OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

RESTRICTED

15878

DP/ID/SER.A/763
14 October 1986
ENGLISH

PESTICIDE DEVELOPMENT PROGRAMME IN INDIA

DP/IND/80/037

INDIA

Technical report: Findings and recommendations*

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

Based on the work of Dr. Jan Bondam,
expert in clay mineralogy

Backstopping officer: B. Sugavanam, Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

* This document has been reproduced without formal editing.

V.86 60859

CONTENTS

Project : DP/IND/80/037/11-65

Duration : From 22 June - 21 September 1986

Abstract:

The report mainly deals with the research and development activities in the clay mineralogy laboratory of the Pesticide Development Programme in India (PDPI) Research Centre, Udyog Vihar, Gurgaon-122 016, Haryana, India. The PDPI is a UNDP/UNIDO executed programme in cooperation with the Government of India through the public enterprise Hindustan Insecticides Limited (HIL), with head office in Hans Bhavan, Bahadur Shah Zafar Marg, New Delhi 110 002, India.

A number of suggestions and recommendations is made with respect to testing facilities, communication of test results and post-gradual training. Proposals are made for the successful continuation of the on-going routine survey of indigenous pesticide carrier materials, for imminent research topics, as well as for medium to long term tasks in enlarging the choice of mineral carriers and diluents for pesticide formulation.

Acknowledgement

My task has been considerably eased by the existing attitude at the PDPI Centre that clay mineralogy studies are an integral part of pesticide research and development of activities.

Far from being regarded as a necessary nuisance to concentrate on carrier properties also, the spirit of the Centre mirrors the understanding that meticulous carrier studies offer the pesticide industry on opportunity to develop superior brands of a variety of toxicants, both in quality and in efficiency in use. The centre is to be congratulated with the adopted concepts of integrated research units within its framework.

I wish to express my gratitude to all those, who have made my stay at the Centre a fruitful one. My thanks are due to Dr. S.P.Dhua - Chairman of HIL, and to Dr. K. Hussein, SIDFA, UNDP for keen interest in my work. The scientific, as well as the technical staff of the Centre I am indebted for having made my job that pleasant. Dr. S.K. Khetan, Dr. P.K. Ramdas, S.Khattar, M.Sc., and Miss. Mani have in all possible ways been at my side.

Dr. S.K. Khetan is acknowledged for animated discussions and for accompanying me in the field.

Indeed, everybody at the Centre has accepted me as one who belongs, and that have made me feel at home from the very first day. It greatly contributed to give me a flying start in the job.

Mr. Sat Pal from the UNDP office in New Delhi has provided me with all possible assistance whenever needed. To Mr. R.R. Pillai I extend my thanks for typing the draft report.

A concluding word of appreciation and a friendly thought goes to the staff of the entomology laboratory of the Centre, Dr. N.R.Bhateshwar, Dr. Y.P. Ramdev and Mr. S.P. Yadav, M.Sc. for helping me to get some insight in beekeeping in India. I will surely communicate the little knowledge I acquired during my stay to my fellow hobbyist beekeepers in Denmark.

Introduction and explanatory notes

1. Mineral carriers and diluents in pesticide formulations are inert materials, which allow the toxicants to be prepared in a convenient and effective form for use in the fields.

To obtain the desired effect it is essential that the mineralogical, chemical and physical properties of the carrier material have been determined in order to facilitate a proper choice to be made.

While most choices will be based on price and performance, coupled to availability, a surprising number of carrier choices continue as a result of habit and established formulation practice. Replacement of a carrier or diluent in pesticides frequently requires some sort of redressing of the formulations, a task the industry is not likely to embark upon unless cost or performance improvements are apparent.

To this end an institution like the recently established PDPI Centre in Gurgaon is viewed as a main instrument for the pesticide industry,

- to inform the formulators on the properties of marketed carriers and diluents,
- to introduce the proper uses of carriers and diluents,
- to specify the desired grades or qualities to the suppliers of carriers, as a measure of consumer guarantee.

2. It has been in the above sense that the content of the project job description was understood to be interpreted, as a continuation and development of the initiated evaluation of a number of indigenous clay mineral carriers, undertaken by the PDPI Centre so far.

After consultation with the management, it was decided to proceed in the same view with the routine determinations of carrier properties, and to make the results available to both the pesticide industry and the suppliers of mineral carriers, on data sheets that are to be grouped according to a mineralogical classification.

Simultaneously an approach has been made as to what topics of mineralogical research are likely to contribute to better applications of indigenous clays and other mineral carriers and diluents in pesticide formulations in order to improve performance of the active ingredients in field use.

2. In Annex I, a short explanatory description is given of the various mineral carriers and diluents currently in use in the pesticide industry, and their availability on the Indian market.

Annex II is a brief manual in the use of simple quality control tests on clay carriers, preferably to be carried out by the supplier.

The ultimate aim of this exercise is to gradually introduce uniform, comparable standards for carrier materials on delivery, which can be utilized in quotations.

Annex. III is an actual example of a ready data sheet on a lump china clay from Gujarat.

4. Recommendations made in the running text of the report, are marked with an (R) in the margin. Subsequently these recommendations have been collected and summarised in a separate concluding chapter.

Remarks of particular interest are denoted with two strokes,- -, in the margin of the text.

