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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

Based on the work of A.R. Woodford,
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Contents

Introduction

The UNDP programme in India is sponsoring until 1988 at the present time, a pesticide development programme under the title PDPI (Pesticide Development Programme India) under the general management of HIL (HIndustan Insecticides Ltd.) a Government of India Corporation.

The main objectives of this programme are to act as a focal point within India for technology dissemination in the area of formulation development, quality control, pilot scale studies and other related disciplines.

The author first became associated with this project in 1986 and spent six weeks working at the PDPI centre at Udyog Vihar near Gurgaon. During this visit, some very useful progress was made particularly in the area of suspension concentrates and their scale up to pilot scale size. At the same time, a number of recommendations were made both for the purchase of additional equipment and for training of personnel. As a result of their recommendations, three persons from PDPI were sent to the UK for training during the summer of 1987.

This report covers the second six week visit to PDPI to both assist in a Quality Control training programme and to follow-up on the work previously started.

1. **Follow-up from previous visit**

a) **Flowables** : It way very pleasing to see that the work started on the development of a Carboxin flowable had been brought to a successful conclusion. A modest quantity had been prepared on a pilot scale with no serious problems.

Samples of this product were re-examined as it is approximately one year since the formulation was completed. This examination showed that after this time there was some very hard clay like settlement. However, further examination of this deposit showed that it represents only 2-3 % of the solids content and thus the formulation is still suitable for use.

In view of this settling it is proposed that the formulation is re-examined when time permits in order to improve the wetting and dispersion of the carboxin.

b) **Dressed seed** : The result of field trials on seed dressed with this flowable are being reported elsewhere, so it will suffice here to say that these results show quite clearly that the flowable is as effective as the power dressing and on average seems to give better control of the fungus.

c) **Bacillus sphaericus** : Following the preliminary suggestion for an oil based spreading formulation, a formulation has been developed based on a vegetable oil. This formulation gives the desired spreading effect and does effectively kill stephansivariety but does not seem to be anything like as effective on culificarae. During this visit some tests were carried out to observe the feeding habits of both species. For the purpose, a stereo-microscope was used to observe the effects of the spread oil formulation on feeding.

Small dishes were partly filled with water on the surface of which the formulation was floating. Larvae were then introduced into the water and observed under the microscope using the zoom attachment to obtain close pictures of their behaviour. Both species appeared to eat the oil dispersion, although this was made obvious in the case of stephansi.

No further alterations were proposed to the formulation since it was felt that more evidence was necessary to determine whether the failure with culiciferae was due to the species of sphericus or the morphological state of the Larvae.

d) **Microscope** : It was very pleasing to see that the microscopes recommended during the last visit had been purchased as suggested. The stereo-microscope proved to be extremely useful particularly in connection with the observation of the Larvae referred to above. It also proved very useful to have a camera attachment as this enabled us to actually photograph the Larvae while they were eating.

e) **General Comments** : The laboratory conditions are much improved over those existing at the time of the previous visit and most of the suggestions in the last report seem to have been implemented.

2. **Points arising from the visit**

a) **Clay examination** : The results of the work of Dr. Khandal and his assistant were received and discussed. This was a very comprehensive piece of work and

much useful knowledge of the properties of clays is now available. As a result of these discussions, the following comments and suggestions were made.

i) When trying to establish correllation between various tests, it is easier to assess the results graphically and it was suggested that Dr. Khandal tried this technique.

ii) It is not valid to compare powder properties of clays with widely differing average particle sizes. It is better to mill the coaser powders to give comparable size distribution to the finer products and then carry out the comparative tests.

iii) Although the data recorded is of great use to clay supply company and the PDPI as both are in a position to carry out the necessary tests. However, for less well equipped laboratories, it is essential to find some simple test procedures which do not require elaborate and expensive equipments. Some tests which can be looked at are oil absorbtion wetting and suspensibility with a standard combination of wetter and disperser.

B) **Surfactants**

There still exists a problem in connection with the quality control of surfactants. One possibility is to use the infra red spectra of surfactants but this is not available to all laboratories. For this reason, tests were started to try to see if cloud point determinations could be used by making use of the fact that small addition of anionics increase the cloud point. By using salt solution to lower the cloud point and then addition of anionics to increase it, perhaps a graphical relation will be possible. Work to determine if there is any such correlation has been started but at the conclusion of this visit this work was still in progress.

C) **NEW WORK**

i) **Water dispersible granules**

Some tests were started using the Aeromatic to produce isoproturon water dispersible granules. This work went very well partly due to the training Mr. Sarin had received in the U.K. Good granules of 75% and 80+% active ingredient were prepared with excellent dispersion and suspensibility. It was suggested that further work is directed to understanding the effect on quality of granules of changing the various parameters.

a) Rate of spraying slurry
b) Air pressure
c) Slurry concentration
d) Drying Temperature

Although there are several other parameters many of them are interlated and above selection were the most liekly paramters to effect product quality.

