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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, expert in pesticides formulations

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Vienna

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* This document has not been edited.

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Finally, I would like to thank Dr. Dhua and the staff at UNDP for their co-operation in many areas relating to my visit.

CONTENTS

Abstract

This report briefly summarises the work carried out during the author's assistance as lecturer at the "Workshop on Pesticide Formulation Technology" organised by PDPI/RENPAP/UNIDO at the PDPI Research Centre at Gurgaon. This workshop took place from 27th March to the 15th April but the author was only present for the second two weeks. Four lectures of a general nature were given during this period and the author also acted as Chairman at two sessions. Additionally, assistance was given by discussion and comment with the participants during the practical sessions. On the final day the author helped and guided the participants in formalating the courses recommendations.

Introduction

The author visited India for two weeks commencing 3rd April 1989 in order to take part and assist in the "Asia and Pacific Regional Workshop on Pesticide Formulation Technology" organised by Pesticide Development Programme India (PDPI) and "Regional Network for Production, Marketing and Control of Pesticides in Asia and the Pacific" (RENPAP) under the auspices of UNIDO.

The Workshop

During the time of the author's stay at the 'Workshop', the programmes were divided into a series of lectures during the morning, followed by demonstrations,generally relating to the subjects of the lectures,during the afternoon.

The author acted as session chairman on two occasions and deputy chairman on two occasions as well as giving four lectures. The practical sessions were generally very good, but because of the numbers of participants, were not quite as useful as they could have been. However, much of the time not directly taken up by lectures was used for informal discussions on general topics relating to formulation ,manufacture and control which the participants seemed to find very useful.

The interest shown by all the participants was of a very high level as was clear from the many pertinent questions they asked, both during the lectures and during the informal discussions. It was apparent that the language problems encountered by some of the participants during the formal sessions was less of a problem during private discussions where they seemed to be more relaxed and ready to try their English.

Considering all the lectures which were presented throughout the whole three weeks of the Workshop, the coverage of the subject was excellent. The whole workshop gave the participants an insight into most of the techniques involved in formulation development and testing and a chance to see first hand the type of equipment used for both formulation development and analysis.

One point which may require consideration in future courses of this type is how to cover such subjects as Registration. The lecture on the Indian Registration process was very interesting but only to the Indian participants because of the very specific local nature of such regulations. Perhaps a more general lecture on the guidelines used in setting up such systems and the good and bad points of how it is done in various countries would be more generally useful.

The main criticism of this course relates to the practical sessions. Although these were well organised there were too many participants at each session. It was thus difficult for them all to see what was happening and have any hands-on experience. It would be very advantageous if the numbers at each demonstration could be reduced to say 4 or 5. This would, of course, mean that more of the staff of PDPI would be engaged in the demonstrations but in the author's opinion this should not be too difficult to achieve and at the same time I am sure the participants would benefit greatly from this experience.

The lectures presented by the author is attached to this report together with the full programme and the course recommendations.

Recommendations

1. The final course recommendations which the author helped to draft were very pertinent and should be implemented where possible.

2. In future courses, because of language difficulties, the papers to be presented should be available to the participants before the sessions.

3. The numbers at each demonstration should be kept small and certainly not more than 4 or 5 so that all can see what is going on.

4. Some difficulties were encountered in relation to the way the participants received their DSA, and it is strongly recommended that means are sought whereby they can receive this without having to make several visits to the UNDP offices. In addition, the work and time involved in preparing so many sets of documents can surely be reduced. The courses are relatively short and even half a day lost is a significant part of the time available for training.

5. An excellent lecture was presented on Safety but it would have been even more useful if a demonstration session on safety including types of safety equipment had been included.

6. As recommended by the participants it is also recommended that one or two visits are made to formulation plants. Such visits should be carefully selected to show units where the standard of plant and work practices is of good quality. This would enable the participants to see some of the ideas and procedures discussed on the course being put into practical use.

APPENDIX I

Regional Network for the Production, Marketing and Control of Pesticides in Asia and the pacific.

Workshop on Pesticide Formulation Technology, New Delhi, India, March 27 - 14 April 1989.

RECOMMENDATIONS

In the concluding session of the Workshop held on 13th March 1989, all the participants of the Workshop adopted the following recommendations.

1. The Workshop recommends that Pesticide Development Programme India (PDPI) to ender into discussion with member countries with a view to extending technical cooperation in the development of formulations specific to these countries.

2. The Workshop recommends that PDPI/UNIDO investigate means by which technical assistance can be provided to those countries which do not as yet have any formulation plants such as Afganistan and Tanzania.

3. The pesticides industry in some countries such as Thailand, Philippines and Sri Lanka is dominated by the private secter. The Workshop recommends that consideration should therefore be given to extending the membership scheme available to India Pesticide Industry, to these countries.