CLAY MINERALOGY STUDIES AT THE PESTICIDE DEVELOPMENT PROGRAMME IN INDIA (PDPI) RESEARCH CENTRE IN GURGAON, HARYANA

Introduction

The general scope of work in any research institution like the PDPI Centre is always of a dual nature.

The main objective, to serve a particular industry by carrying out specific R&D tasks on contract is backed by a certain volume of internally generated scientific research on particularly chosen subjects with a potential for acquiring advanced knowledge useful to that industry.

For carrier technology a well-equiped clay mineralogy laboratory has been established at the PDPI Centre. It was rightly seen as a priority to initiate a survey of indigenous carriers used in pesticide formulations in India, in order to gain a firsthand knowledge of these materials with the objective to be able to advice potential users in making proper choices.

The evaluation of carrier material is done on a routine basis, which is more than adequate for that purpose. This survey must certainly be continued, as it will create data on which more specific studies can be based, and further
(R) material specifications worked out. To create files with material characteristics for different classes of carriers and diluents available from indigenous sources must be looked upon as a priority task for the PDPI Centre. The routine range of carrier analyses will always be wanted for contracted studies on pesticide formulations anyway. As to the second prerogative, generated research, no particular advanced studies are being undertaken as yet. However, a number of research subjects is already in sight. To reach such targets the laboratory has to adopt a broader range of research methods and tools. In the following chapters, the possible ways for future clay research at the PDPI Centre will be outlined in detail.

Properties related to clay composition

Particular physical properties inherent to clays are very much dependent on the chemical and mineral composition, on the crystal habit and on the degree of crystalinity.

The physical properties of importance for the use of clays in the pesticide industry are particle size distribution, surface area per unit weight, sorptive capacity, cation exchange capacity, wettability and suspensibility. Important technical parameters aze the aizeated and compacted bulk density of the carrier, as well as the flow characteristics of prepared dusts and powders.

In order to determine the mineral composition of the clays, use is made of X-ray diffraction (XRD), infrared spectroscopy (IR) and of thermal analytical methods (TGA, DTA, DSC). Chemical analysis is mainly carried out to the extent as to determine compositional elements which are of influence on the interaction between the clay carrier and the toxicant, and secondly for mineral identification purposes also. For a proper understanding of the interrelated combination of the above mentioned physical and chemical characteristics of a given clay product, it is essential to have a good insight in the mineral nature of the clays and their crystalline structures.

To reach that stage the PDPI Centre has initiated a systematic evaluation of clay products and other mineral carriers from all the states of the union, and to that avail received samples from different producers and suppliers of clays and fillers, and collected samples in the field as well. An array of determinations of the physical and chemical properties of these samples has been carried out on a routine basis. Part of the on-going analytical work has been completed and the results have been communicated in a number of reports.

A greater part of these analysed clay samples consist of kaolinitic clays. This group of clays is singled out for a closer view of subjects inherent to the study and evaluation of clay carriers in the pesticide industry, and problems encountered in this context.

Kaolinitic Clays (See also annexure I):

The group of kaolinitic clays have suitable properties to which many pesticide formulations have been adopted, in particular for wettable powders. For this reason the use of kaolinitic clays in the pesticide industry in India and elsewhere, is well-entrenched. Another reason for the industry's adaption to these readily available clays is the fact that kaolin or china clay is used in quantity is the paper industry, and in ceramic works. The exploitation of the primary kaolin deposits in India is therefore well organised and processing of these clays is carried out in such a way as to meet the standards set by the major consumers, either for use as a paper filler, or as an integral part of the body used for making, china ware, sanitary ware and technical porcelain. The desired physical properties for pesticide carriers cannot however, be deduced from the specifications for filler use or from the standards set for ceramic purposes.

On the other hand, kaolinitic clays which cannot be used as a paper filler, or in whiteware ceramics, may very well be applied in pesticide ... ulations where specific brightness of the end-product is not required.
(R) The pesticide industry is bound to set its particular set of guidelines for the use of kaolinitic clay carriers. To this end, a first approach is to continue the work initiated at the PDPI Centre, to get an overall view of available kaolinitic clays in India. These includes clays used to produce terracotta ware, ceramic from potteries, or glazed tiles.

Since kaolinitic clay carriers are an ingredient of wettable powders, the carrier behaviour in clay-water suspensions is crucial for the suspensibility
(R) properties of the end-product. A study of clay water system using the indigenous kaolinitic clays is considered to be an important subject for further research at the PDPI Centre.

To a great extent the tendency for flocculation depends on the surface area of the kaolinitic clays. Other subtile clay properties such as stacking order of the particles and their crystal habit exert some influence on the behaviour in clay-water systems. Flocculation of aqueous kaolinitic suspensions is due to the presence of loosely adhered cations on surfaces and edges of the clay particles. For practical purpose the balancing of the flocculation by addition of dispersing or peptizing agents can only be measured empirically.

As water suspended kaolinitic particles are slightly hydrolized by absorbed water molecules which can enter sites of crystalline imperfection, the degree of crystallinity become. a characteristic parameter for hydrolysis. Resulting dissociation of free radicals in this process confers with the pKa (or pH)of the aqueous suspension.

