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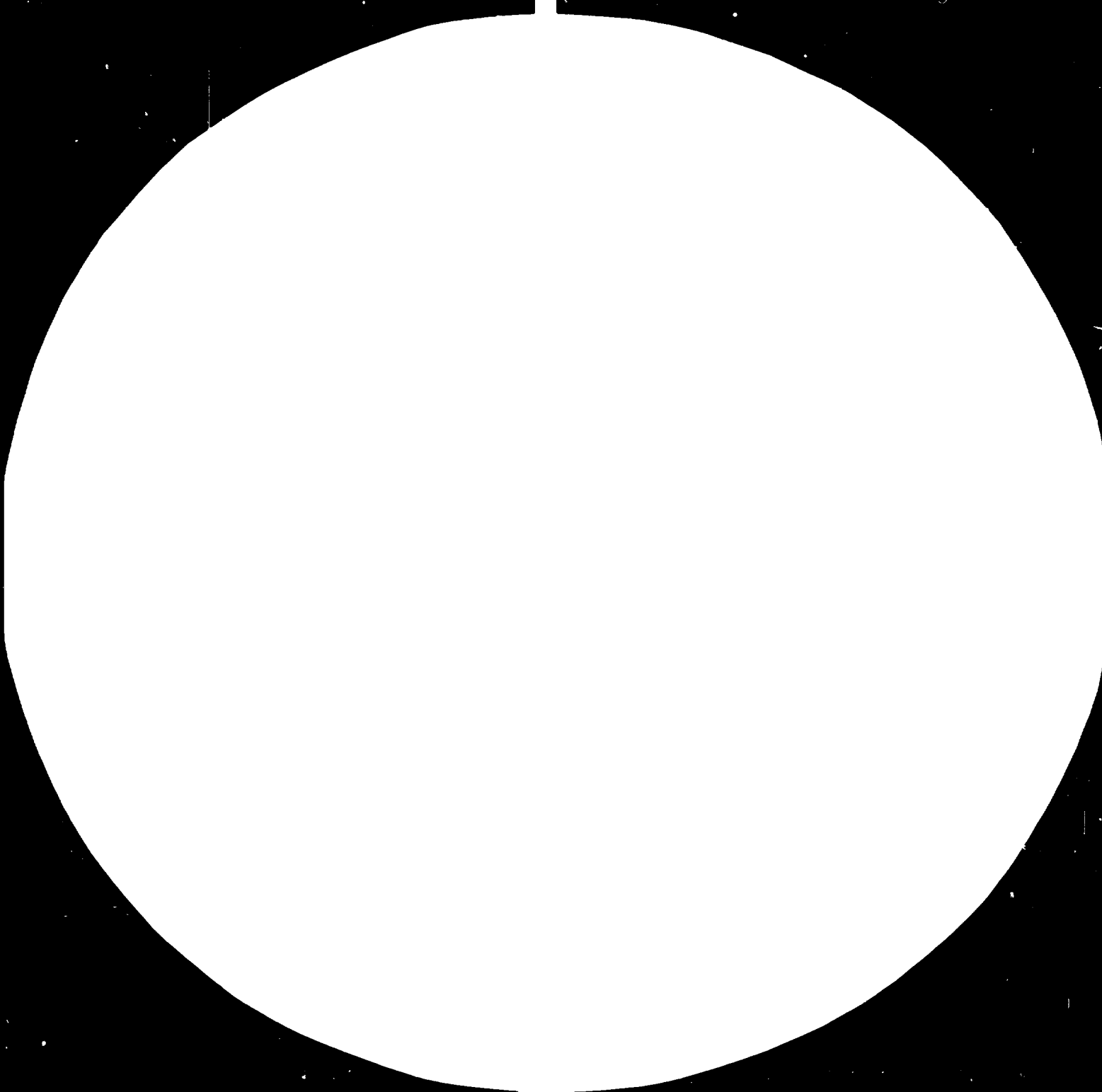

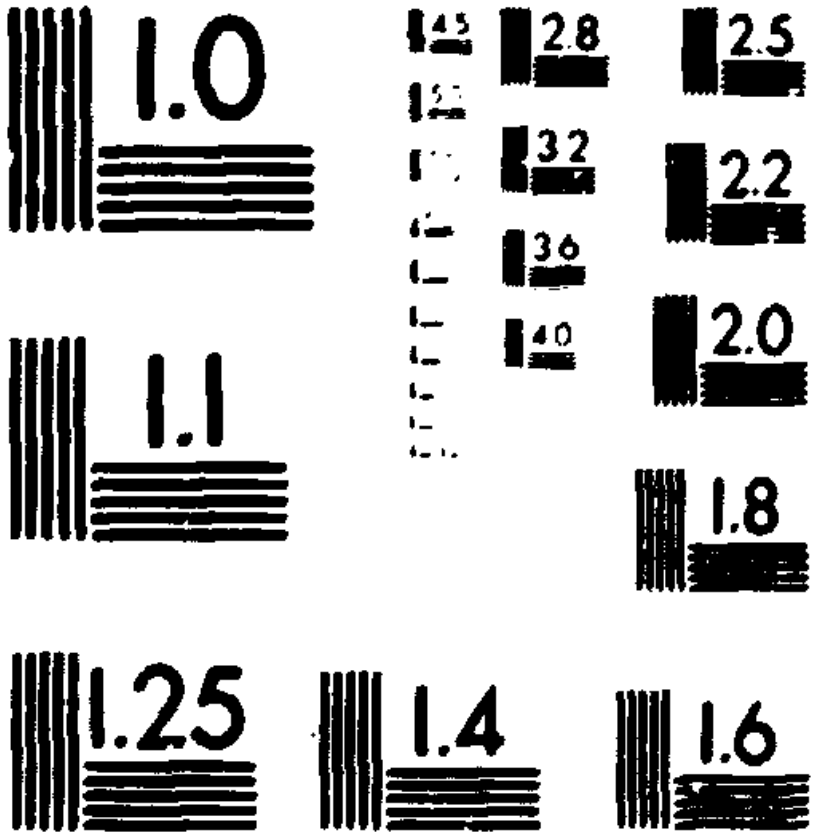

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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION

Project: Modernisation of Copper Phthalocyanine Technology at Wolskie Dyestuffs Works [illegible] Poland

SI/POL/89/801.

Contract: 90/072/GYL.

FINAL REPORT

November 1991.

ABSTRACT

The Wolskie Dyestuffs Works Organica at Wola Krystoporska in Poland had for many years been making the important blue pigment Copper phthalocyanine, which is widely used in the coloration of paints, plastics and printing inks, by the so-called 'Dry Bake' process. Because of the low yield obtained, the costs of production were too high. For this reason and because of the pollution caused by the need to dispose of a large amount of chemical waste, a change to a better process had become essential. The poor physical state of the existing plant added a further reason for making radical changes.

An alternative method of making this pigment, called the 'Solvent' process, gives better yields, lower costs and less pollution. A number of solvents can be used in this process. However, some of them have been found to produce a very dangerous by-product, the carcinogen PCB. In selecting a solvent for use in the new process, which had to be one available at reasonable cost in Poland, it was necessary to provide very sensitive methods for the chemical detection and analysis of these PCB's, both to minimise their production by suitably controlling the process and also to be able to certify that the content of these substances met the very low specification limits, without which the pigment cannot be sold on the international market.

This Report includes six appendices with the technical details of the research and development work which has been carried out and which has resulted in the following:

1. A laboratory scale chemical process for making crude blue copper phthalocyanine pigment in high yield and of low PCB content.

2. An analytical method for measuring the PCB content of pigment. The necessary gas chromatograph apparatus has been supplied by UNIDO and installed in the Polytechnik at Lodz.

3 A general design for a plant to manufacture crude blue copper phthalocyanine on the scale of four tonnes per annum

4. Laboratory screening methods for use with crude pigment produced for further processing to pigmentary form.

The aims of the Contract have thus been fulfilled.

CONTENTS

Page

1. Abstract

3. Background.

5. Overall Plan of the Work.

8. Conclusion and recommendation

9. Appendix 1

   Interim Technical Report, February 1989.

12. Appendix 2

   Second Technical Report, March 1990.

16. Appendix 3

   Development of Solvent process for making crude blue.

28. Appendix 4

   Development of method of PCB analysis.

43. Appendix 5

   General Process for the manufacture of crude blue copper phthalocyanine by the Urea Solvent method.

50. Appendix 6

   The conversion of crude blue copper phthalocyanine into pigmentary form -
   laboratory screening method for assessing crude blue samples for conversion to pigments.

Background.

This report is formally concerned with the work that has been carried out under the terms of UNIDO Project No SI/POL/89/801 during the period June 1990 to August 1991. However, to put this into context, it is necessary to mention the background of happenings since 1988 when a request was made by the Polish Government for technical assistance to improve the performance of the Wolskie Dyestuffs Works 'Organika' plant at Wola Krystoporska, where the blue pigment copper phthalocyanine had been made for some thirty years by the Dry Bake process.

The problems needing attention were that the yield was low, the quality was poor and the cost of production unsustainable. Elsewhere in the world, the Dry Bake process was regarded as obsolete, and only one other plant was known to be operating it successfully, and then only because of the special circumstances which applied there. General industrial practice is to use the so-called Solvent process in place of the Dry Bake Process.

A preliminary visit to the 'Organika' plant at Wola was made in January 1989. It was found that the plant was in a very poor physical state, causing much pollution in the immediate area and giving rise to considerable difficulties in disposing of the large amount of chemical waste produced. My advice was that a new plant should be built using the solvent process. There existed at Wola buildings which could be adapted for this new process and there was also available a considerable stock of unused reaction vessels which could possibly be used, although these were in open storage (Appendix 1).