4. The Workshop reinforces the recommendation made by the earlier regional workshop that cooperation amongst the countries of the region in collaborative research programmes is necessary. In particular, it is recommended that services of PDPI are made available to member countries in the areas of technical trouble shooting, formulation improvement, quality control and training.

5. The Workshop recommends that RENPAP principle is extended to African countries, particularly to the English speaking Africa like Tanzania, Zambia, Malawi, Zimbabwe,Ghana, Nigeria, Egypt, Sudan, Kenya, Uganda, Ethopia and others in the light of their similar climatic and socio-economic conditions.

6. The Workshop strongly supports the FAO/GIFAP recommendation concerning time-barred products in the countries of the region, by disposing of these materials wherever possible in the normal way.

7. The Workshop recommends that PDPI/UNIDO broaden their base to include the provision of technical know-how on disposal of pesticides, such as by incineration, in those countries where no such facilities exist, such as Sri Lanka.

8. The Workshop reinforces the recommendation of the earlier regional Workshop that the RENPAP programme continues for at least further five years in order to be fully effective.

9. With respect to this specific training programme, the Workshop recommends increased hands-on practical training in small groups to make the training more effective and also, if possible, to include visit to some manufacturing plants.

APPENDIX II

SPECIFICATIONS

A. R. Woodford
Rhone Poulenc, UK.

This talk will be mainly about the situation in Europe with regard specially to the U.K.

Types of specification

A) Registration
B) Production
C) Sales

A) Registration : Sales specification

This is the specification which is submitted along with all the other relevant documents to support the registration of either a technical ingredient or a formulation.

i) Technical Chemical

In the case of a new technical ingredient this specification will be concerned not only with the active ingredient purity but also with the nature and quantities of any impurities present. Normally the specification for a new active ingredient takes several years to develop because the impurity pattern is dependant on the method of manufacture and until a compound is manufactured in a commercial plant a definitive impurity pattern cannot be established.

When this is achieved it is normal to give the total analysis of five typical batches and to derive the specification on the basis of this data. Normal FAO limits are then placed on the active ingredient and upper limits placed on the impurities.

The other tests included will vary according to the nature of the product. Such tests as melting and boiling points, free acid or alkali, solubility, density appearance etc. are often included and relevant limits be placed on these based on experience and using the FAO guidelines as an absolute maximum tolerance.

This specification would also be used as a basic sales specification. As the sales specification is used as a basis for discussion between buyer and seller the final agreed specification may or may not be the same as the registration specification. However, it is important to remember that if the buyer is proposing to use the sellers product registration then the specification must not be different from that registered.

ii) Formulation

In the case of a formulation, the principle is the same as for an active ingredient specification. However, there is one main difference. In the case of formulations the biologically active component or components will always already be registered as technical chemicals and it is only necessary state the source of the

chemicals to which the specification refers. So there is no need to include the impurities in the technical active ingredient in the formulation specification.

Therefore for a registration specification it is only necessary to include additionally those tests which indicate that the product is suitable for its end use. Some typical examples of the type of tests included are given below.

a) Wettable Powder :

* Appearance
* Assay
* Wetting time
* Suspensibility

b) Suspension Concentrate :

* Appearance
* Assay
* Dispersion
* Suspensibility
  (Pourability - possibly in some cases)

In both these cases an identity test may be included but only if the assay method is not very sufficiently specific.

This type of specification would also be used as a basis for a sales specification. If the buyer is intending to use the sellers registration then this latter must be at least the minimum specification but quite often a buyer would require a more detailed specification if he was really concerned about quality. The difference in this case from that of an active ingredient is that the buyer may have some specific properties he requires in the formulation.

The normal approach with respect to limits to be placed on these specifications is to use the FAO tolerance as a basis. These limits are strictly of course only applicable to active ingredient assay and are not normally applied to other physical test such as are included in a formulation specification.

B) Production specification

This specification is the one which is used to ensure that the product meets the companies own in-house requirements both with respect to quality and control over the production process. In addition this specification must be such that any product which complies with it will comply with the registration and sales specification.

i) For active ingredients :

In this case there is very little difference between the registration specification and the production specification. The main difference lies in the presence of additional tests to ensure that for example, residual solvent, residual moisture or residual acidity or alkalinity are correct; or to ensure the physical form is correct etc. There features are usually not

of concern to the registration authorities provided the active ingredient and its associated impurities remain the same. Thus we are able to sell dry mecoprop acid and damp mecoprop acid containing say 5-10% moisture under the same basic registration package.

Normally in this specification the tolerance limits are tighter than F.A.O. to ensure that the product always meets these requirements.

One point often raised in connection with active ingredients is, what happens if the active purity is higher than the standard, say 95% instead of 90%. In this case the same registration will still hold provided that the impurities present are present in the original specification and are below the limits specified. The only time the matter has to be raised again with the registration authorities is if some new impurity appears Then further work is necessary to define this impurity and determine its effect on all the properties of the active ingredient.

