KN-47-51 "MONASTRAL" FAST BLUE LB: LABORATORY PROCESS STUDIES By: F. F. Ehrich 2/46 - 12/47

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

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LABORATORY PROCESS STUDIES

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

PROGRESS REPORT

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Period Covered: February, 1946 - December, 1947.

SUBMITTED BY: F. F. Ehrich DATE SUBMITTED: January, 1948

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I. INTRODUCTION

Phthalocyanine synthesis studies were initiated by the Newark Research Group in November, 1945. The initial studies were concerned primarily with the development of a process for the synthesis and finishing of chlorine-free CPC ("Monastral" Fast Blue B) for the proposed plant. Study of the synthesis of the chlorine-free type of CPC was discontinued in the interests of producing a "can-stable" variety of copper phthalocyanine and accordingly, an investigation of the synthesis of a partially chlorinated variety of CPC, "Monastral" Fast Blue LB (LB/CPC) by the phthalic anhydride-urea route was started in February, 1946, utilizing the background experience embodied in I.C.I. Technical Reports.

The major problem was the production of a "can-stable" type of copper phthalocyanine, of suitable strength, and possessing tinctorial qualities essentially equivalent to those of the current standard pigment prepared from acid-pasted, semi-chlor CPC synthesized by the phthalonitrile route. Originally, the accepted standard, quality-wise, was BT-172-D toner, which material has since been shown to be tinctorially inferior to BP-173-D despite the fact that it is derived by acid-pasting from the same source crude material as is BP-173-D. The latter product (BP-173-D) has been found to be the best of the DuPont standards in tinctorial properties and accordingly has been established as the goal product in the more recent work.

Solvent-ball-mill grinding was specified for the particle-size reduction step for the purposes of the proposed plant, in contrast with the less novel and more expensive acid-pasting and salt-milling techniques. The use of the solvent-milling procedure presented quality problems, to which it was necessary to devote a considerable portion of the studies reported here.

The present report covers laboratory investigations of the process development from February, 1946 to December, 1947, and to some extent represents process studies suggested by semi-works operations which were started in August, 1946. The work summarized here was concerned largely with the LB/CPC condensation reaction and "sulfation" step and, to a lesser degree, with subsequent processing steps. Only certain special aspects of the processing steps of ball-milling, and acid and alkaline extractions are covered in the present report. The major portion of the work done in this laboratory on the ball-milling, drying, and the acid and alkaline extraction steps, as well as additional information regarding lake preparation following the LB/CPC synthesis will be presented in subsequent reports by other members of the phthalocyanine research group.

The preparation of the 4-chlorphthalic acid intermediate is dealt with, in another report (see references).

The considerations presented here represent information acquired through various stages of the development process, and all contribute to some greater or lesser extent to the laboratory process described in Appendix I. Some of the information presented is no longer pertinent to the proposed plant process but is included in the interests of completeness.

II. SUMMARY AND CONCLUSIONS

A procedure for the laboratory synthesis and finishing of "Monastral" Fast Blue LB of satisfactory strength and tinctorial properties has been set up (Appendix I). Alternative procedures are described.

"Monastral" Fast Blue LB prepared in the laboratory by the phthalic anhydride-urea process, employing the "sulfation" step, and solvent-grinding for particle-size reduction, is strong in extension, superior in hue to present duPont standard commercial semi-chlor CPC toner BT-172-D, and is a close hue match to standard "Ramapo" Blue BP-173-D.

The following factors have been shown to be significant in their effect on the tinctorial properties of LB/CPC finished by solvent-grinding.

1) Synthesis
   - a - Effective agitation is necessary to permit optimum distribution of the chlorine in the final product and to the attainment of optimum tinctorial properties.
   - b - Choice of reaction medium: Trichlorbenzene invariably yields superior products, quality-wise, to those obtained in kerosene.
   - c - The presence of iron, whether derived from the starting ingredients or from the reaction equipment, gives rise to undesirable pigment quality when the synthesis is conducted in kerosene.
   - d - Quality of the crude 4-chlorphthalic acid: The use of the free acid, rather than the sodium salts of the acid, insures a more homogeneous reaction slurry and, therefore, better chlorine distribution throughout the reaction mass.
   - e - The presence of more highly chlorinated phthalic acid derivatives contributes to greenness of the product.

2) Conditioning (Crystal-Phase Considerations)
   - a - "Sulfation": The sulfation process permits the use of solvent grinding as a particle-size reduction method consistent with the production of good quality LB/CPC.

3) Extraction
   - a - Solvent extraction employing acetone or trichlorbenzene removes a green impurity not removable by aqueous acid or alkaline extractions. The resulting pigments are superior, tinctorially to their unextracted counterparts.

4) Grinding
   - a - The presence of kerosene residues in the crude pigment hinders grinding in 91% isopropanol. Acetone (99.5%) grinds are less affected.