At about this time very extensive political and economic changes were taking place in Poland and the whole future of the Wola plant was in doubt at the time of my second visit there in February 1990. The management however made a provisional decision to abandon the Dry Bake process and to change over to the Solvent process (Appendix 2.)

One technical problem with the Solvent process is that some of the solvents which have from time to time been used, and which are intended to act only as heat transfer agents, have been found to give rise to side reactions. These can lead to the formation relatively small amounts of poly chloro biphenyls (PCB's) but since these are known to be dangerous carcinogens, the result is that copper phthalocyanine can generally only be sold on the world market if produced using a solvent the status of

individual batch analysis has shown that the PCB content of the product offered for sale is below a few parts per million.

This requirement has caused producers considerable difficulties. They are making, in some cases, many hundreds of tons of copper phthalocyanine per annum, and on this scale it is not easy to maintain such high standards of purity.

Careful selection of the solvent employed, together with close control of conditions in the synthesis to minimise the formation of PCB's, is necessary. Very sensitive analytical methods for the detection of PCB's and efficient purification methods for their removal, should any be formed, are also essential. These considerations were very much to the fore in the work plan of this Contract which was begun in June 1990.

The project staff were as follows

Dr David Patterson	University of Leeds,	Contractor and Team Leader
Prof Jan Kracka	[illegible]	Consultant
Dr R Barraclough	Consultant on industrial procedures	
Mr K Divan *		
Mr G Edmondson	Environmental Monitoring Unit, Dept of Colour Chemistry University of Leeds	Sub-contractors for method of PCB analysis

Overall Plan of the Work.

1. Research to be carried out in the University of Leeds, UK.

In the Department of Colour Chemistry of the University of Leeds, there are full laboratory facilities both for the synthesis on a laboratory scale of organic pigments including copper phthalocyanine. Perhaps more important, however, is that in the Watson Organic Powders Research Unit which forms part of this Department, there are available the most modern physico-chemical facilities for the preparation of pigments from crude reaction products and their technical assessment. Techniques available include electron microscopy, particle size distribution measurements for sub-micron sized particles and instrumental colour measurement methods. Additionally, gas chromatographs are available for the development of analytical methods necessary for the determination of any PCB's present in the pigments prepared using various solvent systems.

The first step in the programme had two aims. First to make crude blue copper phthalocyanine on the laboratory scale using a range of different solvents and to adjust the reaction conditions to get high chemical yields of the product. The second aim was to develop an analytical procedure for detecting and measuring any PCB content of the products produced. Since pure samples of copper phthalocyanine were available together with standard PCB preparations, the development of the analytical methods could proceed at the same time as the work on copper phthalocyanine synthesis and the analysis of the samples so produced could await the completion of the analytical method.

The work on the laboratory syntheses was completed in June and July 1990 and is reported in Appendix 3.

The development of the method for PCB analysis was finished in September 1990 and is contained in Appendix 4.

2. Development Work to be carried out in Poland.

At this stage it was necessary to order a gas chromatograph for installation in Poland so that further development work on the laboratory scale could be continued there. The samples of copper phthalocyanine produced there could then be analysed for their PCB content. The development of a method of synthesis producing a minimum of the PCB by-product was, of course, one of the principal requirements of the whole project and one of the conditions by which progress was judged.

Consequently, an order for a Varian Model 3300 gas chromatograph plus necessary accessories (Purchase Order No 15-0-1116T, dated 4 September 1990) was placed by UNIDO. The delivery dated requested was the end of October 1990.

The apparatus was sent by air freight from London airport on 23 November 1990 contained in two packages and duly arrived in Warsaw, where it was sent into Customs for the necessary clearance. Only one of the two packages emerged from this process. When I found out about this, I went to Poland on 6 December and stayed there until 13 December. My efforts to find and if possible get delivery of the missing package were completely unsuccessful. I contented myself on working with the experimental syntheses being carried out in Lodz. I also took with me to Poland a small ultrasonic dispersing bath and a standard sample of PCB compounds needed for the analysis.

It was not however until 17 February 1991 that the missing package turned up from Customs and the gas chromatograph was later installed in Lodz Polytechnic. This 3½ month delay completely upset the progress of this Project. The overall delay was longer than this because of the need for experience in the running of the apparatus and the analytical procedures.

The financial support of the development work subsequently carried out in Lodz following the installation of the gas chromatograph has been a Polish responsibility.

3. Other support work in the United Kingdom.

However, to support the work in Poland with the final object of assisting in the building a full scale plant for making both crude blue copper phthalocyanine and converting this to pigmentary form, two further technical reports have been written by Dr Barraclough and myself.

These reports, entitled General Process for the manufacture of crude blue copper phthalocyanine by the Urea Solvent Method and Laboratory screening method for assessing crude blue samples for conversion to pigments are given as Appendices 5 and 6 respectively of this Final Report.

Appendix 5 gives typical process methods for a plant producing batches of about 400 Kg of crude blue. It cannot be an exact plant manual for a plant as yet unbuilt and a process which may be subject to further development and modification. But it is the result of long experience of industrial manufacture of crude blue.

Appendix 6 gives important information about testing crude blue samples as to their suitability for conversion to pigmentary form. This is needed whether or not the operators of the crude blue plant themselves intend to continue the finishing processes leading to the production of phthalocyanine pigments, or whether they intend to sell the crude blue to others for finishing. Both courses are currently followed and some producers finish part of their production while selling the rest.

Conclusion and recommendation.

Despite the much extended time scale of this project, the request for high level technical assistance in the production of copper phthalocyanine has been met.

Admittedly, this has resulted in the closure of the previous highly polluting, uneconomic plant, but this would almost certainly have happened even if this project had not been embarked upon.

The present situation is that the stage has been reached at which a process has been developed on a laboratory scale for the making of crude blue copper phthalocyanine by a method which is economically viable, is non-polluting and uses a solvent which is available from Polish oil refineries.

The most modern apparatus has been provided for the analysis of the crude blue, so that it can be certified as meeting intrenational requirements with regard to its freedom from carcinogenic PCB impurities and could therefore be sold , if desired, on the world market when in full production.

The project has stimulated development, funded by Polish resources, which is now at the stage where pilot-scale trials could now be begun, leading in turn to the construction of a full-scale plant for crude blue production and its conversion to good quality alpha phthalocyanine pigments.

It is to be hoped that economic and political conditions in Poland will enable this course to be followed, but this is beyond the scope of the present project.

The technical content of this report is such that in due course, it could serve as the basis for assistance to other countries who might approach UNIDO for help in this field of synthetic organic pigment production.

November 1991 David Patterson.

Appendix 1.

Interim Technical Report February 1989

Findings

As a result of my visit in February 1989 to the copper phthalocyanine plant of "Organika" at Wola Krzystoporska it became clear to me that the plant was in no state for further production. The last batch had been made in early December last year and various parts of the plant had apparently been dismantled since then. I was informed that the Polish Health Authorities had insisted that the plant should be completely closed by the end of 1989, and it seemed that the process of closure had already begun. The reasons for this move were obvious. The plant was in a very bad state of repair and had been causing a great deal of pollution, both atmospheric and also to ground water since a large amount of sulphuric acid had to be disposed of, as a result of the purification process that was being employed. The Management of the plant clearly realised the position and were quite prepared to go along with the decision which had been made.

A change to the solvent process will necessitate a complete re-design of the plant and the installation of new types of machinery. A building containing another unwanted plant is available for the installation of this new plant and after the removal of the existing machinery should not require too much building work to be done. In the yard at the works there were quite a large number of reaction vessels of suitable sizes for the new solvent process plant. They were glass lined, which may cause some wear problems when making copper phthalocyanine, but I was informed that there was also available a stainless steel reactor which it might be possible to use.

In view of the time that the construction of new plant must inevitably take because the reactors are not the only new plant which must be installed, it is my view that the most advisable [illegible] would be to carry out laboratory scale development work to find the most suitable for the process as a first stage.

The "Organika" plant has only laboratory facilities for testing their production materials. The development laboratory is not at present equipped to carry out the required development work for the changeover of the process for making copper phthalocyanine from the existing Bake Process to the proposed Solvent process. As part of the overall UNIDO programme however, I would suggest that some assistance should be given to upgrading the development laboratory.

During my stay I paid a visit to the Polytechnic at Lodz, where there is a Department of Colour Manufacture with which I have had contacts for some twenty five years. They are well equipped for carrying out development work at the laboratory scale of new processes, having adequate resources of reaction vessels, chemicals and other laboratory techniques, but more importantly in this case, have modern instruments, including spectrophotometers, an electron microscope and a gas chromatograph.

The latter is essential for detecting the presence of substituted biphenyl which are a dangerous by-product in the production of copper phthalocyanine by the Solvent process using nitrobenzene. Process conditions can be adjusted to minimise the amount of biphenyls produced but not usually completely eliminated. For health reasons therefore it is necessary to monitor the process very carefully and safely dispose of any such by-products.

At Lodz there are additionally members of staff in the Department who are well qualified to assist with the organic synthetic aspects of the project and they also have access to a well stocked technical library. I had a long discussion with Professor Jan Krasko and he is agreeable to providing facilities for Mr. Kowalchyk of "Organika" to carry out the necessary work there, subject to a suitable agreement as to payment for the facilities provided being arranged.

Mr Goreczny, the Deputy director of the Organika factory, accompanied me on the visit to Lodz and is in agreement with this suggestion.

To further the project, a schematic design for the plant was produced in conjunction with Mr Goreczny. This is not yet in the state of being an agreed design.

