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SPECIFICATIONS FOR PESTICIDES USED
IN PUBLIC HEALTH
FIFTEENTH REPORT
OF THE WHO EXPERT COMMITTEE ON INSECTICIDES

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WHO EXPERT COMMITTEE ON INSECTICIDES

Geneva, 19-25 October 1965

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SPECIFICATIONS FOR PESTICIDES USED
IN PUBLIC HEALTH

FIFTEENTH REPORT
OF THE WHO EXPERT COMMITTEE ON INSECTICIDES

The WHO Expert Committee on Insecticides met in Geneva, Switzerland, from 19 to 25 October 1965 to review specifications and analytical methods for pesticides used in various public health programmes. The meeting was opened by Dr P. Dorolle, Deputy Director-General, on behalf of the Director-General.

Dr G. W. Pearce was elected Chairman, M. Inspecteur général J. Prat Vice-Chairman, and Dr J. Treboux Rapporteur.

1. INTRODUCTION

During the seven years that have elapsed since the Expert Committee on Insecticides last considered the chemistry and specifications of pesticides, the use of DDT powders in malaria eradication programmes has grown enormously and the expansion and diversification of other vector control programmes using other insecticides has been equally great.

The WHO manual Specifications for Pesticides was revised on the basis of the recommendations of the Expert Committee on Insecticides, the second edition being published in 1961. The growth in the use of pesticides has been reflected in the manual, so much so that when a second impression was issued in 1962 corrections had to be made. The wide use of the manual is largely because practically all pesticides used for international, as well as some national, vector control programmes are based on the specifications laid down in it. It was in the light of this situation that the Committee made its recommendations for changes, additions and deletions in the specifications for the next edition of the manual.

The Committee had before it a large number of working papers which provided data on collaborative experiments as well as draft specifications for new materials. This documentation was the basis upon which the Committee considered the various problems and made its recommendations. In the report which follows, details of specifications which the Committee recommended for adoption by WHO have not been given. However, the recommendations are given in sufficient detail so that consistent and correct specifications may be drafted for inclusion in the new edition of the manual. In many cases, the working papers that were in the form of draft specifications will be the basis for the new specification. The Committee agreed that for specifications for materials which are of equal interest in agriculture, such as herbicides, the analytical methods and the requirements should be based on the corresponding specifications approved by the FAO and the Collaborative Pesticide Analytical Committee of Europe.

Probably the most important problem considered was the suspensibility properties of DDT water-dispersible powders. The loss of suspensibility after shipment to the field and the probable causes for this were discussed at length. Recommendations are given which should prevent recurrence of this problem.

The Committee's recommendations are intended to serve as a guide in the preparation of the new edition and deal only with new or revised specifications with the appropriate analytical methods. Specifications not revised will remain in effect.

2. ADDITIONS AND DELETIONS

The Committee noted that there has been a continual increase in the number of pesticides being used in the various public health programmes of interest to WHO. At the same time, some pesticides for which specifications were given in the second edition of Specifications for Pesticides are no longer used on a large scale.

After reviewing these developments, the Committee recommended that certain specifications be deleted from the new edition of the manual. It stressed, however, that these specifications are still useful; consequently the second edition will not be superseded by the third edition in respect of these materials.

Part I. Insecticides

Specifications for the following materials should be deleted from the new edition: methoxychlor technical, water-dispersible powders and emulsion concentrates; chlordane technical, water-dispersible powders, and emulsion concentrates; allethrin technical; chlorthion technical, water-dispersible powder and emulsion concentrate; diazinon dusting powder; larvicide granules.

With respect to larvicide granules, the Committee agreed that not enough data are available to draft useful specifications for granular formulations. However, because of the growing importance of larvicides in vector control programmes, WHO should undertake a programme to develop improved granular formulations. This subject is treated at greater length in section 7.

Part II. Rodenticides

The following materials should be deleted from the new edition: ANTU, technical; arsenious oxide, technical; red squill powder; sodium monofluoroacetate; zinc phosphide, technical; fumarin, technical, sodium salt, concentrate, water-soluble powder.

Part III. Molluscicides

The following materials should be deleted from the new edition: copper sulfate; pentachlorophenol, technical.

Part IV. Herbicides

The Committee reviewed the specifications for herbicides and the draft specifications being considered for the corresponding materials by the Food and Agriculture Organization (FAO), and agreed that it would be desirable that the requirements for herbicides established by FAO, should be recommended for adoption. However, since these FAO specifications have not yet been published, no changes should be made in the existing herbicide specifications, but they should be deleted from the new edition.

Part V. Auxiliary Chemicals

None of the materials in the section on auxiliary chemicals should be included in the new edition.

Part VI. Spraying and Dusting Apparatus

Specifications for spraying and dusting apparatus are given in the recent WHO publication Equipment for Vector Control, 1964 and will not be reprinted in the new edition.

Annexes

The Committee reviewed the method of determining bulk density as well as the bulk density requirements for several specifications. In the course of discussions it became evident that bulk density measurement is not really significant since the supplier can provide a product of almost any bulk density by aeration or compaction; moreover, the bulk density will change depending on the amount of vibration the powder is subjected to during shipment. In view of these facts, the Committee recommended deletion of the bulk density requirements for all dusting powders and deletion of the method for determination described in Annex 13 of the second edition of the manual.