When used in formulations the active ingredient will always be used on a pure basis and changing from 90% to 95% will result in the use of less of the technical material in any given formulation.

Similar considerations apply when selling technical since the customer is paying for active ingredient he should not expect to get 95% technical for the same price as 90% technical material.

ii) <u>For formulation:</u>

Similar considerations apply to the specifications for formulations. There are a number of additional tests included above and beyond those used in the registration specification which are designed to ensure the quality of production and to act as in-process checks. To illustrate this same examples are given below:

a) Wettable powders :

The specification always includes a bulk density. This is important to ensure that the product will fit into the final pack. Aeration during processing can make a big difference to the bulk density.

A wet sieving test is also included to ensure no coarse particles are present.

b) Emulsifiable concentrates :

A suspensibility test in different hardnesses of water is used. The object of the test is to ensure that the correct proportion of emulsifier have been used. It is well known that the emulsifiers have to be balanced to achieve optimum performance in 342 ppm water hardness but the choice is never sharply defined and so tests are carried out at 25 ppm and 500 ppm to ensure that the correct proportions have been used.

The specific gravity is also determined because in fluctuating temperature conditions the w/w content of the active ingredient must be constant as we have to quote both the w/w and w/v content of the formulation on the label.

c) Suspension concentrates :

Particle size distribution tests are always included for these formulations as these tests ensure that the milling operation is being carried out correctly. This is most important for this type of formulation because the long term stability of suspension concentrates is very dependant on the particle size.

Viscosity is another very important property of the formulation and together with particle size controls the long term stability.

From these comments it can be seen that the components of a production specification will differ quite considerably from the registration specification because of the different use to which each will be put. In the case of the production specification there are many components of the formulation for which it is impossible to include a chemical method of determination and so physical tests must be devised which will show whether the correct quantities of al the components have been used.

It follows from this that each formulation type and each different application will necessitate a different range of tests and the tests used for a wettable powder are not the same as would be required for a seed dressing for example.

Summary

The object of this paper has been to show how the components of a specification are chosen and how it is most important to be aware of the purpose for which the specification has been drawn up. Specifications are intended to help ensure a high and consistent standard of product quality and suitability for use.

For registration purposes they are used to define the product in relation to its use as a pesticide particularly in relation to its biological performance, toxicology and effect on the environment. For Production purposes, besides ensuring the product meets the registration requirements it is a tool in helping to monitor and control the production process.

SETTING UP A FORMULATION LABORATORY

A. R. Woodford
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When considering the establishment of a Formulation laboratory it is most important to first of all understand quite clearly the purpose and function of the laboratory. Depending on its intended use the layout and equipment of the laboratory will be rather different.

We can therefore envisage three basic objectives for the laboratory:-

1) General Production and Quality Control.
2) Formulation Development.
3) Basic Research.

Let us now consider each of these in turn but bearing in mind that in practice each of these may be combined with any or all of the others.

Before starting however it is most important to always bear in mind the general safety and hygiene requirements. Thus there must be adequate ventilation and lighting. The ventilation must be such that it draws any pesticide dust or solvent vapour away from the laboratory worker and not towards him; a suitable fume and dust cupboard must be available; adequate fire fighting equipment must be at hand; in fact all the normal safety measures should be fitted as recommended by GIFAP.

Having said this, I will not refer to this again unles there are specific reasons for doing so.

1. General Production and Quality Control.

Under this heading I am referring to a laboratory whose function is to provide support to Production in the areas of physical testing. Such functions as assessing the suitability of alternative fillers or emulsifiers, checking the quality of raw material deliveries, testing finihsed products etc.

Thus the laboratory must be able to carry out basic quality control tests on formulations such as these listed below.

a) Dusts and wettable powders.

b) Emulsifiable concentrates.

c) For suspension concentrates.

d) For storage stability.

With the exception of suspension concentrates the tests used to assess performance of dusts, wettable powders and emulsifiable concentrates can all be carried out in simple glassware. This together with suitable balances, stop watch and a set of sieves is quite sufficient. to enable a laboratory to carry out all the basic tests necessary. Thus for dusts the dry sieve test and flowability can be carried out with just a set of sieves and a funnel which does not have to exactly

corresponse to the CIPAC model to be useful for the comparative assessment of the properties of a dust.

For wettable powders, the additional tests for wettability, suspensibility and foam can be carried out in simple glassware and the assessment of such things as suspensibility, can also still be done without elaborate equipment.

In fact for both wettable powders and emulsifiable concentrates an assessment of performance sufficient to give a very good indication of whether a formulation will meet specification can be obtained by a simple volumetice assessment of settling. By using a graduated measuring cylinder and measuring the volume of compacted sediment in comparison with a good quality sample, the effect of changing surfactants or fillers in a wettable powder can be assessed. In a similar way, but using a graduated conical cylinder a similar assessment of emulsifiers in an emulsifiable concentrate can be made by comparing the volume of settled cream in comparison with a standard.