The degree of crystallinity of the kaolinite material species is probably the single most important correlative index for the physical properties of the clay. Unfortunately no univocal scale can be established, especially not because the crystal habit of kaolinite minerals is not related to crystallinity. Moreover kaolinite minerals can extend different levels of hyderation, only partly related to crystallinity. Whatever method is used to designate a degree of crystallinity to the kaolinite species, as deducted from XRD or IR diagrams, no uniformity can be expected in expressing the physical properties in terms of so determined crystallinity alone, unless one uses a rather crude subdivision well crystallised kaolinite, not hydrated - intermediately disordered kaolinite, partly hydrated - highly disordered kaolinite, hydrated.

This means that any correlation of the physical property in study with the degree of crystalline order of the kaolinite species must be based on simultaneous comparisons between a number of mineral characteristics, including the results of thermal analysis.

Only in this way a particular kaolinite species can be properly classified and erratic values of inter related properties of the clay correctly interpreted. It is imperative to note that in order to study the structural nature of the clay minerals, the analytical procedures must only be carried out on the clay fraction below 2µ obtained from thoroughly dispersed sample materials. It is not desirable to grind the samples to a fineness as practised in the industry before analysis as grinding may exert influence in the test results, tending to give erratic unreproducible values.

(R) Summarising, the following topics of research on an advanced level, are worth while to pursue with respect to the physical and mineral properties of kaolinitic clays found in India. A selected number of clay samples, ranging from well crystallized, and acidic clays to poorly crystalized and hydrated ones should be chosen and compared to available standard clay samples. The American Association of Petroleum Geologists (AAPG) has prepared a standard series of clays, which is available on order.

- a study of clay water interaction, with special reference to different types of natural water occuring in rural areas in India.

- a study of the thermal properties of the clays in relation to the infrared absorption characteristics, under rigidly controlled experimental conditions.

- a series of studies of the dependency of the sorptive capacity on the following physical parameters: pKa (pH), surface area, cation exchange capacity and particle size distribution.

It is emphasised that the selected clay samples should be checked for minor impurities, and mixture with other clay minerals, oxides and hydroxides and carbonates. For that reason the scope of chemical analysis must be broadened.

(R) As the PDPI Centre is not fully equiped for the advanced clay studies, it will be necessary to enter into scientific cooperation with other public research institutions with respect to X-ray diffraction and election microscopy, and to enlarge the range of own facilities for analysis in order to be able to determine surface area and cation exchange capacity of the clays.

(R) Furthermore the atomic absorption spectrophotometer ought to be equipped with lamps to determine the contend of alkalis in clays, and if desired of a number of trace elements often present in clays, such as Ti, Ni, Pb a.o.

Analysis facilities for the determination of the silica and alumina content of mineral carriers ought to be available also.

Attapulgitic clay (see also Annexure I)

The use of attapulgite as a carrier for toxicants in the pesticide industry
(R) has certain advantages which are disussed in detail in Annexure I. Since the occurrenceof attapulgite in India has been confirmed by tests made in the laboratory of the PDPI Centre, and XRD carried out at the Potash Research Institute, Gurgaon, it may be worth while to initiate a further study of attapulgite occurrences in the field, with the goal to develop viable exploitation in case sufficient large deposits can be discovered and identified. It is clear that such studies have to be under taken in cooperation with other state or government agencies, which are concerned with the development of industrial mineral resources.

In a recent paper, Gerstl and Yaron (1981) have presented a good summary of the use of attapulgite as a pesticide carrier, and of the factors affecting its use as such.

Mineral reviews on attapulgite and related sepiolite are by Henin and Calleree (1975) and Zelany and Calhoum (1977), both reviews were made available as photocopies, by the potash Research Institute. A comparison of attapulgite with sepiolite is cited and reproduced in white and Hem(1983).

References

1. Gerstl, Ze'ev and Bruno Yaron:
Attapulgite - pesticide interactions. Residue Reviews, Vol 78, 7099, Springer verlag New York Inc. 1981.

2. Henin, S. and S.Callere:
Fibrous Minerals, Ch. 9 in J.E. Gieseking (ed.) Soil Components, Vol. II, 335-349, Springer Verlag, New York 1975.

3. Zelany, Lucian W and Frank G. Calhoum. Palygorskite (Attapulgite), Sepiolite, Talc, Pyrophyllite, and Zeolites in J.B. Dixon and S.B. Weed (eds.). Minerals in soil environments, Ch. 13., Soil Soc. Amer. Madison, Wisconsin, USA, 1977.

4. White J.L. and S.L.Hem: Pharmaceutical aspects of clay-organic interactions. Ind and Eng. Chem. Product Research and Development, vol. 22, p.665-671, 1983.

All the named publications are available at the PDPI Centre, either as reprints or as photocopies.

The data sheet

The data sheet has been compiled in such a way, as to serve the following purposes:

- as a record of the available data on carriers, useful to the formulator of pesticides,

- as a file for carrier properties, which, in case, can easily be transformed to an edp format,

- as an entrance to additional records of scientific oriented investigations noted on the back side of the sheet.

(R) Furthermore, it will be feasible to reproduce the front sides and distribute these among formulators and carrier suppliers, accompanied by an explanatory note, as "communications from the PDPI Centre". In that case the "remarks and recommendations" could serve as guidelines for the consumer - the pesticide formulator, as well as for the producer, the carrier supplier. This could be done at more or less regular intervals to start with. At a later stage the issue of data sheets, could be evaluated afresh, based on the gained experience as to the value and the use of the disseminated information, and ultimatively revised if necessary, and compiled. The data sheets should preferably be issued for each class of mineral carrier. As an example of an actual data sheet is given in Annexure III.