It recommended that the polarographic method of determination of gamma-isomer content given in Annex 19 should be deleted, since this method is not used for the BHC specifications recommended for the new edition.

Several specifications for new pesticides recommended by previous expert committees on insecticides which were concerned with vector control programmes were reviewed by the Committee and recommended for adoption. These materials are - parathion-methyl; fenthion; dichlorvos; Bayluscide; triphenylmethylmorpholine and Deet. These are given in section 4.1. At the same time, the Committee considered specifications for very recently developed pesticides which have not yet been recommended for general vector control use in the field of public health. Specifications for this group of compounds should be developed by the Secretariat and members of the Expert Panel. These materials are given in section 4.2.

The Committee also recommended that consideration be given to providing an index and an alphabetical list of new proprietary names and synonyms for pesticides included in the new edition.

WHO specifications have been frequently used to purchase materials for agricultural purposes, even though the specifications are based on the requirements and properties necessary for pesticides used in public health programmes. The Committee strongly recommended the inclusion in the new edition of a statement making it clear that the specifications are essentially intended for public health purposes. The title of the new edition should accordingly read: "Specifications for Pesticides used in Public Health".

3. CHANGES IN SPECIFICATIONS

3.1.1. Technical DDT (WHO/STP/1.100)

The Committee reviewed the method of taking the setting point of technical DDT and recommended that the boiling-tube dimensions be more clearly defined, that the maximum bath temperature be 100°C, that a stainless steel rod 1.5 mm in diameter with a 6-turn spiral of 1.6 cm diameter be used for stirring, and that the bath temperature for cooling be 5-8°C lower than the anticipated setting point.

3.1.2 DDT water-dispersible powders (WHO/SIF/1.R2)

This was clearly the most important item brought before the Committee. There is ample evidence that the progress of malaria eradication programmes throughout the world is being adversely affected by the continual arrival at the point of use in the field of significant quantities of DDT water-dispersible powders with unsatisfactory suspensibility. The Committee recognized that the present WHO specification for DDT water-dispersible powders would have to be strengthened in order to correct or alleviate this field difficulty.

Evidence was presented to the Committee which indicated that there are at least two major factors involved in the deterioration in suspensibility of these powders during shipment and storage in tropical climates. One, the tendency of the powder particles to agglomerate and the other, a loss in activity of the surfactants. Published data were presented which indicated that incorporation of a more severe accelerated storage test was an effective way to correct the agglomeration problem. The Committee recommended that this method be adopted to solve this problem. However, there are no data available which would permit the Committee to devise a specification requirement which would prevent suppliers from offering products with a latent defect which results in unsatisfactory suspensibility in the field. It was noted by the Committee that the vast majority of DDT powders used in malaria eradication programmes over many years did not have this defect in surfactants and it was within the capabilities of suppliers to correct this fault so that resort to a warranty clause in the specification covering latent defects was a feasible solution to the problem until further research can provide a test for use in the specification. The Committee recommends that this approach be used.

Although the Committee agreed in principle to the use of more severe accelerated storage requirements, considerable discussion revolved around the methodology involved, especially the method of determining suspensibility. FAO and CPAC have initiated research to develop specifications and methods of analysis for pesticides and WHO has agreed that wherever feasible the three organizations should have the same specifications and methodology. As the discussion proceeded, it became evident that physical properties of water-dispersible powders required by FAO and WHO could differ so that where necessary

FAO and WHO must use methods of analysis and specification requirements that fit their field needs. This applies particularly to the suspensibility determination which is one of the most important properties of water-dispersible powders used in malaria eradication programmes. Since there would be technical difficulties in incorporating a more severe accelerated storage test in the present WHO specification and there were no data available on which to base minimum requirements after such treatment, the Committee was guided by the specification developed by the United States Agency for International Development (AID). This specification is based on extensive research over many years and therefore is backed by the type of data and field experience which the Committee would have to have if they attempted to incorporate an accelerated storage test and establish suspensibility requirements meeting field needs using the current WHO methods of determining suspensibility. AID adopted the suspensibility method given in the WHO specification for DDT water-dispersible powders approved in 1951 (WHO/SIFORM/1), but when this was changed in 1954 (WHO/SIF/1.R1) to the present procedure it was not feasible for AID to change because of the same lack of data relating the change in methods to field needs. In addition to the difference in method of determining suspensibility, the AID specification also includes a suspensibility test in distilled water. The Committee agreed that this was a desirable requirement which should also be used in the WHO specification. The AID specification includes a wettability test, but the Committee felt that this serves no real purpose and should not be included in the WHO specification.

In summary, the Committee recommended that the following requirements be incorporated in a new specification for DDT water-dispersible powders:

- (1) an accelerated storage treatment of $70^{\circ} \pm 0.1^{\circ}\text{C}$ for two hours;
- (2) the suspensibility test method used in the AID specification for DDT powders;
- (3) the suspensibility to be determined in distilled water before and in hard water after the accelerated storage treatment;
- (4) the suspensibility to be a minimum of 70% in distilled water before and 65% in standard hard water after accelerated storage treatment;

(5) a warrant, and suitable sampling procedure be included which will guarantee a shelf life of one year for batch samples. It is recommended that the suspensibility of the powders be a minimum of 50% after storage for one year at ambient temperatures within the limits of approximately 21°C to 30°C.