III. DISCUSSION

1 - Constitution and "Can-Stability"

In the preparation of copper phthalocyanine by the phthalic anhydride urea process, the substitution of 17.3 mol percent of 4-chlorphthalic acid for an equivalent amount of phthalic anhydride results in the formation of a partially chlorinated blue phthalocyanine containing approximately 4.1 percent of organic chlorine. The product is designated as "Monastral" Fast Blue LB in contrast with the chlorine-free material, "Monastral" Fast Blue B.

The introduction of chlorine into the phthalocyanine molecule contributes to "can-stability" (sometimes referred to as "crystal-stability") of the resultant pigment in paint systems in that it prevents a loss of tinctorial strength on exposure to hydrocarbon solvents and particularly to aromatic hydrocarbon solvents. The chlorine-free material (Blue B) suffers considerable strength loss (approximately 30%) when stored in typical paint solvents and this loss makes its use in such systems undesirable.

Statistically, the LB type of copper phthalocyanine (LB/CPC) can be regarded as a mixture of two different molecular species. Assuming the optimum distribution of the chlorine atoms, such a mixture (containing 4.1% of organic chlorine, i.e., 17.3 mol percent starting 4-chlorphthalic acid) would consist of 69.2 mole percent of mono-chlor copper phthalocyanine and 30.8% mol percent of chlorine-free copper phthalocyanine. Presumably, the gross stability exhibited by such a mixture is contributed primarily by the chlorinated portion of the mixture, inasmuch as the instability of the chlorine-free species is known.

The selection of a product containing approximately 4% chlorine, rather than one containing more or less of this element, was originally dictated by the necessity of obtaining a product of sufficient "can stability" to permit particle size reduction by ball milling in kerosene. With the use of alcohol rather than kerosene, for the ball milling step, such a large chlorine content is not necessary and it appears possible to reduce the chlorine content safely to some smaller value. The LB type pigment containing 4% chlorine is better in "can stability" than the current du Pont standard, which contains only 3% chlorine, and approaches mono chlor CPC (5.8% Cl) in stability.

2 - Tinctorial Properties of Solvent-Ground LB/CPC

Initial efforts to prepare LB/CPC by the phthalic anhydride-urea-kerosene route invariably gave rise to products tinctorially inferior to standard materials. Several causes for tinctorial deficiencies have since become apparent, some as a result of semi-works experiences, the presence of iron phthalocyanine in the kerosene synthesis being foremost. Efficient agitation during synthesis has been shown to be of importance in the attainment of good quality. Also, crystal-phase considerations have been found to be significant, as well as the reaction synthesis medium, quality of the crude 4-chlorphthalic acid used in

synthesis, the presence of impurities, the grinding medium, and the condition of the crude prior to grinding.

These possible causes of tinctorial deficiencies (dullness and greenness) of solvent-ground LB/CPC materials have been investigated and all have been shown to be significant in their effect on the tinctorial properties of the pigment. It should be emphasized at this point that the effects are cumulative and that the removal from the process of all the causes is necessary for the attainment of optimum pigment quality.

a - Extraction of Impurities

It appears that the dullness observed with many samples of solvent ground LB/CPC is associated to some degree with the presence of impurities in the pigment, since acetone extraction of samples of such material (in addition to usual extraction) has corrected some of this tinctorial deficiency. It has not been possible thus far to obtain the same improvement thru simple acid and alkaline extractions alone. The use of an acetone solvent-extraction, in addition to the standard acid and alkaline extractions, does not offer sufficient improvement in itself to overcome the objectionable dullness of solvent-ground LB/CPC but application of this extraction procedure to "sulfated" pigment synthesized with good agitation, even in kerosene, yields a product of goal quality.

b - Extraction of Kerosene-Ground Materials

The concept of hindered extraction due to the presence of kerosene is supported by the results of a series ball-milled in kerosene, with and without napthenic acid, and each type subsequently steam distilled with and without caustic soda. All samples were acid and ammonia extracted. The sample having both napthenic acid and sodium hydroxide was strongest and most intense, followed by the sample having sodium hydroxide but no napthenic acid. These results could possibly be explained by the emulsification of kerosene on the pigment particles by sodium naphthenate. Likewise, acetone extraction of kerosene-ground material prior to the acid and ammonia extractions gave a considerable strength and tinctorial improvement. The results indicate that prior removal of the kerosene from the kerosene-ground pigment permits a more efficient aqueous acid and alkaline-extraction due to better wetting of the pigment surfaces.

c - Alkaline Extractions

Extraction of an isopropanol-ground paste with 2.5% sodium hydroxide, in addition to the 2% sulfuric acid and 3% ammonia extractions, or the presence of sodium hydroxide (10% solution) during steam distillation of the crude, kerosene reactor slurry (with subsequent filtration and washing of the slurry), results in definite tinctorial improvement under laboratory conditions. Also, further washing of a crude (steam distilled in 10% sodium hydroxide solution as described above) with a concentrated ammonia solution, or a 1:1 conc. NH_4OH-water solution gives a colored filtrate and a subsequent improvement in tinctorial quality of the pigment. Ammonia extraction apparently offers some advantage even when applied subsequent to a 10% sodium hydroxide, and a 2% sulfuric acid extraction.