Recommendations

In view of the findings it is my opinion the plan for the project should be amended as follows:

1. Instead of a furtner visit by me to the "Organika" works lasting until the completion of the project, work to gain preliminary design data should be carried out at the Lodz Polytechnic in the Instytut Barwnikow, ul Zwirki 36, Lodz. This should be done using the Instytut Barwnikow as a sub-contractor to provide the necessary laboratory facilities for a member of the staff of "Organika".

2. When this has been arranged I should pay a visit to Lodz and Wola to supervise the beginning of a programme of laboratory work to obtain process data for the new solvent process.

3. After about two to three months when the development of the process is approaching its completion, I should make a further visit to check progress and begin the design stage for the new plant.

Appendix 2.

Second Technical Report - March 89

Since my last visit in February [illegible] conditions have changed considerably in Poland. It was felt necessary to re-visit the situation and a visit to the 'Organica' plant at Wola Krzysztoporska and the Polytechnic was therefore made, lasting from 19 to 24 February 89.

Findings

There have been some changes of personnel which make it necessary to alter the proposed plans set out in my Interim Technical Report of February 1989. Additionally, some experimental work has been carried out by Professor Kraska at Lodz to test out a possible solvent system for copper phthalocyanine synthesis.

General Background to the change to a Solvent Process

There are two principal methods used for making crude phthalocyanine. The first is the Baking Process at Wola (it now being dismantled and the second is the Solvent Process which is to be used in its place. Both these processes produce a material termed 'crude blue'. Despite this description, crude blue is chemically nearly pure copper phthalocyanine but its particle size is far too great for the material to be used as a pigment. It must be submitted to a 'finishing' process which reduces the particle size very greatly and also ensures that the crystal structure of the particles is either the alpha or beta form.

This 'finishing' process may or may not be carried out at the same factory that prepares the crude blue. Crude blue is also an internationally saleable product, provided that the content of carcinogenic poly chloro biphenyls (PCB's) is sufficiently low, particularly for sales in USA and EEC countries.

Consequently, as well as for the prevention of pollution and general safety, there are important commercial reasons for designing the production process for making copper phthalocyanine crude blue so that it has a minimal PCB content.

There are thus two considerations to bear in mind when formulating a process for copper phthalocyanine production. One is to get as high a yield as possible from the input of raw materials and the other is to reduce the amount of by-products. Some of the by-products are tar-like compounds which cause technical difficulties in the subsequent finishing processes, while others are the carcinogenic PCB's already referred to.

The change from the Baking process to a solvent process will increase the yield from the 62 to 72% previously attained at 'Organica' to at least the required minimum of 93%, while at the same time reducing atmospheric pollution almost to nothing, and considerably diminishing the previously high consumption of sulphuric acid with its attendant disposal problems.

The solvent process is not without its own problems, however. It is necessary to choose a solvent for the process which produces minimal amounts of PCB's, to monitor very closely the actual PCB content and further to remove it entirely from the 'crude blue' before it is subjected to finishing processes either by the producer or by a customer.

When choosing a suitable solvent, there are many considerations to be taken into account. These include the cost and availability of supplies of that solvent in the country where the synthesis is to be carried out, together with the cost of recovering as much of the solvent as possible at the end of the reaction. The cost and availability of solvents may change from time to time, so that as a precaution against this, technical experience with more than one solvent would be very useful should supplies cease for some reason.

Practical Considerations

1. The Project Document number S/[illegible] entitled 'High level technical advisory assistance for the rehabilitation of the technological process and quality improvement of the phthalocyanin[illegible] pigments' contains a plan which is a sound basis for the objectives in the title. The plan is capable of successful implementation in the current situation in Poland and has the support of the Management of the [illegible] Works and the Head of the Colour Institute of the Technical University [illegible]

2. The Professor of Colour Chemistry in the University of Leeds, Prof. D M Lewis, is willing to provide all necessary laboratory facilities in the Wolfson Organic Powders Research Unit for the development work necessary to prepare a Solvent Process for the manufacture of copper phthalocyanine crude blue. The necessary analytical facilities are available for the determination of the PCB content of samples made during the course of the development work. Full pigment testing methods are on hand for the quality testing of development samples. The charge for the use of these facilities, which will be on a 'cost per test basis', would be met by me from the contract budget. Testing of samples made in Poland by Prof Kraska using his solvent system will also be tested at Leeds on a similar charge basis.

3. Prof Kraska is also willing to spend two months, preferably June and July of this year, working in Leeds using a different solvent system which in is more general use commercially. The entire cost of this work could be met from the contract budget, excluding his transportation costs between Poland and Britain, which should fall to the Polish Government.

As a result of this development work, two solvent processes should be available so that a choice between the two can be made. The principal factor in making this choice will probably be in the PCB content of the respective products, but in advance it is not possible to be certain. Advice from a Consultant who has had long practical experience on copper phthalocyanine production will be taken.

4. It will be necessary to provide a gas liquid chromatograph or similar type to that available in Leeds for the analyses necessary at the end of the programme when subsequent work is carried out in Poland. It is not practicable to set up this chromatograph in the factory at Wola, but this could be done in the Institute at Lodz. The distance between Lodz and Wola is only about 50 Km and the samples only weigh a few grams, so even for a factory in full production, this would be only a minor disadvantage. The management at Wola have no objection to the Gas chromatograph, which would be provided from the budget, in place of the equipment listed in Annexe II of the Project Document, being sited in Lodz. Contrary to the doubts expressed in my earlier letter of about it being possible to provide this gas chromatograph within the budget, further enquiries have shown that these doubts were incorrect. An instrument can be provided, together with a supply of spares and consumables for the £ 20,000 available. It may additionally be possible to arrange training for a Technician in the operation of the instrument in the UK.

4. Some progress has been made in clearing the buildings for the new phthalocyanine plant at Wola. One at least, in which the actual Solvent process is to be carried out, will have to be equipped with electrical gear of flameproof standards, on which the Polish Government (quite rightly) now insists. In connection with the provision of an operational plant for phthalocyanine, I understand that 'Organika' has been approached by consultants in Warsaw with an offer of finance from American sources for construction but without any technical input. Whatever the outcome of this, the design and process instructions for a full scale plant which are called for in the Project Document can be provided.

Recommendation

Overall I am of the opinion that it is possible to begin a programme as soon as the contract is agreed, which will lead, within both the time scale and the budget available, to the scientific and engineering design of a solvent process for making copper phthalocyanine in crude blue form which is what the Polish government originally requested.

I recommend that steps should be taken to begin this project at the earliest possible date and am willing to act as subcontractor in this project.

March 1990.

Appendix 3

Basic method for the Preparation of Copper Phthalocyanine Crude Blue using Ortho-nitrotoluene (ONT) as Solvent

The reaction is between 4 moles phthalic anhydride + 12 moles of urea + 1 mole of a copper salt eg. cuprous chloride.

Working on the scale of 0.25 mole of [illegible] yield of 144g, the following are needed:

Phthalic anhydride	148g
Urea	432g - 468g
	100% excess - 50% excess
Cuprous chloride	24.8g
Ammonium molybdate	1g
Antioxidant	
sodium phosphite	
1-2% on weight of	
crude blue	1.44g - 2.88g
Orthonitrotoluene solvent	400 - 800ml
Theoretical yield	144g
in practice 93 - 96% of this	
should be achieved	

Procedure

Once the solvent has been added to the mixture, allow to stand at room temperature for approximately 1hr to allow reactants to dissolve in the solvent. Then raise temperature to 120°C and hold 1 hour to remove any traces of moisture in the solvent (mainly applicable if the solvent was re-cycled after the emulsion - drowning-out process).

Then raise the temperature to 160-180°C (preferably 170°C) and hold for 8 - 12 hrs. or until reaction is complete (indicated when no more ammonia is evolved from the top of the condenser [illegible] by formation of white fumes when a glass rod dipped into aqueous HCl is held at the mouth of the condenser or by change in colour of mixture to bluish violet from green to violet. pH of 8-14). Normally a [illegible] of 10hrs is required.

Isolation of Crude Blue

Once the crude blue reaction is complete, isolate it by one of the following methods:

1. Steam Distillation

Transfer the reaction mass to a steam distillation vessel.

Add approximately 200-300mls of water. Adjust the pH to 8-9 with aqueous sodium carbonate and also add a small amount of an anionic surfactant (approx. 1% on weight of crude blue, eg Turkey red oil or Nansa SSA). The surfactant helps to prevent bumping during steam distillation and the formation of hard lumps of crude blue ('balling').

The advantage of this method is that it is simple to operate and also doubles as an aqueous alkaline purification step.

The disadvantage is that it is relatively expensive. The cost of crude blue by this method is approx £200/kg at 1991 prices.

2. Emulsion Drown-out Method

When the crude blue reaction is complete, cool to room temperature.
Raise the temperature to [illegible] and [illegible].

In a beaker

Place 100ml of oNT and then
200ml of water

Stir for 15min to mix thoroughly

then add carefully and slowly
40g sulphuric acid.

Stir as vigorously as possible for [illegible]

Next add the hot reaction mass and stir the resultant emulsion at approx 90°C for 1-2 hrs.

Then filter. When filtration is complete, wash the presscake with hot water until the mother liquor is neutral, this removes all traces of impurities and leaves the presscake neutral.

The presscake is then dried in an air oven at approx 80-90°C.

The mother liquor from the initial filtration and the subsequent washings are added to a large settling beaker and left to stand until the solvent and aqueous acid phases separate. The upper aqueous acid phase is then carefully poured off and the liquid remaining in the beaker is put in a separating funnel to obtain a clean separation of solvent and aqueous acid layers. The solvent layer is used in the next crude blue reaction while the aqueous acid layer is discarded.