The Committee recommends that a new specification based on the above requirements be adopted and designated as DDT water-dispersible powders for overseas shipment. However, for domestic and local use in the country of origin the present specification (WHO/SIF/1.R2) is recommended for use with the modification that the requirement for suspensibility be changed to a minimum 60% in distilled water before and 60% in standard hard water after "tropical storage" treatment. It is suggested that this modified specification be made available in one of the WHO series of publications.

3.1.3 DDT Dusting Powders (WHO/SIF/16.R1)

The tolerances allowed for variation from the nominal content for low active ingredient dusting powders were reviewed for the three dusting powders for which specifications are in effect. It was agreed that improvement is needed to define these tolerances better since they depend to a certain extent on the method of analysis and the stability of the formulation. No agreement was reached on a way to handle this problem. The Committee recommended that the tolerances be defined for each specification; the tolerance for DDT dusting powders is recommended to be changed from $\pm 5\%$ to $\pm 10\%$.

3.2.1 Technical and refined HCH (WHO/SIT/2.R2)

The Committee reviewed the specification and recommended that the nitric acid clean-up step, in the preparation of the sample for analysis, be deleted in view of the generally improved manufacture of this material. However, the deleted part should be entered as a footnote so that this step could be used when oily ingredients are present.

The Committee reviewed the acidity requirement and recommended that the value expressed as β w calculated as HCl be changed to a value expressed as % w calculated as H_2SO_4 . The present figure of 0.1% will thus be changed to 0.15% w.

3.2.2 Gamma-Isomer HCH (WHO/SIT/3.R2)

The Committee recommended that the same change as recommended for expression of the acidity value of technical and refined HCH (item 3.2.1) should be made for this material. The present value of 0.1% w will thus be 0.15% w.

3.2.3 HCH water-dispersible powders (WHO/SIF/2.R2)

The Committee recommended that the suspensibility of HCH water-dispersible powders should be determined before accelerated storage in distilled water and after accelerated storage in standard hard water in order to prevent use of surfactants which fail to perform satisfactorily in both hard and soft water.

The Committee reviewed the conditions of performing the suspensibility test and recommended that no changes are necessary and that the test concentration for gamma-isomer should remain at 0.5% w/v, that the 250-ml cylinder be used, and that the bottom 25 ml be analysed.

The Committee also recommended that a note be inserted in the method for the analysis of the gamma-isomer indicating that an aliquot of the extract must be taken so that the weight of gamma-isomer to be applied to the chromatographic column lies between 60 and 80 mg. This is especially important when heavy sediments are noted.

3.2.4 HCH Dusting Powders (WHO/SIF/17.R1)

The Committee noted in the analysis of this formulation for the gamma-isomer content that insufficient solvent was allowed for the extraction process and recommended that this part of the specification be changed so that an appropriate weight of the formulation be subjected to Soxhlet extraction.

The tolerance for HCH dusting powders was reviewed (see item 3.1.3) and it was recommended that the present value of $\pm 5\%$ be changed to $\pm 10\%$.

3.3.1 Technical dieldrin (WHO/SIF/6.R2)

The Committee reviewed the results of a collaborative experiment made to test the accuracy and reproducibility of the analytical method for dieldrin now given in the specifications for technical dieldrin, water-dispersible powder and emulsion concentrate formulations. It was noted that the results showed excellent agreement and that the experimental trial was thus quite successful. The Committee recommended that small changes which were used in the experiment be incorporated in the method, such as that the agreement of values from the three-band technique should agree to within 5-10% and only those differing by greater than 10% be rejected, and that the standard solutions and the sample size should be altered slightly.

The Committee noted that maximum allowable acidity for technical dieldrin is expressed as % w acetic acid and recommended that this be changed to read as % w calculated as sulfuric acid.

3.3.2 Dieldrin water-dispersible powders (WHO/SIF/3.R2)

Collaborative research on the stability and suspensibility of dieldrin water-dispersible powders was reviewed. The Committee recommended that the requirements and accelerated storage conditions for this material be changed as follows:

- (i) the suspensibility of the powder in distilled water be not less than 80%, and
- (ii) the suspensibility of the powder in standard hard water be not less than 60% after being subjected to accelerated storage at $90^{\circ} \pm 0.1^{\circ}\text{C}$ for two hours.

The improved analytical method which was recommended for technical dieldrin (item 3.3.1) was also recommended for analysis of dieldrin powders.

3.3.3 Dieldrin emulsion concentrates (WHO/SIF/6.R2)

The improved analytical method recommended for technical dieldrin (item 3.3.1) was recommended for the analysis of dieldrin emulsion concentrates. A proposed method for clean up of the sample before analysis was reviewed. This procedure incorporates passing the sample through a column with activated charcoal and

extracting with light petroleum (40-60°C) before the infra-red analysis is undertaken. This modification to the specification was recommended in order to remove the substances which interfere with this determination.