Some trials were also initiated working with a sulphur slurry but only early trials were carried out during the visit. The results obtained indicated that the technique would be successful but required optimisation. This would mainly take the form of adjustments to slurry feed rate and drying condition.

ii) **Sulphur Flowable**

This project was discussed but no trials were started. The lines of work suggested were thus already established for the carboxin flowable and carried selection of this dispersing and thickening agents and setting the milling rate Somefull scale trial carried out about a year previously indicated that Tamal DN was good dispersant for sulphur.

iii) **Microencapsulation**

This project was discussed at some length. However, in the time available it was not possible to obtain the necessary chemicals to try out polyamide encapsulation as is used for methy parathion

A proposal for the work was discussed and the following outline procedure was drawn up.

1) Dissolve the diamine as its hydrochloride in water
2) Dissolve the acid as its acidchloride in the pesticide together with an emulsifier.
3) Emulsify the pesticide in the water phase
4) Slowly add sodium hydroxide solution to release the amine and thus control the rate of reaction.

It was proposed that work on the techniques is carried out first before actually using a pesticide as the procedure does require some technical skill which can only be acquired by practical experience.

iv) **Sulphur Wettable Powder**

Although the techniques for producing wettable powder are well known some time was also usefully spent on this project. PDPI had received a request for an 80% sulphur WP and thus a work programme was drawn up. A possible formulation was drawn up based on the wetting and dispersing agents currently used for DDT using a kaolinite clay as filler and this was used in the trials.

The main interest in this work is concerned with safety. Milling sulphur is a potentially hazardous operation and so the plant to be used was very carefully inspected. The first and most important thing was to ensure that all parts of the plants were interconnected and atearth potential. This was all carefully checked electrically. It was then necessary to ensure that all nonmatalic parts had inside then a conducting wire also earthed and connected to the metalic wires.

The area of most concern was the dust collection and it was decided to conduct the trial relying on the explosionpanel in case of problems.

RECOMMENDATIONS

Work on flowable formulations is still held up because of the lack of efficient and quick equipment for particle size determination. It is therefore recommended that PDPI purchase the following instruments which will not only use for particular size measurements on flowables but also for emulsion and droplet size of sprays.

Malvern Model MS 1001 Complete

MS 1 - S small volume sample cell

This model is particularly useful as its size range goes down to 0.1 micron. If this model proves too expensive then the following is proposed :

Malvern Model 2601 E

There is already, in PDPI a particle size measuring instrument based on rate of sedimentation. Although this equipment is useful for relatively coarse particles it is not suitable for fine particles due to the very slow rates of sedimentation even under the centrifuge. Further more the results are dependant on the density of the solid, a property which it is often difficult to determine. The Malven measures actual particle size and thus suffers from none of these defects and directly gives 0 particle size distribution with out the need to rely on sedimentation or artificial increases in gravity to accelerate settling. Further, the results are obtained in a matter of a few minutes rather than more than 1 hour.

2. The usefulness of both micro copies will be enhanced by having a measuring grating so that qualitative anessments of particular size can be made. The following additional items are recommended for this purpose:

For Model BHT	
Micrometer eyepiece	Micro WHK 10X
For Model ZSH	
SZH-STADI	Stage adaptor
BHZ-SH	Mechanical stage
OSM-4	micrometer eye piece

3. The Aeromatic fluid bed granulation, although very useful for preliminary laboratory studies is not exactly suitable for pilot scale work. Continuous fluid bed spray granulators are now available from both Niro of Denmark and Alpine of Germany. The former has a topentry spray and the latter a bottom entry one. Although the Niro plants are in a more advanced state of development i.e. they have full scale plants in operation, the Alpine works on a rather better principle and is the model recommended. As it is not clear how far Alpine have developed their model it is suggested that they are contacted immediately concerning the models available.

4) The KDL Dynomill for producing laboratory scale sample of flowables is in most cases quite satisfactory. However, it does have a relatively high residual capacity which is a serious disadvantage with small quantities. It is thus suggested that a mini mill such as the Eiger Mini mill is purchased. Thus mill can operate on as little as 50 mls of a flowable and is especially useful for preliminary trials with small quantities of pesticides.

5) It is apparent that the period of training given to persons of PDPI has had a very good affect on their laboratory technique. It is strongly recommended that this process continues and in particular it is recommended that Mr. Singhal from Dr. Ramdas's laboratory is given the opportunity receiving such training. Once again the author is willing to offer the services of his company in this respect but it may be possible to make similar arrangements through another company either in the UK or America.