The advantages of this method are:

i. Quick

ii. Combines isolation and acid purification steps

iii. Requires less capital investment than the steam distillation method

iv. Relatively cheap manufacturing [illegible] compared with deep pot eg using the steam distillation

3. Isolation by Vacuum Distillation.

The reaction mass is simply transferred to a vacuum distillation unit.

The advantage is that it is relatively simple and quick.

Purification methods

1. Hot Solvent Washing

The presscake is washed with hot ONT solvent at 80-90°C. Purities as high as 96% can be achieved.

All manufacturing/isolation processes require a purification step before the crude blue can be used to manufacture high quality pigments, except when using the emulsion drown-out method.

2. Normal Purification Step

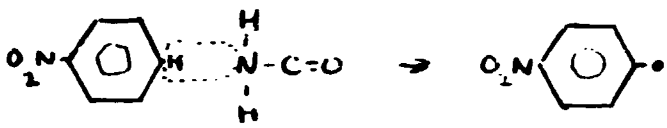
This is an aqueous acid procedure, [illegible]

The crude blue is added to 10% aqueous acid and stirred at 90°C for 1-2hrs. It is then filtered, washed neutral with warm water at 60°C and then dried in an air oven at 60-80°C. This should produce crude blue with a purity of 98-99%. Dilute sulphuric acid can be used instead of hydrochloric acid.

Mechanism for the Formation of Substituted Biphenyls.

When using nitrobenzene as solvent

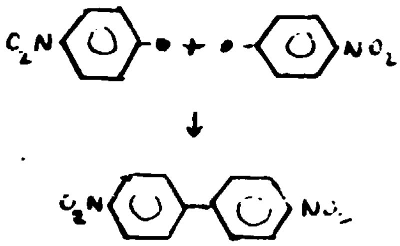
The **1st step** is always H abstraction



nitrobenzene [illegible] radical

This initiates a chain reaction

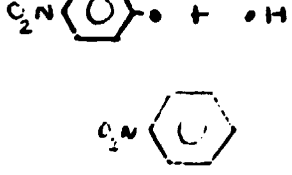
The **2nd step** is add[illegible]



4,4'-nitr[illegible]
(or other forms eg [illegible] nitro biphenyls).

If the solvent had been 1,2,4 trichlorobenzene, then polychlorobiphenyls PCB's would have been formed.

If anti-oxidants are added, these tend [illegible] as chain stoppers, since they produce an H radical and reaction with the main radicals produces less harmful products eg



Preparation of Crude Blue - using Polish refinery hydrocarbon solvent.

In a three necked flask capacity 1000ml. fitted with stirrer, thermometer and a reflux condenser, kept at 80°C by means of a thermostat.

Load: Phthalic anhydride
Urea
Cuprous Chloride
Ammonium molybdate
Hydrocarbon solvent

stir constantly and quickly heat to 90°C.

next Slowly raise the temperature to 130°C, taking not less than 1hr and then hold at 130-140°C for 3hrs.
(A slight foam appears on the reaction mass)

next Slowly raise the temperature to 170-175°C, taking 1hrs and hold for 3hrs

next Slowly heat to 195-200°C, taking 1hrs and hold for 4hrs

After this time the reaction is finished.

Still stirring, allow the temperature to fall and then filter off the phthalocyanine.

Wash the phthalocyanine on the filter with 200ml of fresh solvent.

Press and then wash with 1.5 litres of hot water at 90-95°C.
The wash is complete when no solvent is seen in the filtrate.

Disperse the phthalocyanine presscake in 900ml of hot water at 80-90°C.

Mix with 70ml of 30% NaOH at this temperature and stir for 45mins.

Filter hot at 90°C and then wash with about 2 litres of hot water at 90°C

The filtrate will be neutral and

Redisperse the presscake in 1 litre of hot water at 90°C.

Add 75ml of 50% sulphuric acid at this temperature and stir for 30mins.

Filter and wash with 2 litres of boiling water.

Filtrate will be neutral, colourless and free from any copper salts.

Yield: 103-106g crude blue copper phthalocyanine

June 1990.

Guidelines for process development - Polish Phthalocyanine project

1. Solvent Selection

Prepare a crude blue using the Polish process (see pxxx) but using completely aliphatic based solvents, eg odourless kerosene or Isopar M or L (Exxon Chemical), which have an aromatic content of less than 4%.

If there are problems with reaction mass fluidity, which I suspect will be the case, then we must carry out further experiments, using surface active agents with this type of solvent. Anionic, cationic and non-ionic types are available, but in my experience, anionic surfactants usually give the most satisfactory results, eg Turkey Red Oil at 1-2% by weight of the crude blue to be synthesised.

Using aliphatic solvents with a high aromatic content (over 20%) will improve the fluidity but will also increase the chance of producing substitutued biphenyl toxic by-products, which must be avoided if at all possible. This is the reason for the suggestion above for using aliphatic solvents with less than 3% aromatic content.

If it is necessary to use aliphatic solvents with more than 3% aromatic content to get a satisfactory fluidity, it would also be necessary to use an anti-oxidant such as sodium phosphite at the synthesis stage, as illustrated in Memo 1. The anti-oxidant will prevent the formation of substituted biphenyls.

Some experiments making crude blue using mixtures of odourless kerosene and ONT to give a satisfactory mass reaction viscosity might also be valuable A second series of reactions could be carried out with the addition of an anti-oxidant. The relative amounts of substituted biphenyls produced could be compared, as well as the crude blue characteristics.

Mixed solvents reactions are feasible but make the isolation of the crude blue unnecessarily complicated. Isolation in these cases entails the use of vacuum distillation units and eliminates the use of the economically preferable emulsion drown-out process mentioned in Memo 1.

2. Experiments Using the Emulsion Drown-out Process for the Isolation of the Crude Blue

These should be carried out using both the aliphatic (odourless kerosene) and aromatic (ONT) solvents. These should also be done using re-cycled solvents of both types.

With this type of isolation process, the [illegible] of the sodium acid and solvent layers in the beakers must be carefully observed. Sometimes a secondary emulsion forms between the two layers, making a clean separation of the solvent difficult, especially on a plant scale.

June 1990.

Progress Report No.1 June & July 1990

In accordance with the draft programme set out in my Technical Report of March 1990 on the above Project, Professor Kraska of Lodz Polytechnic spent two months in Leeds in the Department of Colour Chemistry, Leeds University. Fortnightly progress meetings involving Prof Kraska, Dr Barraclough and myself have been held to guide and monitor progress with the work in hand.

Work carried out during this period

This has been carried out with two separate purposes. The first is the investigation of the synthesis of copper phthalocyanine and the second the development of an analytical method for detecting the presence of polychlorobiphenyls (PCBs) in the samples of pigment so synthesised, together with the quantitative measurement of their amount

1. Synthesis of copper phthalocyanine (CuPc)

Some twenty syntheses of CuPc have been carried out in the laboratory using the following solvents:

(i) o-nitrotoluene

(ii) nitrobenzene

(iii) high boiling point hydrocarbon solvents, free from aromatics (Isopar L and M, Exxon chemical products)

iv) high boiling point hydrocarbon solvent containing some aromatics (Polish oil refinery products)

The details of the synthesis were kept fairly constant during each of these solvents, particularly as regards molar ratio of reactants, solvent/reactant ratios and time/temperature of the reaction.

The first important result was that no PCBs were found in any of the resultant products, so that from the pollution viewpoint and using the particular conditions chosen, all these solvents were equally satisfactory. Ortho-nitrotoluene is not readily available in Poland and there are some handling problems connected with nitrobenzene. These two solvents are therefore very much a second choice compared to the two high boiling point hydrocarbon solvents.

From all the solvents, the yield of CuPcy ranged from 90 to 95%, so that any of them can meet the requirement for at least the yield from the bu to 7a% level which was one of purposes specified in the original request of the Polish Government.

2. Analysis of Pigments for PCB content

The basis for the method derives from work carried out by the Dry Colour Manufacturers Association in USA. The method that has been developed as part of this Project, under sub-contract by the Environmental Monitoring Unit of the Colour Chemistry Analytical Service Centre of the University of Leeds, shows equal sensitivity to that required for analytical certification, as regards freedom from PCBs which is required before CuPcy can be imported into USA or any other country. A gas chromatograph of advanced design is required for this analysis. The recommendation of a suitable instrument for supply and installation in Poland is being forwarded to the Chemical Industries Branch of UNIDO under the terms of this contract.

Actual details of the experimental procedure will be included in the final report of this Project, but meantime a copy has been taken to Lodz Polytechnic in anticipation of the provision of the necessary gas chromatograph there.

It is worthy of note that the only sample so far analysed that has been found to contain any PCBs is a sample of crude CuPcy from the old bake process at Wola which is now closed.

Overall, the project has proceeded at a rate which has exceeded our best hopes when it began. The next step is to put the position to the Polish Authorities for them to make a decision about the solvent system to be used. Owing to the continuing economic changes in Poland, it seems that the original 'Organica' plant at Wola may not be the location of the further development of the project. It may be that the Boreta plant, which is closer to Lodz and has more extensive development facilities will take it up. This is something, of course, over which we have no control.

I am planning to make a visit to Poland in mid-September and one of the objectives of this visit will be to discuss this matter, others will be to check the installation of the gas chromatograph in Lodz Polytechnic, to arrange training in its use and to discuss any further development work needed on the synthesis before plant design is begun. The question of solvent recovery is an area requiring more data than is at present available.