Thus a useful assessment of new formulations or changes in adjuvants in formulations can be made without the necessity of carrying out special chemical determinations which require expensive analytical equipment.

The only additional item of laboratory equipment which would be required is a small hammermill or equivalent. However in the event of this not being available even a simple coffee mill can be used equally effectively provided the material to be ground is not too hard.

Ultimately, of course, the formulations have to be checked by the full specification methods but my objective in these comments is to show that even with very simple low cost equipment the suitability of some formulation adjuvants can be checked before they are used in full scale Production and thus a measure of Quality Assurance which should be within the capabilities of any small scale formulator can be introduced into the production of forumations.

ii) Formulation Development.

In laboratories designed for the development of new formulations the requirement is of course basically the same as in the previous type but additionally more sophisticated and specialised equipment is needed.

In particular, more sophisticated powder mills would be required which could be used to yield variable particle sizes including air mills to obtain the smallest particles. Additionally some equipment for assessing particle size is necessary.

At its simplest a small hammer mill with exchangeable screens is required together with a pin mill and if possible an air jet mill. These three mills would enable a range of particle sizes to be achieved and consequently the characteristics of variable particle size wettable powders to be altered and their properties to be studied.

Furthermore a laboratory size wet process bead mill such as a Dynomill is essential if any serious work is to be carried out on suspension

concentrates and any developments in this area of course are only worthwhile if such milling capacity is available in the country concerned.

Incidentally some very useful work even in this area can be done by using a beaker of glass beads with a stirrer in it. Although the grinding is not as efficient as a real bead mill some very ueful early stage development work can be carried out.

The measurement of particle size generally requires sophisticated equipment, though even here some simple qualitative tests are available. The Hegman Gauge is one such. A drop of the suspension is drawn across a slot tapering to nothing. By means of noting scratches which appear due to large particle and the slot depth where they appear, some measure of the maximum particle size can easily be obtained.

However having listed all this equipment, it is often possible to develop new formulations with very simple equipment and many of the techniques used are drawn either directly or indirectly from food processing.

At this stage of the work of this type it becomes more important to have available equipment suitable for carrying out assays of the active ingredients in the formulations and to be able to assess both chemical and physical stability of any new formulations developed. Generally spoeaking this involves at its simplest a UV spectrophometer and at its more complicated GC or HPLC.

iii) Basic Research

To set up a laboratory to carry out basic research into formulations and formulation adjuvants requires considerable expenditure to establish a unit similar to that existing at PDPI. More sophisticated means of measuring particle size such as the Malvern are essential. Similarly equipment to measure surface tension, zeta potentials, absolute density, viscosity etc are all necessary if successful basic research is to be carried out. With regard to the mechanical equipment, spray granulator, spray drier, pan granulator, colloid mill, high energy disperser and drum blenders are all necessary to enable a wide variety of different formulations to be prepared.

The main objective of this paper has been to try to show that it is not necessary to have an extremely elaborate and fully equipped laboratory to do useful work on formulations and formulation development. Even at its simplest level a laboratory can be used to help control incoming raw materials and to keep a check on the quality of day-to-day production. Both of these functions should help to lead to fewer lost batches and hence a better output rate.

Similarly for formulation development, often ideas for formulation types rise from day-to-day observations and as an example as a result of watching a cake being made in a food mixer, I used the same technique to produce my first granular product. I quote this to show that it is innovative ideas not just sophisticated equipment that is required to produce new formulations.

WATER DISPERSIBLE GRANULES

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The background of the Agrochemical Industry is a dynamic one and this dynamicism is reflected in the great deal of investigative work being carried out on new types of formulation. Some of these changes are made for technical reasons, some for economic reasons and some for publicity. However, whatever the reason they are all of technical importance since they advance our basic knowledge of agrochemical formulation.
One such change is the development of water dispersible granules. This is a particularly interesting development and one which may have great possibilities for the future. This paper sets out to indicate the properties that are required in these granules, the techniques that are used to make and test them, and gives an assessment of their future. Because the terminology has not been completely defined, the following have been adopted for the purposes of this paper.

1. Water dispersible granule (w.d.g.). A particle which when placed in water, breaks up and either dissolves or goes into a fine suspension or a combination of both.

2. Granules - Any particle in the range 0.5mm to 5mm.

3. Fine Suspension - This is a suspension which meets the agrochemical criteria for suspensibility as set out in such monography as CIPAC have and WHO hand-packs.

The principal properties required in these granules are:-

1. Ease and convenience of use.

2. Stability.

3. Homogeneity.

1. Ease and convenience of use

They must be easy to place in the spray tank and must not present a dust hazard to the operator. They must disperse readily in water without the necessity of any excessive stirring or agitation. The resultant suspension or solution must meet the normal standards for agrochemical formulations such as good suspension stability as determined by such tests as CIPAC MT15 for suspensibility using a limit of not less than 75% of active ingredient retained in suspension, and there must be no risk of filter or screen blockage (as determined by such tests as CIPAC mt53.3 followed by wet sieving through 60 mesh to determine the presence of large particles).