d - Trichlorobenzene Extraction of Crude LB/CPC

Extraction with hot trichlorobenzene of crude pigment made in kerosene, or synthesis in trichlorobenzene, followed by filtration of the reactor slurry and washing of the presscake with hot trichlorobenzene, results in a product significantly brighter than is obtained by the usual synthesis in kerosene

kerosene (without TCB washing). The improvement resulting from the washing with trichlorobenzene is apparently a consequence of the removal of an impurity from the crude pigment. 1-2% of a dark green compound containing iron (1-2% as Fe), copper (2.9 - 5.7% as Cu), chlorine (3.7 - 5.7%), and nitrogen (12.0 - 16.7% as N) is removed by the extraction. The available information suggests that the green material is a mixture of a chloro-iron phthalocyanine and a chloro-copper phthalocyanine containing more than one atom of chlorine per molecule. This view is supported by the fact that the spectrophotometric absorption curve (Appendix II) of a sulfuric acid solution of the material is very similar to that of a mixture of chloro-iron phthalocyanine (ClFePC) and a copper phthalocyanine of formula approximately Cl$_{14}$ CPC$_{16}$ and by the observation that the iron and copper phthalocyanine of the types in question are tinctorially dull, and are slightly soluble in trichlorobenzene. Formation of the green chlorine CPC's of the type in question is believed to result from:

(1) non-uniform distribution of the chlorophthalic acid during the synthesis, so that more than one molecule of the acid enters into the synthesis of a CPC molecule, thus yielding CPC containing more than one chlorine atom.
(2) the presence of di- and possibly tri-chloro compounds in the crude chlorophthalic acids used in the synthesis.

While the improvement resulting from extraction of the crude pigment with trichlorobenzene is appreciable, this step alone is not adequate to insure production of pigment of the desired brightness by the solvent grinding procedure unless prior crystal-phase change is effected (see later section.)

e - Particle-Size and Dullness

A relationship between particle size and dullness is suggested by the observation that solvent ground (isopropanol), and extracted samples of the strength level of the order of 10-15% greater than that of BT-172-D, are seldom dull, relative to BT-172-D, whereas corresponding samples only equal in strength to this standard are generally (but not always) dull. Dullness decreases with increasing strength development during grinding.

f - Iron Phthalocyanine

Current semi-works LB/CPC contains a quantity of non-acid (HCl) extractable iron, which, when calculated as iron phthalocyanine, represents approximately 3% of the weight of the pigment. The fact that approximately 65% of this iron remains after acid-pasting suggests that at least most of the iron is present as a phthalocyanine-type compound. The iron contamination apparently results from corrosion during preparation of chlorophthalic acid in the equipment (vat with steel cover and fittings) currently in use, and also from corrosion of the steel agitator in the synthesis vessel.

A green, acid-pastable pigment can be isolated from semi-works material by acetone extraction. The extracted material contains iron and exhibits a spectrophotometric curve similar to that of a known sample of iron phthalocyanine. (Appendix III)

A study of the relationship between the presence of iron phthalocyanine and the greenness and intensity deficiency of semi-works LB/CPC suggests that iron phthalocyanine is responsible for at least some of the tinctorial deficiency. BP-173-D, to which was added 3% by weight of iron phthalocyanine was green and dull against the unadulterated standard.

The presence of dichlorphthalic materials in the crude 4-chlorphthalic acid introduces an error in the interpretation of the analyses of the crude acid, the net effect being that for a given gross amount of organic chlorine in the crude acid, there is present a smaller proportion of chlorinated phthalic acid molecules available for Blue LB synthesis. Consequently, a greater proportion of chlorine-free CPC results.

j.--Agitation Requirements

On the basis of these considerations, it appears that those conditions which favor the most uniform distribution of the chlorine throughout the blue synthesis reaction mass, so that no more than one molecule of 4-chlorphthalic acid enters into each phthalocyanine unit, are necessary for the attainment of optimum pigment quality. The importance of good agitation during the condensation step is immediately obvious. The use of free 4-chlorphthalic acid instead of the mono-sodium salt of 4-chlorphthalic acid, will insure a more homogeneous blue reaction slurry, inasmuch as the free 4-chlorphthalic acid is molten (M.P. 150°C.) at reaction temperatures and its homogeneous distribution is probably more assured than in the case of the mono-sodium salt of the acid. It is presumed, therefore, that good mixing of the phthalic anhydride and of the 4-chlorphthalic acid, both of which are molten prior to the addition of the urea in the blue synthesis (165°C. in semi-works), will insure to some extent the optimum distribution of chlorine in the final Blue LB/CPC.