Progress so far

The results outlined above show that the project is currently on schedule. The analytical part of the work is complete and a basic synthesis which meets all the defined requirements for the production of CuPcy has been achieved.

A choice of solvents is available but further detailed work to decide which of them is technically preferable will form the subject of the programme to be carried out in the next few months of the project. There are some problems of handling the 'impressed' reactants in the synthesis and the recovery rate in the subsequent solvent recovery stage. These need to be looked at in considerably more detail before a final solvent choice and design of a production scale plant can be begun.

Overall, progress has been encouraging and it is desirable that it cannot be maintained at such a high rate. However, a firm basis has been laid for the ultimate solution of the technical problems. With the installation of the gas chromatograph, responsibility for a further stage, that of devising finishing processes for the crude blue copper phthalocyanine pigments can hopefully be carried out within the resources available in Poland. This stage is linked to the current Project which is to raise the technical level of production of crude blue copper phthalocyanine, but is not formally a part of it.

July 1990

Appendix 4.

Development of a multi- [illegible] analysis

by R Driver and [illegible]

A FAST SCREENING METHOD FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS IN DRY PHTHALOCYANINE PIGMENTS

This method is divided into Five (5) parts:

A. SCOPE AND PRINCIPLE

B. REAGENTS, STANDARDS, SAFETY, APPARATUS

C. SAMPLE EXTRACTION AND PREPARATION

D. SAMPLE ANALYSIS AND QUANTITATION

E. QUALITY ASSURANCE

A.1. SCOPE

A procedure is described for the determination of polychlorinated biphenyls (PCBs) in dry phthalocyanine blue pigments, or crudes, using gas chromatography with electron capture detector (GC/EC).

There are 209 possible PCB's. Their molecular formula is $C_{12}H_XCl_Y$, where:

X = 0 to 9 and Y = 10-X

In phthalocyanine blue pigments and crudes, only pentachloro - and hexachlorobiphenyls are determined since these are the only PCBs found in these pigments.

Quantitation is effected by the external standard method. In phthalocyanine blue pigments and crudes, the isomeric structures of pentachlorobiphenyl and hexachlorobiphenyls found are unkown. The quantitation of these PCBs is based on the

response factor of a single pentachlorobiphenyl standard and a single hexachloro standard which are chosen.

Since GC/EC is not an absolute identification technique, this method can only be used to screen samples. It is recommended that samples having PCB levels above the allowed limits, as determined by this method, be analysed by CAPILLARY GS/MS, in order to verify the presence and the amounts of PCB congeners in the Pigment.

A.2. PRINCIPLE

Phthalocyanine blue pigments and crudes are dissolved in concentrated sulphuric acid in a culture tube. The PCBs are extracted quantitatively by shaking with hexane. The hexane layer is removed after centrifugation and analysed by GC/EC.

Quantitation is by the external standard method using ^{63}Ni electron capture detector.

B. REAGENTS, STANDARDS, SAFETY, APPARATUS

B.1. Reagents and standards

B.1.1 Concentrated sulphuric acid (98%)

B.1.2 Hexane (Analar) (BDH)

B.1.3 Anhydrous sodium sulphate, granular (BDH)

B.1.4 Standard solution of DCMA-PCB mixture in hexane

This DCMA-PCB mixture is available from:

SUPELCHEM (UK) Ltd.
Shire Hill, Saffron Walden, Essex CB11 3AZ

Individual PCBs can also be purchased from the same company.

The DCMA-PCB mixture contains the following PCB congeners at the given concentrations in hexane.

PCB	Concentration ug/ml
2 - chlorobiphenyl	100
3, 3'- Dichlorobiphenyl	100
2, 4, 5 - Trichlorobiphenyl	10
2, 2' 4, 4' - Tetrachlorobiphenyl	10
2, 3' 4, 5' 6 - Pentachlorobiphenyl	10
2, 2' 3, 3' 6, 6' - Hexachlorobiphenyl	10
2, 2' 3, 4, 5, 5', 6 - Heptachlorobiphenyl	5
2, 2', 3, 3', 4, 4', 5, 5' - Octachlorobiphenyl	5
2, 2', 3, 3', 4, 4', 5, 5', 6 - Nonachlorobiphenyl	5
2, 2', 3, 3', 4, 4', 5, 5', 6, 6 - Decachlorobiphenyl	5

B.2 Safety

B.2.1 Sulphuric acid causes burns, avoid skin contact.

B.2.2 PCBs are suspected animal carcinogens. Avoid skin contact with these compounds and their solutions. Perform evaporation and other manipulations in a hood.

B.2.3 Hexane is extremely flammable. Use in a hood and away from ignition sources.

B.3 Apparatus

B.3.1 Gas chromatograph equipped with a ^{63}Ni detector.

B.3.2 DB-608 (Megabore) 0.83 micron (Available from Jones Chromatography, New Road, Hengoed, Mid. Glamorgan CF8 8AU Wales.

B.3.3 Wrist action shaker

B.3.4 Centrifuge, capable of working at 2,500 rpm.

B.3.5 Glass boiling beads - 4.0mm diameter.

B.3.6 Culture tubes - 125 x 16mm, 15mls. (e.g. BDH, Pyrex 267/0125/02)

B.3.7 Pasteur capillary pipettes

B.3.8 Assorted laboratory glassware

C. SAMPLE EXTRACTION AND PREPARATION

All glassware should be precleaned with sulphuric acid and should be free of abrasions. Heating glassware to 400°C eliminates interfering contaminants.

C.1 Extraction and preparation of Phthalocyanine Pigments and Crudes

C.1.1 Weigh approximately 0.25g (to the nearest milligram) of sample and transfer into a 15ml culture tube.

C.1.2 Add about 5 boiling beads and 5mls of concentrated sulphuric acid to the culture tube. Secure tube to the wrist action shaker, place in a horizontal position and shake for 15 minutes at a rate of about 150 jolts per minute.

C.1.3 **Remove from the shaker. With the tip of a narrow stirring rod, remove a small portion of the sample and examine under a microscope to ensure complete dissolution. If pigment particles are still visible, shake for an additional three minutes and recheck for total dissolution. Repeat shaking until all pigment particles are in solution.**

C.1.4 **Remove tube from shaker and add 3mls of hexane. Replace tube on the shaker and shake for 5 minutes at about 150 jolts per minute. Remove from shaker.**

C.1.5 **Centrifuge at about 2500 rpm for 5 minutes. If separation does not occur, shake gently by hand for about 10 seconds and recentrifuge.**

C.1.6 **Using a pasteur pipette, transfer the hexane layer into a 25ml beaker containing at least 1.5g of anhydrous sodium sulphate. (Alternatively, the sample may be dried by passing it through a small column of anhydrous sodium sulphate). Repeat the hexane extraction two additional times using 2.5ml each time. Combine extracts, mix well and dilute to 10ml with hexane in a volumetric flask.**

D. SAMPLE ANALYSIS AND QUANTITATION

D.1 Instrumentation

Varian Model 3300 gas chromatograph, or equivalent, equipped with ^{63}Ni electron capture detector. Other detectors which give similar results can also be used.

D.2 G.C. Conditions

Conditions for Capillary Column G.C.

Column: DB-608 (Megabore) 0.83 micron

Injection Port temperature	270°C
E.C. Detector temperature	350°C
Carrier gas	Nitrogen
Gas flow rate	30ml/min
Injection mode	Direct injection
Injection volume	3µl

Temperature Programme:

Initial temperature	140°C
Initial hold	2 minutes
Heating rate	8°C/min
Final temperature	270°C
Final hold	2 minutes

D.3 Calibration of the Instruments

D.3.1 Prepare a working standard solution by diluting 1ml of the purchased DCMA-PCB mixture to 50ml in a volumetric flask. This standard is stable for at least six months if kept refrigerated.

D.3.2 Optimise the G.C. and integrator conditions by injecting approximately 3 microlitres of the working standard solution.

D.3.3 Dilute the concentrated DCMA standard solution with hexane by the following factors: 1 to 25ml, 1 to 50ml, 1 to 100ml, and 1 to 500ml. Determine the linearity of the electron capture detector by injecting approximately 3 microlitres of each of the solutions and plotting the response versus the amount (nanograms) injected. A straight line denotes linearity. (Figure 1).

D.3.4 Typical retention times of PCB congeners in the DCMA standard, using the packed column are as follows:

Time (sec) approx.	PCB
271	Monochlorobiphenyl
455	dichlorobiphenyl
510	trichlorobiphenyl
597	tetrachlorobiphenyl
650	pentachlorobiphenyl
783	hexachlorobiphenyl
898	heptachlorobiphenyl
1060	octachlorobiphenyl
1108	nonachlorobiphenyl
1150	decachlorobiphenyl

Chromatogram for 1 to 25ml dilution (figure 2)
1 to 50ml dilution (figure 3)
1 to 100ml dilution (figure 4)
1 to 500ml dilution (figure 5), dilutions are shown.

D.3.5 Calculate a response factor, F, for the PCB's.

$$F = \frac{[\text{Response (area count)}] \times (\text{Attenuation})}{[\text{Volume injected } (\mu l)] \times [\text{Conc. } (ng/\mu l)]}$$

D.4 Selection of PCB Standards

D.4.1 In phthalocyanine blue pigments and crudes, GC/MS analysis has shown the presence of several pentachlorobiphenyls and hexachlorobiphenyls. Most pentachlorobiphenyls were found to elute prior to the hexachlorobiphenyls,

however, some were found to elute after certain hexachlorobiphenyls. Therefore, retention time alone is not adequate for identifying all the peaks as penta - or hexachlorobiphenyls. It has also been shown that even isomeric PCBs may differ considerably in their response factors.