They must be easy to pack in a easily usable form. In other words the granules must be capable of being filled via conventional Auger fillers without the risk of breakdown of granules, and the final packaging must be such that it is easy to open by the operator and easy to empty into the spray tank.

2. Stability

The granules must be stable, both physically and chemically. Chemical stability is an obvious requirement but physical stability is also required. The requirements are slightly different from normal in that such phenomena as efflorescence, hygroscopicity and friability become of greater significance in these products than in other formulation types.

3. Homogeneity

The granules must be homogeneous both in themselves and in the bulk. The latter is particularly important in cases where the product is measured volumetrically as any tendency to settling or to particle segregation can alter the volumetric dose measurement. This is important as one of the advantages of these granules is the simplicity of volumetric measurement. In addition the products also have to have the general properties of any agrochemical formulation such as biological efficacy, lack of phytotoxicity, compatibility in tank mixes, stability of spray solution etc. Faced with this formidable array of requirements it is fortunate that in the development of w.d.g's there are a variety of preparative techniques and there is quite a wide range of procedures from which the formulator can choose for his route and composition.

4. As usual there is still a problem for the formulator in that the capital cost of granule plant is very high and so generally it is the plant which dictates the type of formulation.

The techniques available for making w.d.g's

There are a wide variety of techniques which can and have been used and for convenience I have divided these into two.

1) wet routes
2) dry routes.

In the wet routes the procedure uses either a solution or a slurry or suspension and converts this directly to the granules. In the dry routes the starting materials are mostly dry powders, and a liquid is added to effect the granulation.

1. Wet Routes : drum drying
spray drying
fluid bed drying
others.

2. Dry Routes : pan granulation
extrusion
fluid bed
pelletisation
Schugi.

Wet Routes

1. Drum drying - A solution or suspension of the active ingredients is applied to a heated drum usually by means of a transfer roller and the dry product scraped off the other side. The dried product is then scraped off the roller (when it usually has the appearance of flakes) and screened if necessary to give the required particle range. Undersize and oversize is milled and reprocessed. This technique is relatively crude and can only be used with materials which are heat stable. By its very nature relatively high temperatures are necessary to dry the liquid film before it reaches the scraper if the drum radius is not to be too great, and the drum must pick up a reasonably thick layer of liquid or the dried flake will be very dusty and the yield of useful granules per cycle will be low.

   Normally the overall yield is high (of the order of 80%) and provided that the product is thermally stable, the fines can be submitted to several cycles.

2. Spray drying - This is a well known and well tried technique for the preparation of granules and is used for a wide range of good products such as soluble coffee, milk etc. The technique involves spraying a solution or suspension into a conical cylinder in which hot air is being circulated. The spray droplets dry out and collect in the bottom of the cone and are removed. The type of granules obtained depends on the size of the spray droplets produced, which is dependant on the type of spray nozzle used, the liquid and the spray pressure.

   However, these properties can be controlled and this technique yields good quality granules and fairly high yields. The final reworking is essentially the same as for drum drying and both over and undersize can be reprocessed.

   Both solutions and suspensions can be handled provided that they can be sprayed, and this latter property is usually a limiting factor in selecting this technique.

3. Fluid bed drying - This technique can be used as a wet route granulator. The procedure relies on the spray producing both fine powder particles and agglomerating these particles. This is a difficult procedure to control and relies on the use of a fluid bed adjusted to remove the correct size and oversize particle, and to retain the smaller ones to be further agglomerated. The same problems of sprayability apply here as in the case of spray drying.

4. Others - A range of techniques for wet route granulation have been described in the literature. They often include some form of chemical reaction which yields a granule containing the active ingredient either loosely bound chemicaly or entrapped mechanically in the granule. The procedures which often are complicated and, in some instances, involve chemical reaction, are only mentioned for completeness.

Dry Routes

1. Pan Granulation - This is a well known technique and is currently used for many agrochemical w.d.g's. In broad outline a finely divided powder is placed in an inclined pan and, whilst the pan is rotated, liquid is sprayed onto the powder in such a quantity that the powder 'balls up' and produces granules. The granules are then dried in a fluid bed drier and screened, and the over and undersize reworked as before. Generally the powders are finely ground and the liquid addition is usually in the range 5-15% w/w.

   The quality of the granule is controlled by the speed of rotation of the pan and its angle of inclination, the precise amount of water sprayed in, the reaction time, etc.

   This technique has been extended to make it a continuous process, relying on the fact that the larger particles migrate to the top of the powder bed and then 'overflow' and the bed replenished with further powder. Other pan type techniques uses rotating cutters in the pan to break down any aggregates which form, are available such as the Eirich granulator.