3.4 Pyrethrum extract (WHO/SIT/7)

The Committee reviewed the specification for pyrethrum extract and recommended that the Seil method be deleted and that the mercury reduction method be revised to take into account the latest findings of the Association of Official Agricultural Chemists and the United Kingdom Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry on the Methods of Assay of Crude Drugs.

The Committee also recommended that the formulae for cinerin I and II be included and slight changes in packaging requirements be made. In addition a footnote should be added to allow the fluorocarbon solubility requirement to be waived in those cases where the pyrethrum is to be used for other than aerosols.

3.5.1 Technical diazinon (WHO/SIT/9.R1)

The Committee reviewed the specification for technical diazinon and recommended that the acidity requirement be changed to 0.03% and that an improved procedure for clean up of the sample be used in the analytical method. This procedure utilizes a chromatographic column instead of separatory funnels and is based on experience gained during the past four years.

3.5.2 Diazinon water-dispersible powders (WHO/SIF/9.R1)

The Committee reviewed the specification for diazinon water-dispersible powder and recommended that the suspensibility test be performed on the material as received in distilled water and also after accelerated storage treatment in standard hard water. In both cases a minimum of 50% (0.5% w/v) of diazinon should be in suspension 30 minutes after agitating a suspension containing 1% of diazinon (w/v). The conditions for accelerated storage recommended are $70^{\circ} \pm 1^{\circ}\text{C}$ for two hours.

It was recommended that the analytical procedure be changed to conform to changes made for technical diazinon (see item 4.5.1).

3.5.3 Diazinon emulsion concentrates (WHO/SIF/13.R1)

It was recommended that the analytical procedure be changed to conform to changes made for technical diazinon (see item 3.5.1).

3.6.1 Technical malathion (WHO/SIT/10.R1)

The findings of several members of the Committee showed that the different analytical methods for malathion described in the chemical literature do not have any marked advantages over the colorimetric method now used. This method is based on the alkaline cleavage of malathion and the formation of a coloured complex of copper with O,O-dimethyl phosphorodithioic acid (DMDTPA). Furthermore, the colorimetric method can be used equally well for the technical product and for the formulations. Consequently, the Committee recommended that this method be retained but that improvements which have resulted from collaborative trials organized by the AOAC be incorporated.

In addition, the Committee agreed that, because errors in the precise malathion content may be caused by the presence of free DMDTPA in malathion of inferior quality, the step in the present method which determines free DMDTPA be retained and the method for the assay be modified to conform with the changes recommended above.

The Committee also recommended that minimum requirements for acidity be raised from 0.4% w to 0.5% w calculated as H_2SO_4 .

3.6.2 Malathion water-dispersible powders (WHO/SIF/10.R1)

The Committee reviewed the specification for malathion water-dispersible powders and recommended that the analytical method for the active ingredient be changed to conform to the new method for the technical product (see item 3.6.1).

The Committee further recommended that the following changes be made in the suspensibility requirement:

- (i) The suspensibility test should be made on a 2.5% w/v suspension in a 100-ml cylinder, taking the aliquot for analysis from the centre of the cylinder.

- (ii) The initial suspensibility test on the powder before the accelerated storage test should be performed in distilled water and a minimum of 60% should be in suspension after 30 minutes.
- (iii) The accelerated storage test for this material should be carried out at $90^{\circ} \pm 2^{\circ} \text{C}$ for 20 hours and the suspensibility test conducted in hard water. A minimum of 50% should be in suspension after 30 minutes.

The Committee recommended that the maximum acid content allowable should be raised to 0.5%.

3.6.3 Malathion emulsion concentrates (WHO/SIF/5.R2)

The Committee recommended that the method of analysis be altered to conform to the method recommended for technical malathion (item 3.6.1).

3.6.4 Malathion dusting powders (WHO/SIF/22)

The tolerance for malathion dusting powders (see item 3.1.1) was reviewed and it was recommended that the present $\pm 5\%$ be changed to -10% to $+25\%$. The larger tolerance for above than for below nominal content is to allow the manufacturer to formulate with an excess to compensate for the expected deterioration and thus to ensure delivery of dusts with the nominal content. The analytical method for malathion dusting powders should be modified to conform to the method recommended for technical malathion (3.6.1).

3.7.1 Technical parathion (WHO/SIT/11.R1)

The Committee recommended an increase from 1 to 3 g of the amount of zinc dust to be used for the reduction step in the analytical methods for technical parathion. However, if less than 3 g are used for the reduction of the nitro group, the zinc dust should be tested according to known techniques such as given in Farbenchimie by Fierz-David.

It was also recommended that the substances used for determining the f correction factor in the analysis of parathion be changed and limited to the following:

m-nitrobenzoic acid, m.p.	140.5-141.0°C
p-nitrobenzoic acid, m.p.	239.6-240.1°C

The advantage of these two compounds is that their purity can be easily checked by titration with normal alkali.

3.7.2 Parathion emulsion concentrates (WHO/SIF/15.R1)

The Committee recommended that the maximum acidity content should not be greater than 0.1% calculated as H_2SO_4 and that the analytical method should be changed as was recommended for technical parathion (4.7.1).

3.8.1 Trichlorfon emulsion concentrates (WHO/SIF/20)

The Committee recommended that the maximum acid content be changed to 1.0% w calculated as H_2SO_4 and that the reference to alkalinity be deleted.