A visit to the kaolin washing plant of Eklera China Clay Works

For an evaluation of particular clay materials it is often advantageous to gain some knowledge of the way the raws are treated in order to be able to suggest possible improvements in the treatment technology, to obtain the desired clay quality for use in pesticide formulations. Repeatedly it is a question of further removal of abrasive finegrained quartz which will greatly improve the grade of the treated clays .

In the case of kaolinitic clays washing of the raw material to remove the coarse grained size fractions and subsequent filler pressing of the separated clay fraction is the refining method universally applied to primary kaolin raws.

A visit has been arranged to a small primary kaolin deposit in Gujarat State. The locality is called Eklera in the Sabarkantha district near taluka* Idar situated about 80 km north of Ahmedabad.

The kaolin deposit at the site of the washing plant is an elongated 200 m wide zone of in-situ weathered crystalline basement rock, probably along a zone of down-faulting or a flexure type of displacement. The depth of kaolinization is between 10 and 15 metres.

The primary kaolin is a hard coarse grained rock with corroded quartz grains, no recognisable altered feldspars and no residual mica. The run of pit raws requires pre-crushing in order to free the clay material, prior to washing.

Summary of recommendations and general comments

A. Testing facilities

As pointed out in this report the proper testing for carrier material properties is crucial for pesticide formulation. To that end the clay mineralogy laboratory is reasonably well equiped. To be adequately equiped it will be necessary to enlarge the scope of instrumentation as follows:

- for measuring the cation exchange capacity, specially designed columns must be acquired,
- for determination of the surface area per unit weight suitable methods ought to be introduced, such as the BET-method utilising liquid nitrogen,
- for chemical analysis, the choice of lamps for use in the existing atomic absorption spectrophotometer should be gradually enlarged.
- for determination of zeta-potential, in case clay-water systems are to be studied, micro electrophoresis apparature must be purchased.

Furthermore the Centre has to secure admittance to an X-ray diffractometer : the estimated need for XRD clay identification will be of the order of 50 to 100 determinations annual.

There will also be a need for transmission images in particular in a study of kaolinitic clays. The number of TEM, SEM exposures will not exceed 50 per annum

B. R&D Activities

The first priority in clay studies must be given to the already initiated inventory of indigenous mineral carriers and diluents, as a basis for further clay studies.

The gradual acquisition of data on mineral carriers should lead to efforts to set grade standards, in order to improve the overall quality of the formulations.

The following topics for more advanced basic research are proposed.

The further treatment at the plant is the usual for low level refinement, sufficient for obtaining ceramic grades of refined china clay. The sand and silt fractions of the slurry settle, in 50 cm wide concrete gutters, over a total length of approxmiatley 50 m. The fines are subsequently settled in slurry tanks; the water is siphoned off and re-used for washing. No floculants are added. The settled clay slurry is pumped to the filter presses in order to bring down the content of water to approximatley 10 weight per cent. The filter cakes are dried in the open air, lowering the moisture content to about 2% . Subsequently the cakes are broken, bagged and weighed, ready for sale. There are no milling facilities at the plant. The washed china clay has satisfactory ceramic properties though of late the content of CaO of about 3% has rightly been considered too high by a number of consumers.

The annual output of the plant hovers around 6000 metric tonnes of china clay out of a mined tonnage close to 25,000 m.t., which gives a yield of 22%. The employed washing procedure is appropriate for the present end use but does not permit a production of high quality ceramic clay or filler clay. Basically this washing technique is still the same, as utilized since the end of last century, when filterpressing was introduced as a means of removing water from the clay slurry. It is still widely used for ceramic clay refinement. For more advanced uses of china clay as a filler or as a coating clay, further refinement is adamant.

This china clay has been tested for its possible use as a pesticide carrier, the results of the tests are given on the data sheet ch. Annexure III.

The nature of the kaoline deposit at Eklera, the magnitude of overburden, the depth of the exploitable bed and the very hard consistens of the raw kaolin, does not warrant expansion or further improvement of the washing facilities by investment in new technologies, like magnetic separators, hydrocyclons and improved drying facilities, nor in mechanisation of the winning of the raw boost output. In fact, the selective way of exploitation by hand digging, paired to low capital costs seems to be the most sensible way to operate the pits and works economically under the given circumstances. This type of kaolin deposits can only be exploited on a small scale with comparatively low overheads, or not at all. Softer kaolin deposits of comparable geological setting are mined in a similar way in France, Japan and Portugal. Where more integrated, capital intensive treatment of kaolin is applied, large tonnage kaolin deposits are a prerequisite for economic exploitation.

- Studies of clay - water systems, using indigenous clays, simulating realistic conditions in the field.

- compatibility studies with different classes of toxicants and different mineral carriers and diluents.

- studies of the physical properties of indigenous clays as related to the mineral nature.

It is advised to single out the group of kaolinitic clays for the above research subjects.

For the following medium to long-term tasks-the PDPI Centre is urgently advised to seek cooperation with other governmental institutions, in order to enlarge the range of useful indigenous carriers for the pesticide industry.