In an earlier effort to determine the comparative ease with which the mono-sodium salt of 4-chlorphthalic acid enters into the phthalocyanine reaction, an attempt was made to prepare a symmetrical tetrachlor CPC from a crude sodium acid 4-chlorphthalate which analyzed for 61.5% sodium acid 4-chlorphthalate, 28.2% sodium acid phthalate, and 10.3% sodium chloride. The resulting product analyzed for 11.7% chlorine (calc. 13.8% Cl), and was obtained in very poor yield (24.6%).

The preparation of a desirable quality of crude 4-chlorphthalic acid for use in LB/CPC synthesis appears in another report. (KN-47-48)

k - Crystal phase and Tinctorial Quality

Copper phthalocyanine exists in at least two crystalline forms as shown by X-ray diffraction patterns. Details of these studies will be presented in another report. Some useful correlations between crystal phase and tinctorial properties of copper phthalocyanine materials have been indicated by these x-ray studies. The tinctorially more desirable crystal form is referred to as the α phase and the less desirable form the β-phase. Crude chlorine-free copper phthalocyanine as obtained from a kerosene-phthalic anhydride - urea synthesis exists for the most part in the undesirable (tinctorially) β-phase, whereas crude monochlor CPC is synthesized for the most part as the α material. The LB type of CPC, which may be regarded as a mixture of the chlorine-free and monochlor types, consists primarily of the α phase. Phase change can be effected in a variety of ways, including heat treatment, exposure to aromatic hydrocarbon solvents, salt-milling, acid-pasting, "sulfation" etc. Monochlor CPC which exists primarily in the desirable α phase resists phase change by any of the above treatments, and in addition to an inherent "can-stability", therefore, does not display all the undesirable tinctorial properties of β-phase chlorine-free CPC.

Salt-milling and acid-pasting by the usual method convert β-phase chlorine-free CPC into the redder and more intense ∝ phase material, whereas solvent milling permits only a minor proportion of change to the ∝ phase, the resulting pigment, in the absence of other treatment effecting a phase change, being distinctly green and less intense, as would be expected of β-phase material. Solvent-grinding (alcohol) of ∝ phase material does not reconvert the pigment to the β-phase, although grinding in aromatic hydrocarbon solvents does effect such a phase change. It is readily apparent, that if optimum quality LB/CPC is to be obtained, the product need by primarily in the ∝ phase. The considerations described here explain in part the anomaly previously reported, i.e., the distinct greenness and lesser intensity of solvent-ground chlorine-free CPC materials in contrast with a solvent-ground semi-chlor CPC, despite our knowledge of the fact of increasing greenness with increasing chlorine content of CPC finished by the conventional acid-pasting method.

As a practical test of the relationship between crystal phase and tinctorial quality, and to determine whether the tinctorial deficiencies of BT-172-D as compared to BP-173-D (both are derived by acid-pasting from semi-chlor CPC) could be attributed in part to the soft-texture treatment given the former (toluene emulsified with TEA-C_{12} ester), semi-chlor CPC pulp (source material for BT-172-D) was soft-texture treated as above, and the product compared tinctorially to the flushed, untreated pulp. The very apparent intensity of the untreated over the treated material suggests the adverse effect of the soft-texture treatment, which effect may be related to a phase change which is known to occur when CPC materials are exposed to aromatic hydrocarbon solvents. (X-ray examination suggested that some phase change resulted from the treatment; the method is not sufficiently precise, however, to permit quantitative detection of less than approximately 10% of the β-phase in mixtures with ∝ structure material.)

3 - Synthesis Studies (Without "Sulfation")

The synthesis studies reported here were made for the most part prior to the use of the "sulfation" process as a conditioning step, and all quality references, particularly those of solvent-ground material, unless otherwise indicated are to be regarded accordingly, especially when compared to acid-pasted products. Quality comparisons between solvent-ground materials are directly comparable and essentially valid.

Three comparative series of LB/CPC syntheses (6 runs) conducted in glass reaction assemblies (essentially free of iron), and provided with good agitation (anchor-type agitator - approx. 200 r.p.m.) yielded the following informations:

a - Trichlorbenzene vs kerosene synthesis

Substitution of trichlorbenzene for kerosene as reaction medium, followed by steam distillation of the reaction slurry yielded products slightly more intense than the corresponding materials made in kerosene. If, however, TCB synthesis is followed by filtration of the hot reaction slurry, and the filter cake is then washed with hot (170° - 190°C) TCB, an appreciable improvement in intensity is observed, as compared with kerosene process materials. As discussed previously, the latter improvement is undoubtedly due to a large extent to the removal of a green impurity from the crude pigment by the hot TCB. Whereas the best acid-pasted materials from such TCB extracted crudes are superior

to BP-173-D in intensity, the best acid-pasted materials from kerosene synthesis crudes are only equal to BP-173-D in this respect.