It was noted that the determination of acidity in technical trichlorfon in the second edition of Specifications for Pesticides allowed for the alkali-sensitivity characteristic of the compound but that the method for the emulsion concentrate did not. The Committee recommended that this specification be changed to be in accord with that for the technical material.

4. NEW SPECIFICATIONS

The Committee reviewed several specifications for new compounds not now included in the second edition of Specifications for Pesticides. These were divided into two groups: materials for which sufficient information and collaborative analytical data are available so that specifications can be recommended for inclusion in the new edition of the manual, and materials for which insufficient data are available. As a result, the Committee recommended that the first group of specifications of new materials be accepted as tentative specifications for the new edition and the second group not be entered in the manual but developed by the WHO Secretariat as interim specifications in collaboration with members of the Expert Advisory Panel.

4.1 Tentative specifications

The following specifications were recommended for inclusion in the new edition of the WHO Manual Specifications for Pesticides as tentative specifications:

Technical parathion-methyl

Parathion-methyl emulsion concentrates

Technical fenthion

Fenthion emulsion concentrates
 Technical dichlorvos
 Technical 2',5-dichloro-4'-nitrosalicylanilide
 Technical triphenylmethylmorpholine
 Technical deet

4.1.1.1 Technical parathion-methyl

The Committee reviewed a proposed specification for technical parathion-methyl and recommended that the requirements for this material be as follows:

	<u>Minimum</u>	<u>Maximum</u>
O,O-dimethyl O-(4-nitrophenyl) phosphorothionate content, % by weight	80.0	85
Acidity, % by weight calculated as H ₂ SO ₄	-	0.2
Solid matter insoluble in acetone, % by weight	-	0.5
Water content, % by weight	-	0.3
Specific gravity at 25°C/25°C	1.24	1.26

Methods for determination of chemical and physical properties to be applied should be the same as those for technical parathion (WHO/SIT/11.R1). The modification for determining the f factor as recommended in 3.7.1 should be used unless WHO can arrange for pure samples of parathion-methyl to serve as the standard.

4.1.1.2 Parathion-methyl emulsion concentrates

The Committee reviewed a specification for parathion-methyl emulsion concentrates and recommended that the requirements for this material should be as follows:

The flash point of the concentrate shall not be less than 22.8°C.

The acidity of the concentrate shall not be greater than 0.1% calculated as H₂SO₄.

The cold test shall be carried out at 5°C.

The method of analysis shall be that described for technical parathion-methyl (4.1.1.1), with appropriate modifications.

4.1.2.1 Technical fenthion

The Committee reviewed a specification for technical fenthion and recommended that the requirements for this material be as follows:

	<u>Minimum</u>	<u>Maximum</u>
O,O-dimethyl O-(4-methylthio-m-tolyl) phosphorothionate, % by weight	90.0	-
Acidity, % by weight, as H ₂ SO ₄	-	0.3
Solid material insoluble in acetone	-	0.5
Water content, % by weight	-	0.5

The analytical method given in the proposed specification, which is based on hydrolysis of the compound to the supporting phenol and coupling with a diazonium compound to form a red/violet colour, was reviewed. Its inclusion was recommended.

4.1.2.2 Fenthion emulsion concentrates

The Committee reviewed a specification for fenthion emulsion concentrates and recommended that the requirements for this material should be: a flash point of not lower than 22.0°C, and a maximum acidity % by weight as H₂SO₄ of 0.3%.

The analytical method should be the same as used for technical fenthion (item 4.2.1).

4.1.3 Technical dichlorvos

The Committee reviewed a specification for technical dichlorvos and the results of a collaborative experiment which compared an infra-red and an iodometric method of analysis. The Committee recommended that both methods be used in the specification and that, in case of dispute, the infra-red method should prevail. The requirements for the material should be as follows:

	<u>Minimum</u>	<u>Maximum</u>
2,2-dichlorovinyl dimethyl phosphate, % by weight	93.0	-
Acidity, % by weight, calculated as H ₂ SO ₄	-	0.05
Solid material, insoluble in acetone, % by weight	-	0.5
Water content, % by weight	-	0.02

4.1.4 Molluscicides

The Committee noted with satisfaction that, because of increased research activity, new and more potent molluscicides have been developed in the past few years. Two new chemicals show considerable promise in bilharziasis control; the Committee therefore recommended that tentative specifications for their technical products be adopted. It was recognized that formulations of these products are still under investigation, therefore specifications for formulated products should be developed only on an interim basis.

4.1.4.1 Technical 2',5-dichloro-4'-nitrosalicylanilide

The Committee reviewed a specification for the technical ethanolamine salt of 2',5-dichloro-4'-nitrosalicylanilide, which is known by the trade name of Bayluscide, and recommended that the requirements be as follows:

- (i) the active ingredient of the product should be calculated as the ethanolamine salt of the 2',5-dichloro-4'-nitrosalicylanilide and the minimum content should be 94% w;
- (ii) the melting point of ethanolamine salt should be 191°C;
- (iii) the water content should be determined by the Dean-Stark method and be a minimum of 1.0% w.

The analytical method of analysis provided by the manufacturer was recommended for adoption.