- the occurrences of attapulgite in India,

- a search for deposits of diatomite in India,

- the application of micronized mica and vermiculite in pesticide formulations.

A topic of very particular nature, which only will emerge after a period of routine testing of available carrier clays-, is the encirclement of kaolinitic clays with a minor smectite content. Only a few per cent smectite in the natural clay greatly enhance the sorptivity of the kaoline carrier.

C. Communication of R&D results

It is not advisable to seek results of clay studies carried out at the Centre published in scientific journals only.

The forum to which these results are to be communicated is not a general academic audience; they have to be directed to the professionals in industry in the first place.

An independent series of reports and communications from the PDPI Centre will fill this need. With obtained permission, reports of contracted studies can thus be incorporatedin the series as well as reprints from contributions to journals.

D. **Post-graduate training**

Post graduate training of young staff scientists is generally seen as advantageous for the quality of applied research, and as a rule stimulated by the management. Without any doubt a number of research establishments in India mainly centered in and around New Delhi, willbe in the position to offer advanced training facilities and courses, which could be of benefit for the research staff in the clay mineralogy laboratory.

Participation in fundamental courses such as clay mineralogy and crystallography, special analytical procedures, like X-ray diffraction, X-ray flourescence, infrared spectroscopy and electron microscopy, but in physical chemistry and statistics, ought to be an integral part of job training at the Centre.

As the PDPI is in its infancy, it is advised that managerial staff is given the opportunity to get acquainted with the present level of clay research in other laboratories.

There are several outstanding clay scientists in the world, who each in their tune contribute to the advanced knowledge of clays.

The majority of these scientists are specialists in their field, and follow a restricted course of clay research, usually with only one single application in view.

For that reason, it becomes more complicated to point out integrated centres of clay research in which a team of scientists is covering a broad spectrum of research topics related to applications of clay studies. Right now, only two of such centres come to my mind : there may be some others. The integrated Centres are:

1) Sektion Geologische Wissenschaften,
Ernst-Moritz-Arndt Universität,
Friedrich-Ludwig-Jahnstrasse 17A,
DDR 2200 Greifswald, DDR,
(Prof. Dr. Manfred Stoerr)

2. Department of Agronomy,
Purdue University,
West Lafayette,
Indiana 47907, USA
(Prof. Joe L. White)

The firstnamed institution is in particular used as a state research establishment for the utilisation of kaolinitic clays in general. It covers a whole range of activities, from exploration in the field to mineralogy of the clays, and testing of clay products for industry. The activities of the second named institution are centered around detailed studies of the interactions of clays with organic compounds. Much use is thereby made of infrared spectroscopy.

Annex I

Mineral carriers and diluents used in pesticide formulations

The mineral carriers are grouped as follows:

1. Clays and clay products,
2. Other mineral carriers and diluents
3. Synthetic mineral products

1. Clays and clay products

The clays are subdivided into:

1.a. Kaolinitic clays
1.b. Smectitic clays
1.c. attapugitic clays

1.a Kaolinitic clays

These clays consist predominently of structurally related minerals of the kaolinite group. Mineralogically speaking the kaolinite group of clay minerals are classified as non-expanding phyllosilicates with a 1:1 type of crystal lattice. The lattice is electrostatical neutral because isomorphic substitution doesnot occur. In the natural state interchangeable cations adhere to particle edges as a result of crystal imperfection. For that reason particle size affects the physical properties of the kaolinites. Sorptive capacity, as well as cation exchange capacity will increase with decrease in particle size.

In nature kaolinitic clays occur as primary kaolin deposits, a residual weathered rock type - and as naturally outwashed, redeposited clay sediments. The latter are variously named ballclay, fireclay, underclay, if related to coal measures, and fintclay.

Kaolin, or china clay, the processed, i.e. washed product obtained from quarrying primary kaolin deposits is mainly used as a filler, or in quality grade as a coating clay in the paper industry. Secondly it is used in the ceramic industry as a major component of the body of china ware, sanitary ware and technical porcellain.

It has found less dominant applicatios as a filler in the manufacture of rubber goods, in paints, in pharmaceuticals and in pesticides.

The use of kaolin and kaolinitic clays in pesticide formulations is well-entrenched in India. A number of good grades are available for that purpose. Priority must be given to further studies of indigenous kaolinitic clays, as discussed in the report on page.6..

1.b. **Smectitic Clays**

Synonyms are montmorillonite, bentonite and Fuller's earth, for natural clays predominantly consisting of smectites.

The smectites are a group of phyllosilicates with an expanding 2:1 type of crystal lattice, which means variable spacing of the basal lattice planes under varying conditions. Due to isomorphous substitution in the crystal lattice, the smectites display interlayer cation adsorption.

Consequently on account of the large surface area, found in smectites, including the so-called internal surface between the basal planes the clays of this group exhibit a high cation exchange capacity, while polar liquides of low molecular weight may enter the mineral structure in mono-molecular layers, causing swelling of the clays. Therefore, montmorillonitic clays usually swell in the presence of water, and will easily flocculate if electrolytes are present also.

The natural occurrence of exploitable smetitic clays is mainly restricted to environments in which basic volcanic rocks have been subjected to weathering processes.

Bentonites are used in many fields of industrial applications as a binder, a stabilizer or as an extender. Pretreated clays are the usually available commercial grades.