Solvent ground TCB materials are consistently 3-5% weaker than their kerosene synthesis solvent-ground counterparts, and although intense compared to the latter, are inferior to BP-173-D tinctorially. Even the combined effects of synthesis in TCB, filtration and washing with TCB, and extraction with sodium hydroxide, are insufficient to yield a product of intensity equal to that of BP-173-D, in the case of solvent-ground pigment. The tinctorial deficiencies of such materials are related to the crystal phase in which the material exists; that is, some of the deficiencies of the solvent ground product case appear may be due to the presence of beta phase material. Subsequent acid-pasting of these solvent-ground products derived from the TCB synthesis produces satisfactory color against BP-173-D standard.

The general conclusions obtained in this study may be summarized briefly as follows: (1) acid pasted products are tinctorially superior (more intense or less dull) to their solvent ground counterparts. Only by acid-pasting has it been possible to obtain pigment of goal quality without "sulfation" treatment. By use of this conditioning method, a pigment of properties approximating those of BP-173-D may be obtained from kerosene process crude. (2) Some improvement in tinctorial properties of either solvent milled or acid-pasted pigment results from synthesis in TCB rather than in kerosene, and the improvement is magnified if the slurry is filtered and washed with TCB. Extraction with sodium hydroxide also results in some improvement. (3) It appears that the presence of beta structure CPC in solvent-milled LB is responsible for part of the quality deficiencies of this pigment. (4) The use of "Niagara" chlorophthalic anhydride leads to acid pasted products brighter and slightly greener than those obtained with Newark chlorophthalic acid, but there is no quality advantage to the use of the "Niagara" material when the pigment is finished by solvent milling. (5) The combined effects of all the aforementioned variables (including extraction with sodium hydroxide solution) which promote improved quality is insufficient to raise the tinctorial level of solvent milled pigment fully to that of BP-173-D.

b - "Niagara" Alkali Chlorphthalic Anhydride

The appearance of Niagara Alkali Company crude chlorphthalic anhydrides on the market suggested its possible use in LB/CPC synthesis in place of the currently used 4-chlorphthalic acid. The Niagara Alkali Company product is prepared by the direct chlorination of molten phthalic anhydride in the presence of suitable catalysts, and gives rise to a greater proportion of more highly chlorinated products than does the Newark process involving the alkaline chlorination of disodium phthalate.

b1 - Newark 4-Chlorphthalic Acid vs "Niagara" Alkali Chlorphthalic Anhydrides

"Niagara" chlorphthalic anhydride containing 1.17 atoms of chlorine per molecule of the anhydride (i.e. contains at least 15% of the dichlorphthalic anhydride), yielded acid-pasted LB/CPC (4.5% Cl) more intense but objectionably green compared to BP-173-D.

"Niagara" chlorphthalic anhydride containing 11.5% chlorine (calculated 60% monochlorphthalic anhydride, 40% phthalic anhydride) yielded materials which, when acid pasted, were intense vs BP-173-D and considerably less green than the products from the more highly chlorinated anhydride above, although still green (vvs to vs) against BP-173-D.

Newark (lab.) crude 4-chlorphthalic acid (12% organic chlorine, (i.e., 60% 4-chlorphthalic acid) yielded products less green, but less intense when acid pasted, than those obtained from the "Niagara" chlorphthalic anhydrides. Only on acid-pasting a TCB synthesized material was a product obtained from Newark 4-chlorphthalic acid which was equal to BP-173-D in intensity. The tinctorial differences between the acid-pasted and solvent-ground materials in the "Niagara" series were significantly greater than the difference observed in the "Newark" series, so that while the acid-pasted samples made with chlorophthalic anhydride were intense compared to BP-173-D, the corresponding solvent milled samples were very green compared to this standard.

b2 - LB/CPC Containing 3% Chlorine (from Niagara chlorphthalic anhydrides)

LB type CPC of chlorine content equal to that of current purchased (Orchem) material has been prepared in both kerosene and TCB, using "Niagara" chlorophthalic anhydride. The acid-pasted material is a close hue match to BP-173-D (trace to vvs green) and is also slightly intense.