4.1.4.2 Technical triphenylmethylmorpholine

The Committee reviewed the specification proposed for technical triphenylmethylmorpholine and recommended that the requirements be as follows:

	<u>Minimum</u>	<u>Maximum</u>
Triphenylmethylmorpholine, % by weight (dry basis)	90	-
Acidity, % by weight calculated as H ₂ SO ₄	-	0.1
Water content, % by weight (by Karl Fischer Method)	-	0.1
Tar impurities, % by weight (dry weight)	-	2.0
Volatile matter, % by weight	-	10.0

It was further recommended that:

- (i) the determination of acidity should be in accordance with the recommendation of the Committee on this subject as given in 5.2 and that;
- (ii) for the titrimetric determination of the active ingredient an indicator be used, but a note should be added so that alternatively the end point may be determined electrometrically.

The Committee recommended the Karl Fischer method for the determination of water in this product in view of the probability of impurities in the technical material.

4.1.5 Technical deet

A proposed specification was reviewed for the insect repellent N,N-diethyl-m-toluamide which is known as "deet". In view of the fact that this repellent is widely used, the Committee recommended that this be adopted as a tentative specification. The Committee noted that minimum requirements for meta-isomer and the maximum and minimum requirements for acidity, water content, specific gravity, refractive index and colour which were provided by a manufacturer and accepted by the USDA are acceptable for this product. The analytical method which is based on an infra-red determination and utilizes a standard reference sample was recommended.

Although formulations of this material as an alcohol solution had been proposed, the Committee considered that only a specification for technical material is necessary to guide the purchase of this compound.

4.2 Interim Specifications

The following specifications for new compounds were reviewed by the Committee. However, since only limited data were available to the Committee, recommendations could not be made for adoption of these materials. The Committee therefore recommended that these specifications be developed by the WHO Secretariat in collaboration with members of the Expert Advisory Panel, so that more collaborative experimental results may be obtained. The materials considered for this category

are: trichlorfon water-soluble powder, dichlorvos emulsion concentrate, fenitrothion¹ (technical, water-dispersible powder and emulsion concentrate), BAYGON² (technical and water-dispersible powder), bromophos³ (technical, water-dispersible powder and emulsion concentrate). It was suggested that collaborative experimental work be started on these at an early date.

4.2.1 Trichlorfon water-soluble powders

The Committee reviewed a specification for an 80% trichlorfon water-soluble formulation based on the recommendation of the manufacturer. Although the analytical method is essentially the same as that for technical trichlorfon (WHO/SIT/13), insufficient information is available on the acidity and accelerated storage tests. The Committee suggested that this type of information be obtained to support the interim specification.

4.2.2 Dichlorvos emulsion concentrates

The Committee considered the available information on dichlorvos emulsion concentrate formulation and its analysis and recommended that only an interim specification be made for this material. This interim specification should use the same analytical procedures as recommended for technical dichlorvos (item 4.1.3). The Committee suggested that further data be obtained to develop clean-up procedures for samples especially when the infra-red method is used.

4.2.3 Fenitrothion

4.2.4 BAYGON

4.2.5 Bromophos

The Committee reviewed the proposed specifications and the formulation problems of fenitrothion and agreed that WHO be requested to continue to develop interim specifications. It recommended that in the absence of full research data the WHO suspensibility test of water-dispersible powder in distilled water before accelerated

¹ Common name now being considered by the ISO for O,O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate.

² Trade name used by Farbenfabriken Bayer AG for o-isopropoxyphenyl N-methylcarbamate.

³ Common name now being considered by the ISO for O,O-dimethyl O-(4-bromo-2,5-dichlorophenyl) phosphorothioate.

storage and in hard water after tropical storage should be required. The accelerated storage test should be carried out in capped bottles without pressure at $54^{\circ} \pm 1^{\circ}\text{C}$. The Committee recommended a minimum of 50% suspensibility for both to assure the effective performance of such a water-dispersible powder under field conditions. It also suggested that WHO undertake investigations to develop a reliable method for analysis which could be incorporated in the specifications. Since only limited trials had been carried out so far, a collaborative experiment should be arranged so that sufficient data can be obtained to properly determine the analytical method.

The above considerations apply to Bromophos, since it too is an organo-phosphorus compound. For the carbamate insecticide BAYGON, the Committee recommended the same approach as above but, since it is a solid, the accelerated storage test should be carried out at $54^{\circ} \pm 1^{\circ}\text{C}$ for 24 hours with the sample under 25 g/cm^2 pressure.

4.2.6 Technical diphacinone

The Committee considered the proposals for including a specification for diphacinone, which is a widely used rodenticide. In view of the lack of technical data and other information, it recommended that a specification for this compound be prepared only when these data become available from the manufacturer. The interim specification can then be used until sufficient data on analysis and minimum requirements are obtained for a tentative or full specification to be made.