So called Ca-bentonite, treated with a calcium chloride solution, is in general of a non-swelling type and for that reason preferred for the use as an insecticide dust diluent.

In India the use of betonite in pesticide formulations seems to be restricted.

1.c Attapulgite clays

Attapulgite also named palygorskite, is a non-expanding clay mineral which structurally can be described as being an intermediate phase between the layered phyllosilicates and the chained inosilicates. In this respect attapulgite exhibits a unique crystal lattice, only encountered in a closely related mineral spicies, called sepiolite. Isomorphic substitution in the crystal lattice of attapulgite is a common phenomenon.

The fibrous nature of attapulgite with structural microchannels, of the order of 4-6 A in width, gives the attapulgitic clays their characteristic colloidal and sorptive properties, which allows for high percentage mixes with liquid toxicants. The clays are equally well suited for the formulation of wettable powders and concentrated dusts.

The use of attapulgitic clay as a carrier or diluent in the formulation of pesticides in preference to more commonly available clays such as china clay and bentonite, stems from the fact that it is not easily flocculated in the presence of electrolytes and it does not cake at high relative humidity but remains free-flowing.

In nature attapulgite occurs in a variety of different weathered rock types. However, exploitable deposits are invariably found in ancient lacusurine marine environments, often associated with calcarous sediments.

Occurrences of attapulgite in India have been identified. Further attention ought to be paid to these occurances, as well as to the possible occurance of sepiolite.

An eleborated view on attapulgite as a preferred mineral carrier for pesticides is presented in this report on page 9....A number of recent reviews are cited as well in that chapter.

Other mineral carrier and diluents

Only a few commonly used mineral carriers and diluents will be discussed. These are

2.a. diatomaceous earth or diatomite,
2.b. pyrophyllite and talc,
2.c. mica and vermiculite

2a. Diatomaceous earth or diatomite

Diatomaceous earth is a fine grained sediment predominantly composed of the skeletal remains of diatoms, unicellar organisims which mainly thrive in slightly acidic waters, in both marine and fresh water environments.

The individual skeletons consist of opaline silica, and measure only a few micrometres in diameter.

In nature diatomite may occur mixed with organic matter in recent deposits, it usually carries clay minerals in minor quantity.

Due to the open texture of the diatom skeletons, diatomaceous earths are of a highly porous nature, which gives a low dry bulk density, and a high percentage of voids or pore space. consequently diatomite exhibits a high sorptive capacity as compared to precipitated silica. See page....in this annexure.

The fact that diatomite mainly consist of silica, in the range of 80-95 per cent, the remaining chemical constituents being moisture, alumina and ferric oxide, makes it an attractive alternative carrier in formulations in which precipitated silica is prescribed.

The particle size distribution is such that it can be utilised in wettable powders.

Diatomite finds other industrial applications as anti-caking coating in NKP-fertilizer, as a fiter-aid agent, as an inert filler, and finally it is utilised as a raw material in the fabrication of low density, insulating fire bricks.

Its occurrence in India is unknown to me, but it is well worth to search for economically viable deposits.

2.b. **Phyrophyllite and talc**

Although structurally being phyllosilicates, these isomorphous minerals are not found in natural clays, but do occur in crystalline rocks, from which they are concentrated and milled for further use as an industrial filler. An often used trade name for the raw material is soapstone, on account of its softness.

Contrary to the layered silicates in clays, the individual mineral particles of talc and pyrophyllite are structurally dense and non-porous which affects the physical properties. It means that surface area, cation exchange capacity and sorptive capacity are low as compared to clays.

As in kaolinitic clays, particle size has a marked effect on the sorptive capacity. In general however, the mean particle size of milled talc products is an order of magnitude larger than that of clays, for which reason talc cannot substitute kaolinitic clays in wettable formulations.

The main application of talc and pyrophyllite is as a filler in the plastics industry. Further more it is used as an anti-stick dusting powder throughut the rubber industry.

The use in pesticides is mainly restricted to dust formulations, as a diluent. In India talc filler is readily available from indigenous sources.

2.c. **Mica and Vermiculite:**

Structurally mica is a phyllosilicate, which commonly occurs as a mineral component of crystalline rocks. Its clay mineral variety is called illite. Both these names designate groups of mineral species which are structurally and chemically different, but related. Illite is never found in a monomineralic clay: it is always presention a mixture of clay minerals often as socalled mixed layer mineral species of varying composition.

On account of its dense, rigid crystalline structure, mica lacks internal porosity, and hence the sorptive capacity is rather low, compared to the other group of 2:1 silicates, the smectites. Ground mica has found application as a filler in paints. As a diluent in dust formulations mica is occassionally used in the pesticide industry.

India is the worlds largest producer and exporter of mica, accounting for approximately two-thirds of the total trade volume. However, the world market for mica is shrinking. The Mica Trading Corporation is currently engaged in an EEC sponsored research projects, to find new uses for mica. Micronised mica powder, one of the available products, could in this context conveniently be tested for its applicability as a carrier for polar toxicants.

Vermiculite is weathered hydrated biotite and may thus conveniently be included in the mica group of phyllosilicates. Like mica, vermiculite has a platy crystal habit. Contrary to the true micas, its lattic expands on heating due to dehydration. This property is utilised for making fireproof insulating materials. The fines residue of this utilisation is used as an extender in paints and as a diluent in pesticide dusts. Its sorptive capacity is better than that of true mica. Vermiculite is likely to occur in quantity in India. The use of indigenous vermiculite as a pesticide diluent is worth-while to be tested.