b3 - Crystal Phase - Niagara Chlorphthalic Anhydride Products

As stated above, the use of "Niagara" chlorphthalic anhydride in the preparation of LB/CPC results in pigment of good tinctorial quality if the product is finished by acid-pasting, but leads to an objectionably green product if the crude pigment is finished by solvent grinding (Unsulfated). This has been found to hold for LB type pigments (from "Niagara" chlorphthalic) of 3% chlorine content as well as for those containing 4% chlorine. The results of recent X-ray studies of the "Niagara" LB/CPC samples show that solvent ground LB/CPC made with "Niagara" chlorphthalic anhydride contain a very much larger proportion of the tinctorially undesirable beta structure CPC than do comparable samples made with "Newark" chlorphthalic acid. The presence of this material accounts for the greenness of the solvent milled product;

since acid-pasting converts the beta form into the redder alpha material, such extreme greenness is not evident in acid-pasted samples made with the "Niagara" material. The greater proportion of the beta structure pigment in LB/CPC made with the "Niagara" product, as compared to pigments (LB) of comparable chlorine contents made with the usual reactants, is believed to be a consequence of the presence of di- (-and possibly tri- and tetra-) chlorphthalic anhydrides in the "Niagara" material, so that the pigment made with its use contains a larger proportion of chlorine-free CPC than is obtained when Newark chlorphthalic acid is used. (Chlorine-free CPC, either crude or solvent milled, exists largely in the beta structure).

b4 - Salt-Milling (Niagara Chlorphthalic Anhydride Products)
Salt-milling of LB type CPC prepared with use of "Niagara" Chlorphthalic anhydride, yielded products superior to BP-173-D in intensity (although greener) and superior in all respects to the unsulfated, solvent-ground counterparts. However, in view of the aforementioned presence of an abnormally large proportion of beta structure material in the crude or solvent-ground CPC made with use of the "Niagara" products, there is question as to whether LB/CPC derived from "Niagara" chlorphthalic anhydride can be considered representative solvent-ground LB type pigments.

Enamels prepared from the above products show the salt-milled samples to be tinctorially superior to the acid-pasted which in turn are superior to the solvent-ground ones.

c - Reaction Media for LB/CPC Synthesis

Various inert diluents for LB/CPC synthesis have been investigated as possible substitutes for Use-Base kerosene, a highly refined, washed, odorless distillate marketed by L. Sonneborn Sons, Inc. At the time the major portion of this study was made, the considerations which are now appreciated as essential for satisfactory LB/CPC synthesis, yieldwise and colorwise, were not fully known. The yield values are, therefore, comparative only, inasmuch as some have since been considerably improved. The quality shown is that of acid-pasted material and, in view of the aforementioned considerations, is not representative of the tinctorial quality inherent in these LB/CPC pigments. Poor agitation, and the use of an iron-contaminated mixture of 4-chlorphthalic acid and mono-sodium 4-chlorphthalate, are presumed for the syntheses discussed in the present section. All runs were made in a one-liter, 3-necked flask under conditions (poor agitation foremost) which gave considerable foaming.

Solvent	Boiling Range °C.	Acid Pasted Yield	Rubouts vs. BT-172-D Tint	Rubouts vs. BT-172-D UT	Rubouts vs Deo-Base Product Tint	Rubouts vs Deo-Base Product UT
Deo-Base Kerosene	185-265	(83.7 (82.8	(s dull (s green	s dull s green	-	-
Esso Mentor 28	270-325	(88.6 (91.3	-	s dull	-	s dull
Esso Kerosene	170-280	91.5	s green	s green s dull	s green	(s green (s dull
Esso 340 Oil	F.B.P. 370-425	83.9				
Esso Bayol D	205-265	81.4		intense	intense	intense
Heavy Aromatic Naptha	179-285	19.5	green dull	green dull	-	-
o-Dichlor-benzene	177-179	20.2	s green s dull	s green s dull		
(90% Deo-Base (kerosene (10% Trichlor-benzene		69.4	s green s dull	-	-	-

c1 - Esso "Bayol" D"

Esso "Bayol" D"appears to give yields as great as those obtained with "Deo-Base" although the former appears to give a slightly cleaner product. The material shows promise as a "Deo-Base" substitute. Both "Deo-Base" and "Bayol D" are highly refined kerosenes consisting essentially of paraffins and napthenes. The use of "Bayol-D" is suggested for economic considerations.

c2 - Trichlorbenzene

Comparative runs (3) of the kerosene process for LB/CPC versus the trichlorbenzene process indicated that in the case of the TCB runs, the acid-pasted yields were 6-14% lower than in the kerosene runs, although the products in the former were stronger and cleaner. The yield comparisons are, however, subject to further study. Less foaming was experienced in the TCB runs although it can be shown that in iron-free, kerosene syntheses provided with good agitation, foaming is essentially negligible.