5. MODIFICATIONS OF TEST PROCEDURES (ANNEXES)

5.1 HCH gamma-isomer content: infra-red method (Annex 1)

The Committee reviewed the results of two collaborative trials for the analysis of HCH and concluded that there were insufficient data upon which to base major changes in the method described in the second edition of Specifications for Pesticides. However, the Committee was of the opinion that this method could be improved in some respects and made the following recommendations:

- (i) a simpler chromatographic column than that used at present should be illustrated and described in the text;
- (ii) more detailed instruction should be given on the removal of solvent from fractions containing the gamma-isomer in order both to minimize loss and preserve crystalline form;

- (iii) new photographs should be used which illustrate more clearly than the present ones the typical crystalline forms of the various isomers.

The Committee agreed that the main error at present in this analysis is in the chromatographic stage and recommended that instructions bearing on this be incorporated in the specification. In particular, it recommended that the column should not be overloaded, a cautionary note at the beginning of the Annex should indicate the dependence of the method on the absorption characteristics of the silica gel, and the specification of the silica gel in Appendix I should include only the "Preliminary Test".

The Committee noted with interest the comment regarding the silica gel found satisfactory by the Pechiney-Progil laboratory and suggested that this material be examined by another laboratory.

5.2 Determination of acidity (Annex 2)

The Committee recommended that the method for the determination of acidity or alkalinity in Annex 2 of the second edition of Specifications for Pesticides should continue to be used. The Committee agreed that an alternative method based on determination of the end-point electrometrically could be used in cases where the material is so coloured that the use of an indicator is difficult.

5.3 Determination of melting-point (Annex 8)

The method of determining melting-points and the accuracy of the results were reviewed. The Committee recommended that changes be made so that the method conforms to that described in the most recent International Pharmacopoeia. The Committee noted that the apparatus adopted by the Collaborative Pesticidal Analytical Committee (CPAC) allows somewhat greater accuracy and suggested that reference be made to this in Annex 8. At the same time, it noted that the International Pharmacopoeia method allows use of any apparatus of equal accuracy or a heating rate different from those recommended depending upon the individual requirements.

5.4 Sieve test (Annex 10)

The Committee recommended that the sieve test for water-dispersible powders described in Annex 10 be retained, with the following modifications:

- (i) paragraph 1, page 496 should be deleted and the method of pre-treatment incorporated in each respective specification;
- (ii) the diameter of the sieve should be defined as "about 20 cm";
- (iii) the term "accelerated storage" should be substituted for "tropical storage" and an appropriate explanation given to indicate the reason for the change in terminology;
- (iv) the International Standards Organization (ISO) specification for mesh size should be added, if available;
- (v) paragraph 3, page 496 and the reference to water-dispersible pastes should be deleted in view of the fact that the revised manual will contain no paste formulations;
- (vi) paragraph 2, page 497, under dusting powders should be modified to clarify the directions for performing the test. In particular, the time of shaking by the machine should be more clearly defined. This paragraph should read: ". . . restart the machine and screen for an additional five minutes. Completion of screening is determined by shaking the sieve by hand for four minutes. Weigh the residue on the sieve. Calculate the portion passing through and express it as a percentage of the weight of sample taken."

5.5 Emulsion stability (Annex 12)

The emulsion stability test and the requirements for separation of emulsion concentrates for the various specifications were reviewed and the following changes were recommended:

- (i) the test should be made at field concentrations;
- (ii) if 5 ml or more of emulsion concentrate are taken for the test, the maximum separation or creaming allowable should be 2 ml;

- (iii) if the amount of emulsion concentrate taken for the test is less than 5 ml, the maximum separation or creaming allowable should be 1 ml;
- (iv) the stirring time should be three minutes from the beginning of the addition of the emulsion concentrate. The description of this test should follow the general format given in test method 20, adopted by FAO;
- (v) the test should be made in standard hard water and in distilled water;
- (vi) since few concentrates to which water must be added to prepare the emulsion are now being marketed, the second paragraph on the test procedure applying to this type of emulsion concentrate should be deleted.

In reviewing this item, the Committee noted that the property of re-emulsification should be determined and recommended that an interim method to test this be developed by the Secretariat in collaboration with CPAC. At the same time, the Committee noted that CPAC had undertaken considerable work to develop a method for evaluating low concentration emulsions and suggested that WHO co-operate in this work where feasible, so that more data may be obtained upon which more accurate requirements and procedures can be based.

5.6 Sampling procedure (Annex 20)

The Committee reviewed the present sampling procedure described in Annex 20 and recommended several changes. Composite samples should not be taken and only individual samples representing single batches should be recommended in the guide to collecting samples. It has been found that if batch samples with good suspensibility are mixed with those which do not comply with the requirements the composite sample may pass the test and so make the detection of poor suspensibility batches impossible. The following changes in Annex 20 are recommended.

For sampling by the purchaser a 200-g sample should be taken to represent not more than 5000 kg of material, and for production control sampling a 200-g sample should be taken to represent not more than 2500 kg of material.

Changes to clarify the procedure were recommended in the quick visual suspensibility test under the section for sampling of water-dispersible powders. This section should read as follows:

"Quick visual suspensibility test. Weigh 3.3 g of the sample into a 100-ml beaker and 50 ml of standard hard water at 30°C, and allow to stand for 30 seconds. Stir the mixture by hand with a glass rod for 30 seconds, then transfer into a 100-ml glass-stoppered graduate cylinder, 18.0 cm \pm 1.5 cm in internal depth from the bottom to the 100-ml mark and 5.5 cm \pm 0.5 cm from 100-ml mark to stopper and add standard hard water at 30°C to bring to the 100-ml mark. Stopper the cylinder and invert 30 times at the rate of one inverting and righting cycle every 2 seconds, then allow to stand for 12 minutes. At the end of this time, observe the volume of sediment in the bottom of the graduate. If the sediment is above the 4-ml mark, the sample should be subjected to the normal suspensibility tests."