2. Extrusion - This is also a well known technique for granulation. In this case the active ingredients with a small amount of water are forced through a screen perforated with small holes. The resultant cylindrical rods are dried and screened, the reject material is sent back for reworking.

   There are a wide variety of extrusion granulators ranging from simple paddles or rotors which push the powder through a screen to the more sophisticated single and twin screw extruders. The paddle type generally give soft uncompacted granules, whereas the screw extruders can submit the powders to quite high pressures and lead to well compacted granules.

   This technique seems to have been most commonly used for granules which are totally or mainly water soluble. A wide range of additives can be used and by the use of lubricants and varying the extrusion conditions, changes in hardness can be produced. Like most of the 'dry route' techniques the granules have to be dried and screened, but as this technique uses very little water, drying is not difficult.

3. Powder compression - In this procedure a blend of the dry ingredients is compressed to form a thin sheet, and this sheet is then broken up into granules and screened. Very little liquid is necessary and virtually no post drying is required. However, the technique is very specialised and requires considerable 'know-how' in order to obtain suitable granules, and its commercial use is limited.

4. Fluid bed - The normal fluid bed technique is used in which the bed is charged with the powder, fluidised and liquid is sprayed on. The technique has been developed from its original batch type process into a continuous one, so that powder can be fed to the fluid bed continuously, and dry granules discharged.

This procedure is very versatile and can be used for both soluble and insoluble products. The spray patterns can affect the type of granule produced but only in a very general way. Various additives can be used either added to the spray solution or the solid, and by suitable choice of components, high yields can be achieved.

5. Others - There are a number of other techniques which have been developed for granulation such as the inclined cylinder as is used in making fertilizers, the Lodige mixers which are based on food mixing, and large scale graters such as have been used for peeling vegetables. The most common of these is the rotating cylinder which is widely used for fertilizers. The others are very much less common and are generally used because circumstances make it expedient to do so.

a) One particular type of plant which has been developed in Holland, the Schugi, is of great interest in granule manufacture. In this plant the powder and aqueous phase are injected simultaneously into a cylinder in which high speed cutters are rotating. The mixture is then discharged to a fluid bed drier. In this instance it seems the powder is coated onto the liquid in the Schugi and the granulation actually occurs in the fluid bed. In practice the powders are in the Schugi cylinder only for a matter of seconds and therefore the relationship between the Schugi unit and the fluid bed drier is very important.

Process Comparison

How do all these processes compare? Well this is quite a difficult problem to answer. There are some basic differences which can be pinpointed but in the final analysis, choice will depend on the type of product required and the plant which is available.

Granule hardness - Decrease in hardness is generally of the order of:-
Extrusion, pan granulation, spray drying, fluid bed, Schugi.
Rate of solution - Decreasing rate of solution in the order of:-
Schugi, fluid bed, spray drying, pan granulation, extrusion.
Friability and abrasion resistance - same as for rate of solution.
Pourability - Only marginal differences but the less regular granules pour slightly less easily than the others.
Pan granulation, extrusion (after marumerisation), others.
Uniformity of granule size - Decrease in order.
Extrusion, the rest.

These are obviously only broad generalizations and it is difficult to distinguish between fluid bed, Schugi and spray dried granules. However there are some clear distinctions between these and extrusion and pan granulation, mainly with respect to ease and rate of solution.

Formulations

Choice of components can make a big difference to the properties of these ganules and this is where the skill and knowhow of the formulator becomes important. Extrusion aids can be used to reduce compaction in extrusion granulation. Additives can be included in any of the granules to aid breakup when they get wet. Other compounds can be added which will cause the granule to become harder, and so on. These are part of the formulators armoury. The main problem with additives, especially those that change their physical form when they dry out, is that rework during processing may not be possible. It is most likely that at least 20% and may be as much as 50% rework will be necessary. Therefore if an important formulation component is added in the aqueous phase, where there is a high level of rework, the composition of the formulation will be continually changing. If any sort of chemical reaction takes place, then of course rework may be impossible.

Testing Granules

1. The standard chemical tests for the active ingredients.

2. Tests designed to assess the physical properties of these formulations. In general the tests required are those which indicate the level to which the desirable properties of the granule have been achieved. Thus the properties tested should include:-

    1. Dust.
    2. Friability.
    3. Pourability.
    4. Bulk density.
    5. Dispersion characteristics.

Dust, pourability and bulk density can be determined by the standard type of methods, e.g. dust by sieving, pourability by the Cipac, 'flowability of powders' test using a suitable size aperture in the funnel and the bulk density by the standard 'tap' method.

In general these tests all work well and are easily adaptable to w.d.g's. However, friability and compaction characteristics are much harder to measure. The final assessment is usually made by measuring the increase in material passing a certain mesh size which is not difficult. The main problem lies in the method used to treat the granules in order to assess their friability.