Appendix I

SHELF LIFE

When a farmer buys a container of pesticide, whether direct from a formulator, from a shop, from a dealer or merchant, he has a right to expect that the pesticide will perform in the way the has been led to expect. This expectation comes from either the product labelling, advertising literature or any official pest control adviser.

What if it turns out that he cannot use the product? Perhaps it will not mix or emvisify, or it has been contaminted in some way. Perhaps he can use it but it does not give the expected pest control, provided this latter is not due to poor application or some climatic effect. Then the farmer has a right to blame the pesticide industry for allowing inferior products to be sold in the market place.

It is precisely to overcome this type of criticism that the pesticide industry must give a great deal of attention to what is called "the shelf life" of pesticides. By this is meant that when a purchaser buys a pesticide product by looking at the information the label, he can tell the length of time within which he must use that pesticide before it will not be gaurenteed to perform properly.

Before going further one or two points need some clarification. We must not expect that pesticide formulations will remain uncanged for ever. They all undergo some degradation with time of steroge and similarly for pachoging materials. Thus there will be some limitation on the time pesticides can be stored before use and a major problem is how this time shelf life can be defined. In other words since some degradation of properties will always occur how much degradation can be accepted before the product can no longer be guaranted to work properly. The use of the word

gaurenteed here is quite deliberate because it is the gaurantee of performance under all normal conditions of usage that is required. No doubt there are conditions under which a product with only 60% of the required active ingredient will work but equally there will be conditions under which it will not work. The main point is that we are not talking of absolute answers but only relative oncs. In other words the performance relates to the fully made product.

Thus the definition of shelf life then becomes the length time the product can be stared under normal local conditions and remain in a satisfactory and safe pachoge and still give the claimed bioligical control.

There are three important points in this.

1. The storage is under normal local conditions.
2. The product performs correctly biologically.
3. The packaging must remain in good condition.

There three points will now be considered in more detail.

1. Storage.

It is not reasonable to expect that products can survive storage under any type of conditions. However it is reasonable to say that in any perticular country or location there are typical storage conditions. Thus it may be a conguated tin shed or similar building in some tropical areas whereas in more temperate ones concrets buildings may be used. There will always be people who will store products in the full heat of the sum sun or above the snow line but there have to be considered as abnormal.

It is generally impossible to cover every possibility . To be realistic the general average must be used.

2. Correct Biological performance.

What the farmer is buying is pest control and this is what he must have throughout the shelf life of the pesticide product. The product at the end of its shelf life, must still be in a condition to be used by the farmer and give the expected biological result. This does not mean that either the chemical or the physical properties of the product are unchanged. In fact it is generally considered that 10% reduction in physical and chemical properties is point at which a product reach the end of its shelf life. This is reflected in many of the FAO specifications where the heat slablity is satisfactory provided the assay after the test is still 90% of its original value. Two examples are mancozeb dispesable power and malathion solution. Perhaps at this point a certain ambiguity in the FAO methods must be mentioned. It is not clear just what this storage slability test means. Is it taken to mean that if the product passes this test it is stable for two years? If this is the case for example, and we retest a sample stored for two years is this stability test to be repeated and if so what result should be obtained? Perpahs 90% of the original value. It is not proposed to answer this question here but merely to point this out as passing one of the problems in connection with the determination of shelf life.

3. The product packaging.

The pesticide must obviously always be packaged in some way and it is with this packaging that the farmer first comes into contact. If this is poor and degraded then it is obviously a danger, either to the person handling the

package or to the contents. Shelf life, must inevitably be associated with the packaging and thus any shelf life testing must be carried out in the relevant packaging.

The recent FAO code of conduct has implicilty taken this into consideration in its Article 10 'Labelling, Packaging, Storage and Disposal'. In this article under paragraph 10.2.6. it says the following.

"The industry should use labels that:

are marked with the date (month and year) of formulation of the lot or batch and with relevant information on the storage stability of the product."

In September 1987 this was subsequently clarified by the Code Expert Committee as follows.

"The date of formulation is the date of the last step in the series of formulation processes at which a sample identified with a batch was tested and shown to meet specification, or the date of last analysis of a sample identified with a batch, before putting the product on the market. This second alternative applies to those situations where formulated product is packed or repacked etc. at source (e.g. manufacturing or formulation plant)."

The underlining does not appear in the original but has been pur in for emphasis. The relevant storage stability in the formulation must appear on the label i.e. on the pack together with the date from which this storage stability applies.

Unfortunately this area is not clarified in the code and although the above clearly refers to the packed product all the standards such as FAO, and other similar standards like ISI only consider tests in glass. No mention is made of the fact that product stability can be affected by the packaging. For example

water based formulations in mild steel containers leads to rusting and contamination, if not degradation of the product; emulifiable concentrates in low density polythene bottles suffer from seepage through the ploythene; water sensitive products in permeable bags can become degraded; and there are many other examples.