Precipitated Silica

Precipitated hydrated silicon dioxide and precipitated calcium silicate are synthetic products derived from ground quartz and quartz sand. The fines are chemically treated with acid and lime in autoclaves, after which the reaction product is precipitated and dried.

It is used in high value pesticide formulations in which the toxicant is not very compatible with other mineral carriers.

Due to the very high price of precipitated quartz as compared to clays and other mineral carriers its use in formulations is limited, and most often combined with the use of clays as diluents.

The sorptive capacity of both these synthetic carriers is good. The products have moreover anticaking properties, comparable with those of diatomaceous earth.

Precipitated silica produced from indigenous sources, is marketed in India.

Annex II

Quality Control with Special reference to clay carriers and diluents.

The pesticide industry, as a consumer of carrier clays, has a vital interest in sources of supply, from which clay grades with near constant properties can be delivered over a long period of time. This is essential in order to ensure an even production, not hampered by shortages, shutdowns for cleaning and repair due to fluctuating carrier grades, other from different suppliers -, and resulting end-product powders of varying quality.

Preferably chosen limits could be adopted for physical properties of clay carriers such as sorptive capacity, wettability, suspensibility and particle size distribution. In addition to these properties abrasiveness is considered to be an important parameter, as carrier clay with a high abrasion index may cause excessive wear and clogging of plant machinery as well as losses in the fields, due to abrasion of pipes and nozzles of spraying or dusting equipment.

By demanding a minimum of quality control, executed by the clay supplier the pesticide industry will gain a better control of its own operations.

It will hardly be conceivable to obtain uniform grades without treatment of the crude clays. Several processes are in use, depending on the nature of the clay. The main processes though are washing and blending or homogenising of the crude clays in order to eliminate minor natural variations in overall composition in the clay pits. Screening and grinding after drying of the clays, as well as air floating, may further improve the grade.

Nekoline clay is an example of a well mixed uniform clay product obtained in the coal washing plant of the Neyveli Lignite Corporation Ltd., in Tamil Nadu..

The kind of simple quality tests which can be carried out on a daily basis at any clay-producing site are wet screening tests, the determination of the bulk density or volume weight, as well as the moisture content of the clay product, all three based on weighing of samples.

Preferably these tests must be demanded in order to certify the clays as pesticide carriers.

According to recommended WHO standard, the residue of grit matter in industrial clay products may not exceed 3% after wet screening on 74µm

(=200 mesh) for reasons of health risks (silicosis) for factory workers in clay consuming industries.

However, referring to above mentioned abrasiveness of the clays as an undesired property, the pesticide industry is well advised to lower this standard considerably. An upper limit of 0.5% residue on a 74 µm screen can easily be obtained for most natural clays. It is good practice also to weigh the residue on a 44µm (=325 mesh) wet screen. It will not be unreasonable to demand a maximum residue of 2% on the 44 µm screen.

Compacted bulk densities vary for different types of clay. While kaolinitic and attapulgitic clays have approximately the same bulk density, bentonites are heavier by a factor 1.7.

For kaolinitic clays the mean bulk density is 0.57 kg/l varying between 0.48 and 0.65 kg/l. For bentonitic clays the mean bulk density is around 0.96 kg/l. It is well known that the moisture content of the clays on delivery has influence on the mixing processes in the consuming industries. On economic grounds, it is an advantage for the clay consumer that the supplier delivers a clay product with a low moisture content, which ideally may not exceed 1% in weight, at a relative air humidity of 60%. As kaolinitic clays, in particular ball clays- are hygroscopic, higher moisture contents in dry clays can be expected. At 60% relative air humidity a ball clay may contain 4% moisture. In as far as hygroscopity is an inherent property of particular clays, no denifite limit can be set. Hygroscopity is influenced by particle size distribution as well.

In the following chapters, 1, 2 and 3, methods for rapid determinations of the above mentioned, underlined clay parameters is given. The basic procedures are all based on weighing only.

1. The proper technique for wet screening analysis

A standardised method for the determination of screen residues on 74µm (=200 mesh) and 44µm (=325 mesh) sieves, which only to a minor degree is dependant on the skills of the laboratory operator is described for kaolinitic clays in particular. A prerequisite for the method is that a peptising agent is added to the clay suspension. The preferred agent is tetrasodiumpyrophosphate ($Na_4P_2O_7$), which can be prepared by dissolving 20 grams of anhydrous $Na_4P_2O_7$, or 33.5 grams of $Na_4P_2O_7.10\ H_2O$= crystals in 1 l distilled water. The procedure is as follows:

1. Add 100 grams of clay to 375 cc water added 25 cc peptiser solution. Stir thoroughly,- preferably in a mixer at high speed-, for 10 minutes. Lump grade clays should be pulverised in a mortar prior to testing.

2. Pour the clay suspension slowly onto the screen, which has been wetted before, and wash the container with care, pouring the washing on the screen. Generally, the treatment with the peptizer is sufficient to produce free screening. In cases where the 44µm screen becomes clogged because one deals with a high viscosity clay suspension or with excessive residue, the screening can be facilitated by a stream of water, directed against the screen, from a rubber hose, with which the force of the water jet can be regulated by squeezing the end of the hose. **Do not rub the material through the screen.**

3. Wash the clay through the screen until the water is clear again, and free of clay particles. This operation, can be completed in the course of one minute.