The quality differences between Deo-Base kerosene and trichlorbenzene (Dow, technical) synthesized products have been discussed in more detail in a previous section of this report.

c3 - Fractionated "Esso" Kerosene

The fractionation of "Esso" kerosene yielded 35% of a water-white distillate boiling in the range 195 - 225°C.; below 195°C, 6 - 10% of the material distilled. The 195-225°C fraction was found to be a satisfactory substitute for "Deo-Base" kerosene in the synthesis of LB/CPC. A 93.5% yield (extracted) of pigment, tinctorially equal to that made with use of "Deo-Base", was obtained with this fraction (195-225°C) in one autoclave run; the yield obtained with "Deo-Base" under comparable conditions was only 89.8%. The use of such a fractionated kerosene material was suggested by its possible use as a grinding medium and subsequent easier removal by steam-distillation in contrast with straight run "Esso" kerosene or "Deo-Base" kerosene steam-distillations. The use of such a fraction is no longer being considered owing to excessive cost of the fractionated material.

d - LB/CPC Kerosene Synthesis Variations

A summary of LB/CPC autoclave syntheses involving several modifications in process is recorded below. All the reactants were initially present except where noted in the case of the urea. The delayed addition of urea implies addition at the 160°C stage of the synthesis. Except where noted, 4-chlorphthalic acid crude was added initially as the dried material. The yields given represent extracted (2% H_2SO_4, 3% NH_4OH) yields. In all cases, the quality of the acid-pasted materials was essentially equal to that of the "Deo-Base" products.

YIELD SUMMARY LB/GPC AUTOCLAVE SYNTHESES

Reaction Medium	Synthesis Variation	Yield(%)	Average Yield (%)
Dec-Base	delayed addition dry urea	88.7 86.2 86.9 91.6	88.4
Bayol - D	delayed addition dry urea	88.5 89.4	89.0
Dec-Base	None	85.9 89.4 86.1 85.2 87.7 87.6	87.7
Dec-Base	delayed addition molten urea	89.8 87.3	88.6
Dec-Base	delayed addition molten urea wet 4-chlorphthalic acid pulp	91.9 90.4 88.6	90.3
DecoBase Medium	delayed addition molten urea 4-chlorphthalic acid slurry	85.6	
Dec-Base (once used for synthesis)	delayed addition dry urea	95.8 93.4 90.5 90.1	92.5
Esso Kerosene (195 - 225°C fraction)	delayed addition molten urea	93.4	
Esso Kerosene	delayed addition dry urea	79.1	
Esso Kerosene (Foster-Wheeler fractionated 195-225°C)	None	87.0 85.7	86.4
Dec-Base (twice-used for synthesis)	None.	86.4 87.7	87.1
Dec-Base (three times used for synthesis)	None.	89.0	

d1 - Delayed Addition of Urea
The delayed addition of urea in the synthesis step offers little advantage, if any, yieldwise. Four runs (autoclave) employing delayed urea addition gave an average yield of 88.4% (of theory) as compared to a yield (average) of 87.7% for six syntheses with urea present at the start of heating. The process employing the delayed urea, however, has other remaining advantages attendant on its use -

1) Although foaming is not a problem in Newark operation, the tendency of a charge to foam is materially reduced when the urea addition is delayed. When all of the reactants including urea are initially present, foaming begins at approximately 105 - 125°C. The addition of urea at 160°C permits a very active but rapid and easily controlled reaction which quickly subsides. The rate of urea addition is the controlling factor.

2) The addition of urea at 160°C permits the use of a wet crude 4-chlorphthalic acid pulp inasmuch as heating of such a cake to 160°C in the course of syntheses guarantees the removal of the water present prior to the urea addition. Destruction of some quantities of urea prior to its utilization in the synthesis would otherwise result.

d2 - Molten Urea - Kerosene Slurry
The addition of urea to the reaction mixture at 160°C as a molten urea-kerosene slurry (kerosene used to facilitate heat transfer during the urea melting) does not appear attractive. Although the procedure is satisfactory yieldwise and colorwise, the greater gravity of the molten urea causes complete separation of this material, even with vigorous agitation, and precludes the formation of a homogeneous slurry.

d3 - Reuse of Kerosene for Synthesis
The reuse "as is" of kerosene filtered from the kerosene reaction slurry apparently permits satisfactory syntheses, yieldwise. Subsequent process modifications, with elimination of the filtration step, however, preclude the recovery of kerosene at this stage of the process.

d4 - Use of Wet 4-Chlorphthalic Acid Pulp
Wet (undried) crude 4-chlorphthalic acid presscake can be used satisfactorily in the LB/CPC synthesis. The use of a wet 4-chlorphthalic acid pulp obviates the need for drying with its attendant corrosion problems.

d5 - Ammonium Carbonate Accumulation in Reactor Condenser
To provide information for design purposes, it was established that operation of the LB/CPC reactor condenser at 75°C. insures the removal (b

d5 - Ammonium Carbonate Accumulation in Reactor Condenser
To provide information for design purposes, it was established that operation of the LB/CPC reactor condenser at 75°C. insures the removal (by decomposition) of a major portion of the ammonium carbonate formed in the course of reaction. Phthalimide continues to condense under these conditions, however, and tends to clog the condenser.

4 - "Sulfation" Process

In view of the considerations already discussed regarding the relationship between crystal phase and tinctorial quality, it appeared desirable to convert any beta phase of LB/CPC material to the more desirable form by means other than acid-pasting or salt-milling, applying a method which would permit the use of solvent-grinding for particle size reduction.