A wide variety of techniques have been tried:

i) Vibrating in a sieve for a given period of time either on the bare sieve or on one on which brushes or ball bearings, or other means of encouraging breakdown are used.

ii) Rolling in a drum or cylinder, possibly containing light beads or stars.

iii) Shaking in a vessel either by rotation or by turning it end on end.

iv) Stirring with some sort of fingers, either metal, rubber or some other material.

Various techniques of this type have been examined and some useful results have been achieved, but only when comparing like with like. When different types of granule are involved, e.g. smooth round compared with very angular particles, the correlation is not so good, and perhaps even misleading.

This is not an easy area to decide on a test and a screen vibration test is the most useful since the granules will inevitably have to be screened at some stage in the manufacturing process, they should not be so friable that they break up under this treatment.

4. Compaction - One important criteria to test for is compaction or aggregation of the granules on bulk storage. This effect is often connected with residual moisture in the granules and a test to determine the likelihood of this phenomena occurring is very important. Such a test enables an assessment to be made of the level of residual moisture which can be tolerated in the granules. There are strong economic reasons for not trying to completely dry the granules; the lower the moisture level the more expensive it becomes to try to remove the last traces. Obviously the limits have to be selected after assessment of the properties of the granules, and it may be possible to leave more residual moisture in some granules than in others.

5. Dispersion - dispersion characteristics are perhaps the most important aspect of these granules. This is what the user really notices. Do the granules wet readily, do they disperse quickly and without undue agitation and, when dispersed, do they remain so until used.

   To take the last first, the suspension characteristics of the prepared spray solution can be determined by the standard methods as used for any other type of agrochemical formulation.

   Similarly, for the wettability of the granules, the classical tests work very well and no greater degree of sophistication is necessary.

   The big problem lies in assessing the ease of breakdown of the granules in water and the rate of dispersion in the water. In this respect w.d.g's are more like wettable powders than either E.C's or flowables, but unlike wettable powders the granules also have to break up themselves as well as being evenly dispersed.

   Some typical tests are:-

   a) Place the proposed field use rate of granules in a cylinder containing the required volume of water, and cound the inversions until complete dispersion.

   b) The granules are placed in water and allowed to stand for about 1 minute and then poured into a funnel with a small diameter mesh at the outlet. The time for the suspension to pass through the mesh is noted and the residue on the mesh examined.

c) The material is placed in a simulated spray tank with stirrer and sprayed out through a standard jet. The filters are then checked for residue.

All these tests are useful in that they provide some information on the behaviour of granules but, in the end, a full scale field tank test is the only safe way of being certain

The most useful test is to use the simple cylinder test a). The agitation is very low if the cylinder is simply inverted at a constant rate, and the behaviour of the granules can be followed visually. In the final analysis the results have to be confirmed in field trials but if the granules disperse readily and completely in this test, then there is a high probability that the product will work properly in the field.

The use of these granules in the Agrochemical industry is still only really in its infancy and the special requirements of this industry make the granulation more difficult.The granulation of soluble products is relatively simple but the the problems become more acute when solid pesticides or mixtures of pesticides are used. Nevertheless, the industry has gone a long way to achieving its objectives and in a relatively short time has made great strides foreward in a technology that seems certain to play an important part in future Agrochemical formulations.

APPENDIX III

Regional Workshop on

Pesticide Formulation Technology

27 March - 15 April 1989

SCHEDULE

MONDAY, MARCH 27

14.00 Registration

Introduction to Workshop

Visit to PDPI Laboratories

15.30 Inaugural Session

Welcome - Dr. B. Sugavanam, UNIDO

Address - Dr. S.S. Khanna
Advisor (Agriculture)
Planning Commission

Inaugural
Address - Shri M.S. Gill,
Secretary
Chemicals & Petro-chemicals

Vote of Thanks - Dr. S.P. Dhua

16.15 Laying of Foundation Stone for the International Trainees' Hostel

Laying of Foundation Stone

Shri M.S. Gill,
Secretary
Chemicals & Petro-chemicals

At Home

TUESDAY, MARCH 28

Key Note Session

Chairman Dr. S. P. Dhua

10.00 Workshop Outline

10.30 - 11.30 Chemistry of Pesticides
Dr. B. Sugavanam

11.45 - 12.45 Pesticide Formulation Technology
Dr. S.K. Khetan

14.00 - 15.30 Visit to PDPI Laboratories

WEDNESDAY, MARCH 29

Technical Session I

Chairman Dr. B. Sugavanam

10.00 - 11.15 Country Papers

11.30 - 12.45 Synthetic Silicas for Pesticide Formulations
Mr. Rolf Oelmuller

14.00 - 17.00 Experimental Demonstration: Evaluation of Carriers and Diluents

THURSDAY, MARCH 30

Technical Session II

Chairman Dr. G. Nath

10.00 - 10.45 Selection of Mineral Clays for Pesticide Formulations
Dr. R.K. Khandal