Since the structure of all the pentachlorobiphenyl and hexachlorobiphenyls found in phthalocyanine blue pigments in not known, the accuracy of the results is curtailed due to the variation in their response factors.

In this method for the purpose of consistency among laboratories, only one pentachlorobiphenyl and one hexachlorobiphenyl standard is used. All peaks having retention times near the 2, 3', 4, 5', 6 - pentachlorobiphenyl standard are calculated based on the response factor of this PCB. All peaks having retention times near the 2, 2', 3, 3', 6, 6' - hexachlorobiphenyl standard are calculated based on the response factor of this PCB. The exact retention time windows are specified in section D.5.2.

D.4.2 It is recommended that samples found to exceed the allowed limit of PCBs as determined by this method, be analysed by Capillary GC/MS in order to identify and quantify more ACCURATELY the total PCB content. The higher values may be due to interfering compounds with the same retention time as PCBs.

D.5 Sample analysis and calculation

D.5.1 Inject approximately 3 microliters of the sample solution obtained in steps C.1.6. If the response is outside the linear range of the detector, dilute or concentrate the extract to bring the response within the linear range. Concentration of the sample must be done over low heat under a stream of air or nitrogen.

D.5.2 For phthalocynanine blue pigments and crudes, record the response (peak area or height) of all the peaks eluting from 0.2 minutes prior to the 2, 3', 4, 5', 6 - pentachlorobiphenyl standard up to 0.3 minutes prior to the 2, 2', 3, 4, 5, 5', 6 - heptachlorobiphenyl standard.

The peaks eluting up to 0.3 minutes prior to the 2, 2', 3, 3', 6, 6' - hexachlorobiphenyl are calculated as 2, 3', 4, 5', 6 - pentachlorobiphenyl.

The peaks eluting from 0.2 minutes prior to the 2, 2', 3, 3', 6, 6' - hexachlorobiphenyl standard up to 0.3 minutes prior to the 2, 2', 3, 4, 5, 5', 6 - heptachlorobiphenyl standard are calculated as 2, 2', 3, 3', 6, 6 - hexachlorobiphenyl.

Obtain the concentration (ng/µl) off each PCB by dividing the sample response by the response factor (F) of the corresponding PCB standard and by the volume of sample injected (ml) as shown below:

$$ng/\mu l = \frac{\text{Area Count or Peak height}}{(F) \times (\text{microliters injected})}$$

Add the concentrations (ng/µl) of all the PCBs found and calculate the total PCB content (ppm) of the sample as follows:

$$\frac{[\text{Sum of PCBs found (ng/µl)}] \times [\text{initial volume of sample (ml)}]}{[\text{Sample weight (g)}] \times [\text{dilution or concentration factor}]}$$

D.5.3 Example

If PCB Concentration = 0.5 ng/µl
Initial Volume = 25 millilitres
Weight of sample = 0.5g

(a) Concentration of sample volume - 25ml to 5ml

Then PCB content = $\frac{0.5 \times 25}{0.5 \times \frac{25}{5}}$ = 5.0 ppm

(b) Dilution of sample volume - 1ml to 25ml

Then PCB content = $\frac{0.5 \times 25}{0.5 \times \frac{1}{25}}$ = 625 ppm

E. QUALITY ASSURANCE

This programme involves the validation of the procedure described above. This includes GC/MS analysis, determination of the efficiency of recovery from spiked samples and the analysis of blind and spiked samples. Repetitive analysis of a retained sample (blind sample) should be one of the tools used to train new analysts and to

check the performance of already trained analysts. Spiked samples should also be analysed periodically. Although spiking cannot be done by adding known amounts of PCBs within the ultimate pigment particle, the experiments are still necessary in order to prove that once the PCBs are released from the pigments by dissolution, they are carried throught the other steps quantitatively.

E.1. Verification of the method

Whenever a significant process change has occurred, including a change in the raw material, or the amount of PCBs found exceeds the allowable limit, the type of sample affected should be analysed by capillary GC/MS to demonstrate that no PCBs other than the ones previously present, are being generated by the process change and that the distribution is still consistent with previous data.

E.2 Quality Assurance (Blind sample)

A sample typical to each of the manufactured pigment should be available. The sample must be analysed by trained analysts, as a blind sample, once every 50 samples or at least once every six months. The sample should also be used to train new analysts until they develop a sufficiently good level of analytical expertise.

E.3. Spiking Experiments

Several spiking experiments with the standard PCB mixture, or with other PCBs, depending on the pigment analysed, should be done when the methods are first established. After that, these experiments should be repeated whenever

significant procedure changes have to take place. In the absence of any significant changes, such experiments are to be done every 50 samples, but not less than once every six months.

Samples Analysed

1. POLISH CRUDE*
2. POLISH CRUDE (A)
3. POLISH ALPHA (α)
4. SAMPLE 4
5. SAMPLE 5.1
6. SAMPLE 6
7. SAMPLE 9
8. SAMPLE 26
9. SAMPLE 32A
10. SAMPLE 38
11. SAMPLE 40
12. SAMPLE 42
13. SAMPLE 46
14. SAMPLE 48
15. SAMPLE 49
16. SAMPLE 50
17. SAMPLE 52
18. SAMPLE 26 (A)

Results of Analysis

The method gives an excellent separation of all the PCBs present in the test mixture, and a sample 'spiked' with 0.4 ppm of the test mixture clearly showed the presence of all the components. A significant amount of polychlorobiphenyls was only found in two of the samples. - Polish Crude A and Sample 10.

In each case, this appeared to be a hexachlorobiphenyl, but this would require confirmation by GC/MS.

Many of the samples had minute traces which could be hexachlorobiphenyls, but in such small quantity that they would be difficult to confirm or estimate.

Conclusions

The method should be quite satisfactory for screening copper phthalocyanines for the presence of polychlorobiphenyls.

References

1. An analytical procedure for the determination of polychlorinated biphenyls in Dry Phthalocyanine Blue, Phthalocyanine Green and Diarylide Yellow Pigments proposed by the Dry Color Manufacturers Association (1980).

2. M. Uyeta, S. Tawe and K. Chikazawa, Bull. Environ. Contam. Toxicol. 16. 417-421, 1976.

Appendix 5

General Manufacturing [illegible] type of [illegible] plant given by

[illegible] Solvent [illegible]

1. INTRODUCTION.

This is a general [illegible] solvent. The intended function of these is [illegible] that they are [illegible] intended and give rise to various side reactions [illegible] those is the production of small amounts of [illegible] by-products. These are carcinogenic and many countries will not import copper phthalocyanine pigments unless the producer can certify by direct analysis that the products on offer contain less than a specified content of PAH's. This content is very low -parts per million- and special methods of analysis are called for to detect such amounts. In the production of phthalocyanine pigments on relatively large scales (hundreds of tonnes per year) which meet this specification, manufacturers will need to meet the problems from the outset.

It will clearly be sensible to [illegible] solvent and operating facility which minimise the amount of PAH [illegible] in the first place, for even though they can be separated [illegible], the manufacturer is then faced with their safe [illegible]. [illegible] safer and better [illegible] has guided the present [illegible].

Solvents which can be used in [illegible] boiling kerosene fractions and [illegible].

The process method which follows [illegible] applies to all the solvents mentioned, but will inevitably vary somewhat from solvent to solvent and also with the design of the plant used. In particular, the overall time taken for the reaction will depend very much on the heating capacity of the oil circulating system in the reactor jacket to raise the temperature [illegible] values.

The layout of a suitable plant [illegible] is given in the diagram on page [illegible].

[illegible] safety notes [illegible] operation of the [illegible]

2. PROCESS METHOD.

All weights are for a yield of [illegible] using a [illegible] litre reactor provided with stirrer and an integral liquid heated jacket. The ancillary vessels and equipment are shown in the accompanying diagram.

(i) Charge to the raw materials [illegible]

425 Kg PHTHALIC ANHYDRIDE

800 Kg UREA

102.5 Kg anhydrous [illegible]

or

preferably, [illegible]

GOGGLES AND DUST MASK MUST be worn [illegible]

(ii) Charging solvent and [illegible]

After checking that there is no water [illegible] sample from the bottom [illegible]

Charge into the [illegible] below

770 Kg [illegible]

This quantity is based on the general rule that the solvent : crude dye ratio should be 2 : 1. The exact amount of solvent needed will vary from solvent to solvent, depending on the solubility of the product / solvent mixture during the course of the reaction, especially during charging and at the end of the reaction. The quantity should be high enough at this stage to allow easy removal of the material from the reactor, but the use of too much solvent will increase the cost of it's recovery. Although high boiling solvents tend to need [illegible] ratios of 2 : 1, but this can be lowered by using [illegible]

Catalyst and agent for suppressing [illegible]

Because of the importance of these [illegible] crude blue, they should be weighed [illegible] charged by him to the reactor, after [illegible] solvent is present in it. He should [illegible]

The amounts of catalyst and anti- [illegible]

2.4 Kg AMMONIUM [illegible]

and

7.7 Kg SODIUM [illegible]

The anti- substituted biphenyl agent [illegible] the formation of nitro biphenyls and [illegible] aromatic solvents such as [illegible] trichlorobenzene are used. [illegible] aromatic content are used as [illegible] low aromatic content are used, [illegible] less than satisfactory quality in [illegible] the pigments prepared from them by [illegible]

(iii) Charging the reactants [illegible]

With some solvents, [illegible] hazard from electrostatic charges [illegible] are travelling down into the reactor [illegible] of earthing straps on the discharge [illegible] nitrogen so that the oxygen content [illegible] purging is not, however, [illegible] solvents such as nitrobenzene, [illegible] is used as the solvent.