6. MISCELLANEOUS

6.1 Packaging requirements

The Committee reviewed the packaging requirements for water-dispersible powders and dusts having a low active ingredient. It was evident from current information and the discussion that the packaging requirements for DDT, HCH and dieldrin water-dispersible powders should be modified to permit a wider choice of containers, including boxes. The Committee agreed that the critical factors in packaging of these powders are compaction and hermetical sealing, and within conventional limits the package size is unimportant for these powders. The Committee therefore recommended that the packaging requirement for the powders mentioned above be modified by deletion of any reference to container size and substitution of a minimum capacity ratio of 2 litres per kg. Hermetic sealing in a polyethylene or equivalent liner should be retained. The Committee also suggested that a footnote be added in the Manual in the case of DDT powders to the effect that specifications for boxes of adequate strength are available from WHO for packaging of these powders.

The Committee also reviewed the packaging requirements for malathion and other water-dispersible powders and recommended that they remain as in the second edition of Specifications for Pesticides.

In the case of malathion dusting powders, where the content of active ingredient is low, the Committee recommended that the packaging requirement be so worded as to prevent the use of polyethylene or other absorbent liner.

6.2 Glassware standards

The Committee reviewed the specifications for graduated cylinders at present used for conducting suspensibility tests and recommended the following modifications:

- (i) the 250-ml graduated cylinder should be retained essentially as described in the present specifications, but with the additional requirement that the distance from the 250-ml mark to the top of the graduate, excluding the neck, be from 4-6 cm. A more accurate description of aliquot removal should be incorporated and reference made to the special apparatus described in Test Method 10 of FAO for the suspensibility test. This apparatus, although not required for the test, facilitates carrying out the procedure;
- (ii) the dimensions of the 100-ml cylinder should be defined more accurately, namely 18 ± 1.5 cm in internal height, from the bottom to the 100-ml mark, and a proper limit placed on the height from the 100-ml mark to the top of the graduate, excluding the neck.

6.3 Suspensibility test standards

The Committee, after reviewing the procedures of the suspensibility of the specification for water-dispersible powders, recommends that as a general principle the 100-ml cylinder should be used for a suspensibility test in cases where the active ingredient of the powder is at a high concentration, for example 50%, and that in these cases the aliquot should be taken from the centre of the graduate but that in those cases where the powder has a low active content, the existing method should be retained.

7. RESEARCH RECOMMENDATIONS

During the course of the discussion the Committee agreed that certain aspects required further information in order to clarify either the minimum requirements or points of procedure. As a result, the Committee listed the following research needs and recommended that they be used as a guide to carrying out future work.

7.1 Technical DDT setting point

More information is required to correlate the minimum setting point with quality for technical DDT. It was suggested that WHO obtain information on DDT manufactured throughout the world with a view to more accurately determining this requirement.

7.2 DDT water-dispersible powders

The problem of loss of suspensibility of DDT water-dispersible powders suggested several lines of research:

- (i) the results of laboratory tests on suspensibility after accelerated storage need to be related to the field performance of the water-dispersible powders;
- (ii) the causes of loss of suspensibility of DDT water-dispersible powders need to be determined more definitely; and
- (iii) since a 100-ml graduated cylinder test is now recommended, work should be carried out to relate the results of this test procedure to the results obtained with the 250-ml WHO test procedure.

7.3 DDT dusting powders

It was suggested that the problem of accurately defining the tolerance for low active ingredient powders as well as other powders be studied in collaboration with FAO in order to develop a more uniform system of defining these requirements.

7.4 Technical malathion

The Committee noted that methods for the assay of malathion often give faulty results when applied to poor quality products and that, in particular, methods based on the alkaline cleavage of the molecule might be greatly improved if the mechanism of this cleavage were known. The Committee recommended that this mechanism should be investigated and an attempt made to develop other methods based on a characteristic property of the molecule.

7.5 Trichlorfon

Research is needed on the method of determining acidity to more clearly define conditions which will not cause acid reaction of the trichlorfon to form dichlorvos or even involve further reaction of the dichlorvos thus formed.

7.6 Larvicidal granules

The Committee noted the growing importance of larvicides in vector control and recommended that WHO undertake a programme of research which would lead to the development of improved granular formulations and permit future committees to draft specifications for these products. It was suggested that WHO should seek the co-operation of FAO and other organizations interested in granules. The Committee also urged that a part of the research be devoted to development of techniques and methods of formulation of larvicidal granules which would permit the user to import technical insecticidal products and formulate with local fillers in order to save the cost of shipping dilute formulations over long distances.

7.7 Sieve test

Research is needed on a wet sieve technique for evaluation of dusting powders.

7.8 Emulsion stability

Development work is needed on a method of evaluating emulsion concentrates and it was suggested that WHO co-operate with FAO so that the resultant methods may have wide applicability.