11.00 - 12.00 Role of Surfactants in Pesticide Formulations
Dr. V.K. Belavedi

12.00 - 12.45 Size Reduction and Blending Techniques in Pesticide Formulations
Mr. S. Kumar

14.00 - 17.00 Experimental Demonstration: Development of WP Formulations

FRIDAY, MARCH 31

Technical Session III

Chairman Dr. S. K. Khetan

10.00 - 11.00 Dust & Wettable Powder Formulations-Development and Manufacture
Dr. R.K. Khandal

11.15 - 12.45 Emulsifiable Concentrates - Development and Manufacture
Dr. P.K. Ramdas

14.00 - 17.00 Experimental Demonstration: Evaluation of Emulsifiers

SATURDAY, APRIL 1

14.00 hrs Visit to Indian Agricultural Fair / Indian Tourism Fair

MONDAY, APRIL 3

Technical Session IV

Chairman Mr. W.J. Osmer

10.00 - 11.15 Packaging of Liquid Pesticide Formulations
Mr. W.J. Osmer

11.30 - 12.30 Country Papers

14.00 - 17.00 Experimental Demonstration: Granular Formulations

TUESDAY, APRIL 4

Technical Session V

Chairman Dr. A.R. Woodford

10.00 - 11.00 Granular and WDG Formulations
Dr. A.R. Woodford

11.15 - 12.45 Suspension & Emulsion Concentrates
Dr. P.K. Rasdas

14.00 - 17.00 Experimental Demonstrations: SC Formulations

WEDNESDAY, APRIL 5

Technical Session VI

Chairman Dr. B.N. Singh

10.00 - 11.00 Controlled Release Formulations
Dr. A.R. Woodford

11.15 - 12.00 Process of Standard Making - Indian Experience
Mr. A.K. Sen

12.00 - 13.00 Specifications for Pesticide Formulations
Dr. A.R. Woodford

14.00 - 17.00 Experimental Demonstrations: Water Dispersible Granules & EW Formulations

THURSDAY, APRIL 6

Technical Session VII

Chairman Dr. S.K. Mukherjee

10.00 - 11.15 Resistance, Synergism and Pesticide Combination Formulations
Dr. S.K. Khetan

11.30 - 12.30 Packaging of Pesticide Formulations
Dr. W.J. Osmer

14.00 - 15.15 Safety and Hygiene in Pesticide Formulation Manufacture
Mr. V.N. Dutta

FRIDAY, APRIL 7

Technical Session VIII

Chairman Dr. A.R. Woodford

10.00 - 11.00 Specifications of Pesticide Formulations
Dr. A.R. Woodford

11.15 - 12.15 Registration Requirements for Pesticide Formulations
Er. V.C. Bhargava

12.15 - 13.00 Quality Assurance of Pesticide Formulations
Dr. R.C. Gupta

14.00 - 17.00 Experimental Demonstrations: Chemical Methods of Analysis

MONDAY, APRIL 10

Technical Session IX

Chairman Dr. V.P. Sharma

10.00 - 11.00 Shelf-life of Pesticide Formulation
Dr. S.K. Khetan

11.15 - 12.15 Chemical Analysis of Pesticide Formulations
Dr. A.G. Bajaj

12.15 - 13.00 Spectroscopic Methods of Analysis
Dr. P. K. Randas

14.00 - 17.00 Experimental Demonstrations:
Spectroscopic Methods

TUESDAY, APRIL 11

Technical Session X

Chairman Dr. B.S. Parmar

10.00 - 11.00 HPLC - Application in Pesticide Analysis
Dr. S.Y. Pandey

11.15 - 12.15 GC- Applications in Pesticide Analysis
Dr. Anil Nimkar

12.15 - 13.00 Country Papers

14.00 - 17.00 Experimental Demonstrations:
GC & HPLC Analysis

WEDNESDAY, APRIL 12

Technical Session XI

Chairman Dr. B.P. Shrivastava

10.30 - 11.30 Bio-assay and Field Trials of Pesticide Formulations
Dr. N.R. Bhateshwar

11.45 - 12.45 Pesticide Application Technology
Dr. Y.P. Ramdev

14.00 - 17.00 Experimental Demonstrations:
Bioassay & Field Trials

THURSDAY, APRIL 13

Penultimate Session

Chairman Mr. Shyam Suri

10.00 - 11.00 Setting up of a Formulation Laboratory
Dr. A.R. Woodford

11.15 - 12.45 Evaluation of the Course and Feed Back from the participants

14.00 - 17.00 Recommendations

FRIDAY, APRIL 14

Concluding Session

10.30 Welcome
Dr. S.P. Dhua

10.45 Address
Ms. J. Haslett
Asstt. Res. Rep. UNDP

10.55 Remarks
Participant Group

11.00 Distribution of Certificates

11.05 Validictory Address
Sh. Ramaswamy R. Aiyer
Member, PSEB

11.20 Vote of Thanks