Whether nitrogen purging is [illegible] when the reactants are run into it [illegible] electric motor on the stirrer gives [illegible] the charge at any time.

Nitrogen can be used to [illegible] point to the reactor and [illegible] reactor at the end of the [illegible]

After checking that all raw materials have been transfered to the reactor from the hopper the lid of the reactor must be closed and the valve leading from the reactor to the scrubbing system opened. The scrubbing system should be able to remove 99% of the carbon dioxide and ammonia released during the manufacturing reaction.

(iv) Reaction Stage.

As mentioned above, the heating [illegible] actual heat output of the heater [illegible] heat losses in it, but in a well [illegible] cycle

Temperature of oil in reactor jacket [illegible]

1.	kept at	150°C	until	[illegible]
2.	lowered to	105°C	until	[illegible]
3.	raise to	125°C	until	[illegible]
4.	raise to	140°C	until	[illegible]

NOTE

When the reactants have [illegible] the reactor.

5.	raise to maximum	until	[illegible]
6.	hold	until	There is a large rise in temperature. This indicates the completion of the reaction and happens after [illegible] hours. The start stage in the water bath [illegible]

The batch is held in the [illegible] reaction.

(v) Transfer of products from reactor.

The products should transfer to the vacuum drier under gravity. If there are any difficulties because the fluidity of the reaction mass is too low, transfer can be assisted by pressurising the reactor with nitrogen, but after some experience with the plant and adjustment of the solvent: crude blue ratio this should not be necessary.

The heal left in the reactor should not [illegible].

SAFETY GLASSES SHOULD BE WORN WHEN [illegible].

Set the vacuum drier in operation, [illegible] the recovered solvent to the solvent storage tank for re-use.

(vi) Aqueous acid purification

This should be carried out in glass-lined or ceramic tiled vat of [illegible] litres capacity, provided with a stirrer and heater. Mild steel vats should not be used.

Charge the vat with

2,700 l WATER [illegible].

Add carefully, with mild stirring,

270 Kg Conc Hydrochloric Acid.

This will produce a 5-10% solution of dilute acid.

SAFETY SPECTACLES SHOULD BE WORN AT ALL TIMES DURING AQUEOUS ACID TREATMENT.

WHEN CHARGING THE CONCENTRATED ACID, GOGGLES AND PVC GLOVES SHOULD BE WORN BY THE OPERATOR.

With vigorous stirring, carefully add the [illegible] copper phthalocyanine crude blue from the vacuum drier. [illegible] to form in the vat a uniform, fluid suspension of crude blue in [illegible].

Stir for 15 minutes.

Then heat the contents of the vat to 90-95°C with good stirring and continue for 2 hours.

(vii) Pressing , washing and drying.

Transfer the suspension of crude blue, still at 90-95°C, to the filter press.

SAFETY GLASSES MUST BE WORN.

Wash in the press with hot water at 90°C for 1 hours

Check that the washings are then neutral to universal pH paper and are free of chloride ions, by the use of silver nitrate solution

When these tests are satisfactory, air blow the press and drop the purified crude blue into boxes for drying.

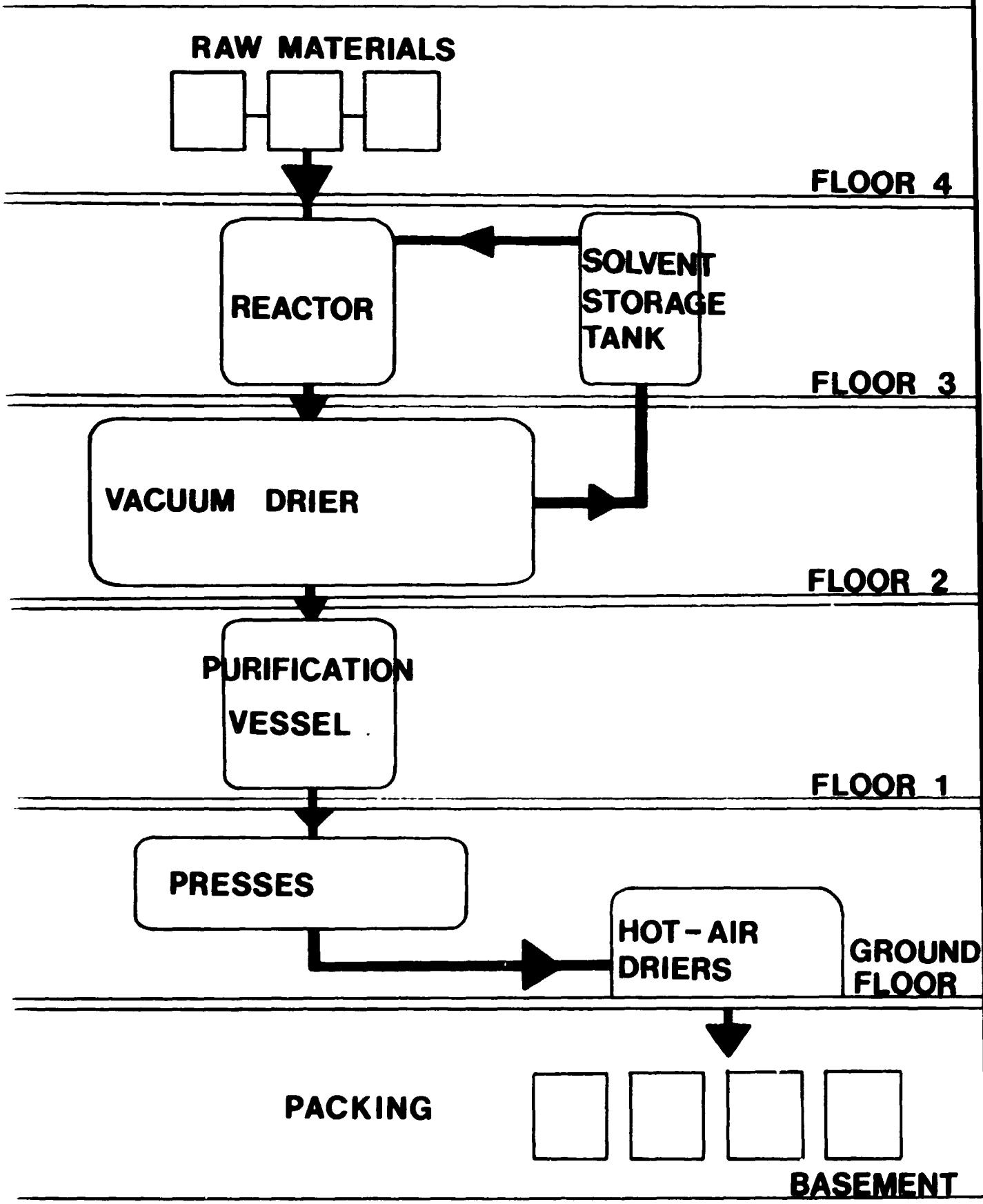
Transfer to a hot air stove drier at 80-90°C until completely dry

Then discharge into drums, seal and weigh.

Yield 385 Kg.

Purity not less than 95%, approximately

August 1991.



LAYOUT OF COPPER PHTHALOCYANINE CRUDE BLUE PLANT, USING THE SOLVENT UREA PROCESS.

Appendix 6.

The conversion of crude blue copper phthalocyanine into pigmentary form.

Laboratory Screening method for assessing the suitability of crude blues produced by various methods for conversion to pigmentary form.

The preparation of copper phthalocyanine [illegible] the first step in the making of copper phthalocyanine pigments. The properties of the crude blue prepared by any process must be tested by converting it to pigmentary form when assessing the value of the preparative process. This report sets out the laboratory screening methods for doing this.

The characteristics of copper phthalocyanine crude blues which influence their colouristic performance when converted to pigmentary form are:

1. Crystal size and shape.

Crystal shape can have a profound effect on the crystal-size reduction step, which is an essential feature in any pigment preparation process. Ideally, sub-micron crystallite sizes are required for good pigment colouristic performance.

In a crystal-size reduction [illegible] the most common are ball milling or [illegible]. Given the same conditions, the shape of the crude blue particles is much more important than the actual crystal size. Long, very thin needles, the finer the better, are the ideal shape since these easily break across their length. Crude blues made using weakly crystallising, high-boiling aromatic solvents such as o-nitrotoluene are often of this type.

The most undesirable crystal shapes are thick cubes or brick-shaped crystals, for obvious reasons.

Thin cube-shaped crystals are usually characteristic of crude blues produced in organic solvents such as xylene or the Isopar range of solvents. Thick, brick-shaped [illegible] strongly crystallising, high boiling, aromatic [illegible] trichlorobenzene are used.

The colouristic properties of [illegible] affected by the crystal [illegible] in inks, [illegible]

A crystal-size reduction step based on a shearing mechanism is the only one which picks out such differences in colouristic performance. Any strong acid treatment (conc 98% sulphuric acid or chlorosulphonic acid) either in acid pasting (total solution of the crude blue) or acid swelling (partial dissolution) destroys any difference which crystal size and shape would otherwise have on the colouristic performance of pigments so prepared.

For this reason crystal size reduction by any acid treatment process cannot be used in any screening process.

2. Chemical Impurities.

These are impurities on the surface of the crude blue, especially if organic. They are often called 'organic tars' and include all substituted biphenyls as well as organic oxides and peroxides.

According to a a patent claim of [illegible] synthesis using a mixed aromatic/aliphatic solvent [illegible] produces a much cleaner crude blue and hence cleaner phthalocyanine blue pigments.