4. Transfer the residue from the screen to a 50 ml or 100 ml preweighed beaker. Dry at 110°C, and weigh the beaker with the residue after cooling to room temperature. An evaporating dish can be used as well, instead of a beaker.

<u>Note</u> : Tap water may carry some grit or other foreign matter and should also be passed through a 44µm screen before use.

The above method insures that each clay particle is wetted by stirring and by the addition of an effective peptising agent to the clay water mixture.

2. **The determination of the moisture content.**

The variety of commercially available test equipment for the determination of moisture content in materials has in common that a weighed sample of the material to be tested is subjected to a predetermined period of heating to 105-115°C, after which the sample is cooled and weighed once more immediately after. The difference between the weighings, the weight loss-, is then expressed as a percentage of the initial weight as a measure for the moisture content of the test sample. The procedure is simple and can be employed after a short instruction.

A common way of obtaining the desired temperature is by utilising the heat which is dissipated from an infrared heat source, usually a bulb. Care should be taken that the test sample is truly representative for the batch or load of clay. This can be done by extracting several samples, which are thoroughly mixed. The final test sample is then again extracted from the sample mixture. Extracting four samples at a time is usually sufficient to obtain a reliable measure for the moisture content of the entire clay lcad.

3. The determination of compacted bulk density

The bulk density, or volume weight, is measured by weighing one litre of dry clay material, thus expressed in kg/l, which is equivalent to t/m^3.

For ali practical purposes it will be sufficient to follow the simple procedure described below:

i) A pre-weighed container with a marked volume of on litre, available as a kitchen utensil-, is filled completely with clay.

ii) The clay material is compacted by bouncing the container on a hard table top, ten twenty times, while turning the container between the two hands, until the surface of the contained clay remains in the same position even after continued compating.

iii) More clay is added upto the 1 litre mark, after which compacting by bounching is repeated.

iv) Repeated filling and compacting multimatively produces a tightly packed litre of clay material in the container.

v) The contained clay sample is then weighed, after which the weight of the container is substracted. The final weight figure obtained is a direct measure for the compacted bulk density.

The compacted bulk density is sometimes referred to as the apparent density. The specific density of clays is the true density of the mineral species exclusively; i.e. without accounting for the voids between the individual clay particles.

Another density parameter used in context with industrial applications is the areated or fluffy density, which is determined by weighing one litre of the powdered material without compacting it.

Annexure III

DATA SHEET FOR MINERAL CARRIERS AND DILUENTS IN PESTICIDE FORMULATIONS

Serial Number 00

Brand Name / Grade :	China clay - ceramic grade
Name and address of the supplier/producer :	Eklera China Clay Works Ltd., 7, Ravi Chambers, 5th Floor, Ahmedabad-380 001, Gujarat
Classification :	Washed kaolinitic clay

Moisture content (110°C): <1 % **Bulk Density :** 0.653 Kg/l (=t/m^3)

Wet Screen Analysis : Residue on 200 Mesh (74 µm) : %
Grit Matter : Residue on 325 Mesh (44 µm): 1.69 %

CHEMICAL DATA:		**AAS DETERMINATION:**			**OTHERS:**	
Loss on ignition	14.0 %	Fe		%	SiO_2	%
Acidity(pKa)	+1.5 to 4.5	Mg	n.d.	%	Al_2O_3	%
Acidity(pH)	8.8	Ca		%		
				%		%
				%		%

PHYSICAL PROPERTIES:

Particle size distribution :	Less than 2 µm	31.77 %
Method used:	From 2 - 10 µm	35.34 %
	From 10 - 20 µm	30.19 %
	Over 20 µm	2.70 %

Wettability/Wetting Time/Water : sec.
Suspensibility (Additive used): %
Maximum sorptive capacity (Malathion): n.d. g/100g
Other parameters:
Cation exchange capacity: n.d. meqv/l
Specific surface: n.d. m^2/g
Method used:

Remarks and recommendations: n.d. = not determined

The clay product is prepared for use in the ceramic industry: its application in pesticide formulations has not been tested yet.
True density : 2.28 g/cc.

MINERALOGICAL DATA

Short description of the natural occurrence/deposit:
(Paragenesis, parent rock, sediment character, geological environment, etcetra)

The kaolin deposit is situated in Sabarkantha district, taluka Jolar in Gujarat.

This primary kaolin deposit, derived from a granitic parent rock, occurs in an elongated zone of disturbance in the crystalline basement, about 200 m in width.

The kaolin is a hard rock, which is precrushed before washing. The residue after washing is predominantly quartz, mica nor feldspar have been detected.

The yield is 22%.

IDENTIFICATION RECORD:

	X-ray diffraction (XRD)
X	Infrared Spectroscopy (IR)
X	Thermal Analysis (TGA, DTA, DSC)
	Electron Microscope (SEM, TEM)
	Optical Microscope (OM)

CRYSTALLINITY AS CALCULATED FROM:

	XRD
0.52	IR
	Other Methods

COMPATIBILITY TESTS ON RECORD:

Toxicant 1

Toxicant 2

Toxicant 3

REMARKS