One point here must be clarified that is that the above refers only to the product inside the pack. There is of course, additionally the problems of the external environment on the pack as was hinted at in the case of water vapour permeable packs used for water sensitive products.

Having outlined the importance of shelf life in regard to pesticide products it is now necessary to consider how shelf life can be assessed. Looking to the international organisations for help is not of all fruitful. Similarly there is no assistance from regulating bodies. In essence their attitude is that if it is wished to claim a two year shelf life, then the product must be kept for two years and be shown to be still satisfactory. As mentioned above the only accelerated tests in the international standards are in glass and may or may not be relevant to the packed product. In any event there is no indication of how long a shelf life can be claimed if a product passes this accelerated stability test.

In the absence of any guidance, most commercial companies develop their own procedures and typical example given below. This particular pattern applies to temperate climates and a different series of temperatures would be necessary for tropical conditions.

TABLE I

Temperature	50C	37C	2o C
10 days	x	x	x
14 days	x	-	-
1 month	x	x	-
3 month	-	x	x
6 month	-	x	x
1 year	-	-	x
2 years	-	-	x

If possible several samples from a batch of the pesticide are packed or if this is very large in a reduced size simulation and then tested at the temperature indicated. At the periods of time indicated by the crosses the best period are arranged to avoid unnecessary time being wasted. If a sample shows degradation at one of the higher temperature then the decision regarding the lower temperatures can be taken.

The basic assumption made is that although many products are stable for considerably longer than two years registration authorities will give registration for products which can be shown to have a two year shelf life.

What tests should be carried out on these samples?
This must depend on the objectives of the shelf life tests. For registration authorities it means testing to the product specification and as indicated above provides no property has degraded by more than 10% of its original value after two years, then the product is satisfactory.

If possible several samples from a homogeneous batch of the pesticide are packaged in the final proposed packaging or if this is very large, in a reduced size simulation and then stored at the temperatures indicated and tested at the periods of time indicated by the crosses. The test periods are arranged to avoiduncessary time being wasted. If a sample degrades at one of the higher temperatures then the decisions regarding the lower temperature ones can be taken.

The basic assumption made is that although many products are stable for considerable longer than two years, registration authoritieswill after given registration for products which can be shown to have only one year shelf life.

What tests should be carried out on there samples? This must depend on the objectives of the shelf life tests. For registration authorities it means testing to the product specification and as indicated above provided no property has degraded by more than 10% of its original value after two years, then a two year shelf life can be assumed. If of course the tests are being carried out not only for registration purposes but also to give more detailed information on the packaging, then other tests should be included such as drop tests to check for embrilttement of the container, weightto see if there has been actual product loss and many others.

The advantage of accelerated tests is that they give early warning that problems may arise. This does not mean than the product at the ambient temperature (20% in the above) will not survive for two years and in doubtful cases the tests must be continued for two years.

Although the proposed temperatures are suitable for temperate climates, the range used should be based on local average conditions. The ambient temperature should be the normal average encountered in average storage depots, wharehouse or dealers shops and the accelerated temperatures adjusted accordingly. If in tropical conditions the general average is about 35 C then a suggested range would be 65^{o}C 52^{o}c and 35^{o}c This change of temperature must of course, be agreed with the local registration authority who should be made aware of the need for realistic condition of test.

Another important point is to ensure that the appropriate packaging is used as this is an integral part of the actual product being sold. It is often very useful to include tests in glass as these will show whether any degradation which does take place is inherent in the formulation or is a result of the packaging.

If large packs are involved then a compromise must be reached due to the physical problems in actually carrying out the tests . It generally is acceptable to use a 5l or 5kg sample in the sample type of packaging as usually, the surface area to valume of the container is greater than in the larger pack and any effects due to contact with the container will be slightly exegerated.

This paper has been concerned with the basic principals of shelf life studies rather than the specific test carried out in these studies. In most cares the usuall product specification tests are satisfactory such as :--

appearance and odour
wt./ml or power density, loose and packed
suspensibility or emulsification properties
mesh and wetting time tests for powers Active ingredient content.

Other tests of course can be included where the product or formulation specially, requires them. In particular the most important tests are those that relate to the suitability of the product for its enduse.

There is however one very important difference between a quality control product specification and one used for shelf life studies. In the latter the method used to determine the active ingredient content must be a product specifie one and not one which includes any breakdown products as well. The object of these tests is to assess stabilty and thus the method for the active ingredient must be able to separate the active ingredient from its breakdown products.

In this paper an attempt has been made to clarify what is meant by shelf life studies and to indicate their importance, this is an important aspect of the pesticide industry and an area where the industry can come into disrepute. Further discusion must take place and a clear international agreement reached so that not only the industry but also the product users understand what is meant by 'shelf life'.