The problem associated with surface organic tars is the tendency of such tars to melt from the heat produced in the particle reduction by shearing mechanisms. This causes fusion of the [illegible] crystallites, and alters the particle size and [illegible] of the pigment. Such fusion is very difficult to eliminate [illegible] the use of a solvent treatment, and the tinctorial [illegible] of the pigment is adversely affected.

Another detrimental side-effect of 'organic tars' is that they tend to stabilise the α-form crystal, which, while [illegible] advantageous in the preparation of α-form pigments, is detrimental when preparing the β-form crystal modification.

Processes occurring in the crystal size reduction step by a shearing Mechanism

All copper phthalocyanine crude [illegible] are basically composed of [illegible]

During crystal size reduction by shearing, the crystals are reduced in size to much smaller, pigmentary crystallites and when the crystallites reach a critical size, the β- form is converted to the α-form. It is normal to mill until the milled material is composed of mixture of 60% α- and 40% β- form and the overall crystallite size is uniformly sub-micron.

An unfortunate side-effect of the shearing process is that the surfaces of α- and β-form crystallites become extremely highly charged, especially the α-form. This causes varying degrees of both agglomeration (crystallites joined together at planar surfaces in a relatively weak manner) and the more serious phenomenon of aggregation, in which the crystallites are bonded together, surface to surface, in a very powerful manner.

Surface fusion by organic [illegible] enhanced and amplified agglomeration and aggregation and makes the groups of crystallites formed, much more difficult to break down by a subsequent solvent treatment process. The reason for aiming to obtain milled material containing 60% α- and 40% β-forms is to facilitate the conversion of any α-crystallites to the β- form, during a subsequent solvent treatment. The 40% β- content acts as a source of 'seeds' which speeds up the α- to β- conversion and produces optimum colouristic performance in the pigment.

A slow α- to β- conversion, on the other hand, generally produces poor colour strength and dirtiness, as well as undesirable shade characteristics.

Normally, the milling process is followed by a solvent treatment step, especially in the preparation of pigment with a 40% β-form content. Solvent treatment aids both 'crystal growth' and 'cemented aggregation'. Any [illegible] of the milled material dissolve in the organic solvent and then [illegible] on β-form crystallites, thus [illegible].

This is a classical "Ostwald Ripening" mechanism by which the pigment undergoes an energy transformation, from the very reactive, unstable α-form crystals to the lower energy, relatively inactive and stable, β-form crystal modification.

Preparation of α-form pigments

To make pigments with as high an α- content as is possible, for [illegible], it is necessary to use a chlorinated [illegible] which stabilises the α-crystal modification, [illegible] transformation to the β-form [illegible] organic solvents.

It is still necessary to use a crystallite reduction step by a shearing mechanism, in order to highlight differences in the crude blues produced using various organic solvents in the urea-solvent process.

The solvent used in the solvent treatment step after the ball-milling operation, serves to de-agglomerate and especially to de-aggregate the pigment particles. These two effects are much more severe when making the very high energy highly surface-charged α-crystal form and their removal, as far as possible, improves the dispersibility of the pigment. This is of vital importance in some applications, especially in plastics systems.

In the crystal size reduction step by [illegible] mechanism such as ball milling, the milling can be carried out either in the presence or absence of inorganic salts such as sodium [illegible]

In screening tests designed to assess the relative suitability of crudes produced by various processes for conversion to pigmentary form, it is preferable to avoid the use of inorganic salts, since these can themselves have critical effects on the severity of agglomeration, aggregation and the surface fusion [illegible] by 'organic rare'.

The choice of the solvent to use after the milling process is extremely important , since the demands on it are severe, many and varied.

The solvent must be able to accomplish [illegible] within:

(i). De-agglomerate, de-aggregate and [illegible] the milled material in order to produce a finely dispersed [illegible] pigment.

These are essential preliminary [illegible]

(ii) α-to β- conversion of the [illegible] in the milled materials when required.

The crystallising power of the solvent must be sufficiently weak to achieve (i) and (ii), without inducing large amounts of crystal growth, thereby producing a pigment with a large and broad particle size range, thus giving a poor colouristic performance.

A commercial consideration, which can be the most important one, is that the solvent should be easily and economically recoverable, thus avoiding environmental problems and unacceptably high manufacturing costs. Butanol usually meets this requirement.
Most polar solvents satisfy points [illegible] but in order [illegible] necessary to use an azeotropic [illegible] 15%). The solvent can then be recovered as the azeotrope and re-cycled.

Thus a screening process for the preparation of pigments of either the β-form from copper phthalocyanine crude blues prepared by the solvent urea-process is usually based on a combination of:

Salt-free ball milling,
followed by an isopropanol/water azeotrope solvent treatment.

In the preparation of β-form pigments or unsubstituted copper phthalocyanine crude blue is used. However in the preparation of β-form pigments, a chlorinated copper phthalocyanine crude blue is used with a the degree of chlorination from [illegible] depending on the application demands.

Laboratory Method for preparing a pigment [illegible] by Ball-Milling/Azeotrope Solvent Treatment.

The first step is:

(i) Ball-Milling

A 1 litre, ceramic laboratory ball [illegible] rotatory type, is used. The charge is stainless steel balls approximately 10mm in diameter and flat-based, [illegible]. These ceramic or glass balls should not be used [illegible] steel balls.

These must first be 'layed' to maximum efficiency. Grinding [illegible] and shearing against crude blue lying in the pitted holes in their surfaces [illegible] and slide over each other with a high [illegible] shearing occurs between the pigment filled in the interstices of the steel balls and that in the pitted [illegible] other steel balls.

The charge for a 1 litre mill is:

2,100 Stainless Steel balls [illegible]

900 [illegible]

100 g crude blue

The charge should fill [illegible]

The function of the flat- head rolling pins is to prevent caking on the walls of the ball mill. An iron ball mill should not be used as there is a risk of the formation of iron phthalocyanine with adverse results on colouristic performance of the pigment.

'Ageing' of new steel balls is done by carrying out several preliminary 'blank' millings before routine testing is begun.

Another method is to put some of the salt from the old ball mill along with the new steel balls and run the ball mill for a short time. Remove the ball charge from the salt with a sieve and remove any adhering salt from the surface of the charge and the walls of the mill. Examine the surface of the steel balls is sufficiently roughened, by examining them under a microscope.

Laboratory Process for the preparation of high purity phthalocyanine pigments

(1) Ball Milling Step

If the crude blue is [illegible]

To prepare an [illegible] pigment, [illegible] chlorine, depending on the [illegible] textiles) in which the pigment is [illegible]

Also, add to the charge 1 ml diethylene glycol per gram unit crude from the mill-charge.

This acts as a milling aid and helps [illegible] material with the desirable content of [illegible] Mill for approximately 12 hours.

Then separate the milled copper phthalocyanine [illegible] using a coarse sieve.

The second step is:

(ii) Solvent Treatment of the Milled Material

a. Making β-form pigment

For this process use a 1 litre [illegible] equipped for stirring, refluxing and distillation.

Put in the flask:

300g isopropanol. [illegible] the milled crude blue to produce a fine pigment of [illegible]
Reflux for 4 hrs, with continuous stirring.
Cool to room temperature and then carefully add 60ml of water.
Stir for ½ hour, then remove the solvent by distillation.
The solvent recovered is an isopropanol/water azeotrope containing about 15% water. It is stored for use in the next solvent treatment. Use the same procedure as given for use with fresh isopropanol.

The temperature at the start of the distillation is 80°C. This rises gradually as the azeotrope is removed. When the distillation temperature reaches 82° the distillation is almost complete.
Cool to room temperature and then add 10% hydrochloric acid to adjust the pH to between 1 and 2 to remove any residual aniline from the surface of the pigment.
Next raise the temperature to 80°C and stir for 1 hour as a further purification.
Cool to room temperature and filter.
Wash until neutral and dry in a fan oven at 80°C.
Do not use a higher drying temperature than 80°C as this can cause pigment aggregation and a reduction of the pigment strength.

b. Making α-form pigment

When preparing an α-form pigment it is necessary to use a partly chlorinated crude blue. The chlorine acts as a crystal growth inhibitor to prevent the α-crystallites against the β-crystallites during the solvent treatment with an organic solvent, which converts the crude blue to the pigment. The chlorine content should be between 0.5 and 1.0 atoms per molecule. The latter is equivalent to about 2% by weight of chlorine in the phthalocyanine.

it is very important to note that the chlorine can only act as an α-form crystal stabiliser and a stabiliser against excessive crystal growth in the presence of powerful organic solvents, when the chlorine atom occupies the 4 -position in the copper phthalocyanine molecule.

Thus, in a multichlorinated molecule, the chlorine atom should be present in the 4 - position, on each of the [illegible] benzene nuclei in the copper phthalocyanine molecule. In any other position the chlorine atom is ineffective as a stabiliser. For this reason, chlorination of the partly chlorinated Crude Blue is normally carried out in the melt of phthalic anhydride and the sodium salt of 4- [illegible] sulphonic acid. The smaller the amount of the latter, the lower the degree of the chlorination product. The synthesis is carried out using the normal organic solvent process. If a mixture of 1 mole of the sodium salt of 4-sulphonated phthalic acid and 3 moles of phthalic anhydride is used, the product obtained will be monosulphonic copper phthalocyanine crude blue. For most application systems less than 6% chlorine is sufficient, but in some flexible formulations, to give the necessary heat-stability, and for the pigmentation of some synthetic fibres, it is necessary to use a 6% chlorine content in the crude blue.

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