230	wax	clear	turbid	clear	clear	turbid	neutr.	1.042	79.5	1.4582	—	44	279	—	95.6	76.5	2	47	> 10
Genapol O-250	wax	clear	turbid	clear	clear	turbid	neutr.	1.042	88.1	1.4587	—	46	280	—	96.2	77.5	2	48	> 10

Characteristics of some of emulsifiers

**Genapol C Products**  
Coconut fatty alcohol polyglycol ether



Name	Nature	Solubility					Density: 10 g/l	Specific Weight/20°C (approximate)	Viscosity/20°C (mPa·s) at	Refractive Index/20°C (approximate)	Softening Point/°C (DIN 51 201)	Flow Point/°C (approximate)	Flash Point/°C (approximate)	Turbidity Point			Line Soap Cleansing Power % (DIN 51 201)	Surface Tension 20°C 1 g/l, d.p.m. (mN/m)	Emulsion Working Power (DIN 51 201) g/l for 100 mg/20°C
		10 g/l		1:10										H <sub>2</sub> O	SDS	NaCl			
		Water	Mineral Oil	Benzene	Tetra	Glycol													
Genapol C-020	liquid, turbid	turbid	clear	clear	clear	insol.	neutr.	0.892	10.6	1.4412	12	—	170	—	39.6	—	7	34	—
Genapol C-050	liquid, turbid	turbid	clear	clear	clear	insol.	neutr.	0.952	17.6	1.4465	11	—	201	—	72.4	—	3	32	0.5
Genapol C-080	paste	clear	turbid	clear	clear	clear	neutr.	0.979	25.4	1.4498	—	26	246	76.7	84.3	49.0	3	36	0.6
Genapol C-100	paste	clear	turbid	clear	clear	clear	neutr.	0.990	30.4	1.4503	—	30	251	90.1	88.2	61.5	3	38	0.8
Genapol C-150	wax	clear	insol.	clear	clear	turbid	neutr.	1.027	45.8	1.4535	—	34	260	—	93.1	74.3	2	43	> 10
Genapol C-200	wax	clear	insol.	clear	clear	turbid	neutr.	1.032	61.5	1.4530	—	37	264	—	95.3	76.8	2	44	> 10
Genapol C-250	wax	clear	insol.	clear	clear	turbid	neutr.	1.055	80.6	1.4564	—	42	267	—	95.8	78.0	2	47	> 10



**Genapol S Products**  
 Stearyl alcohol polyglycol ether



Name	Nature	Solubility					Reaction 10 g/l	Specific Weight@20°C (g/cm <sup>3</sup> )	Viscosity@20°C (Mpa·s)	Refractive Index@20°C (refractometric)	Softening Point@°C (DIN 51 383)	Flow Point@°C (ASTM D-97)	Flash Point@°C (Petrobrans)	Turbidity Point			Lime Soap Dispersing Power % (DIN 53 585)	Surface Tension 20°C, 2% solution (mN/m)	Immersion Wetting Pow. (DIN 53 585) g/l for 100 sec@20°C
		10 g/l	1 : 10											H <sub>2</sub> O	SDS	NaCl			
		Water	Mineral Oil	Benzene	Tetra	Glycol													
Genapol S-020	wax	tur-bid	clear	clear	clear	tur-bid	neutr.	0.890	15.2	1.4458	—	36	198	—	45.4	—	9	50	—
Genapol S-050	wax	tur-bid	clear	clear	clear	tur-bid	neutr.	0.934	21.2	1.4480	—	32	224	—	72.9	—	4	50	7
Genapol S-080	paste	tur-bid	tur-bid	clear	clear	tur-bid	neutr.	0.971	28.4	1.4510	—	30	228	—	64.2	—	3	44	1.5
Genapol S-100	paste	tur-bid	tur-bid	clear	clear	tur-bid	neutr.	0.978	34.0	1.4512	—	33	239	76.0	88.1	46.4	3	45	2.5
Genapol S-150	wax	clear	tur-bid	clear	clear	tur-bid	neutr.	1.009	50.3	1.4540	—	39	266	—	94.2	72.4	2	47	> 10
Genapol S-200	wax	clear	tur-bid	clear	clear	tur-bid	neutr.	1.031	67.4	1.4555	—	41	267	—	96.3	75.4	2	48	> 10
Genapol S-250	wax	clear	tur-bid	clear	clear	tur-bid	neutr.	1.049	106	1.4570	—	47	273	—	97.3	77.0	2	49	> 10

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