The "sulfation" technique devised by Jackson Laboratory for conditioning pigment for chlorination has been investigated as a possible means of improving the tinctorial properties of LB/CPC pigment. The "sulfation" process involves the formation of a CPC sulfate by the addition of 98% sulfuric acid (about 1.25 parts by weight per part of LB/CPC) to the hot kerosene or TCB reactor slurry resulting from the condensation step. Under proper conditions a very granular CPC sulfate can be thus obtained, from which the major portion of the solvent can be readily removed by filtration, or by decantation in the case of kerosene. This sulfate is then hydrolyzed to LB/CPC in the subsequent steam distillation step and may then be processed by the usual drying and solvent milling procedures to yield a redder, more intense pigment than any heretofore obtained by solvent grinding techniques. These products approximate BP-183-D in redness and brightness and, moreover, these properties carry over into alkyd enamels where previous solvent-ground products have been especially green and dull. However, the alkyd enamels no longer show the relative freedoms from flocculation and superior "can stability" of previous solvent ground CPC, but are similar to BT-172-D in these respects.

"Sulfation" undoubtedly permits a change of any beta phase CPC present to the alpha form such as occurs during the acid-pasting process, and also results in the destruction of certain objectionable impurities. In both "sulfation" and acid-pasting, LB/CPC is converted to the sulfate and is regenerated by hydrolysis. "Sulfation" provides a means for effecting the phase change with a much smaller proportion of sulfuric acid than is used in the acid-pasting process. Particle-size reduction is not effected to as great an extent in the "sulfation" process as in the acid-pasting process so that other means must be used for the strength development step (solvent-milling)

a - Effect of Temperature in "Sulfation"

An effort to determine the optimum temperature of sulfation in kerosene (i.e., 60°, 100°, 150°C) produced indefinite results. Only slight tinctorial differences were observed between products sulfated at the different temperatures. The indications are, however, that the lower temperatures may be the more desirable.

A second series, involving sulfation of laboratory synthesized pigment, in kerosene, at 60°C and at 150°C, revealed no influence of sulfation temperature on quality. In all cases, however, the "sulfated" material was appreciably more intense and redder than the pigment processed in the usual way without sulfation.

b - "Sulfation" in Trichlorbenzene

In the case of pigment prepared in the laboratory in trichlorbenzene (TCB), a portion sulfated at 150°C was found to be appreciably more intense than another portion sulfated at 60°C. From the standpoint of pigment quality, preparation and sulfation of the pigment in TCB yields an appreciably more intense product than when the synthesis and sulfation reactions are carried out in kerosene; the TCB (sulfated) products are red and essentially equal in intensity to BP-173-D, whereas the corresponding kerosene product is red and dull compared to BP-173-D. While TCB appears definitely preferable to kerosene as a medium for the reactions in question, insofar as pigment quality is concerned, the use of TCB in the plant may pose difficulties owing to the fact that, unlike kerosene, TCB cannot be separated simply from the sulfated pigment by decantation, and its use will probably necessitate a filtration operation for which no equipment has been provided in the plant. Recent semi-works batches of TCB synthesized and sulfated material have been successfully decanted. The quality advantage of this decanted material in contrast with the filtered material has not yet been established.

TCB synthesis and sulfation conducted at 195°C yielded a product equal tinctorially to one sulfated at 150°C (acetone or isopropanol ground).

c - Role of Salt in "Sulfation"

The presence of excessive quantities of salt derived from the crude 4-chlorphthalic acid (4-CPA) in the synthesis step apparently contributes to some of the agitation difficulties observed during the sulfation of kerosene reactor slurries. Current semi-works 4-CPA contains as much as 45% NaCl, presumably due to process variations made necessary because of equipment considerations. Recent batches, however, have been planned for lower salt content with a view to minimizing agitation requirements.

Present practice is to use a quantity of acid in the "sulfation" corresponding to 1.25 pounds of 98% H_2SO_4 per pound of CPC, plus the additional quantity of acid necessary to react with the salt present.

d - Use of 78% Sulfuric Acid in "Sulfation"

An attempt to sulfate LB/CPC in kerosene at 150°C using 78% H_2SO_4 in place of 98% H_2SO_4 gave sulfation (considerable agitation difficulty) but presumably only after the removal of water together with kerosene (steam distillation effect), and consequent concentration of the sulfuric acid to a level effective for sulfating.

e - Yield Loss Due to "Sulfation"

A series of experiments designed to determine the extent of decomposition of LB/CPC in the presence of increasing quantities of 98% H_2SO_4 in kerosene, at 150°C, for 1-1/2 hours indicated increasing decomposition with increasing acid over and above that required to form the sulfate. CPC sulfate

itself (i.e., 1 mole LB/CPC/4 moles H_2SO_4) showed slight decomposition under the conditions of the experiment. The latter observation was substantially verified by an actual synthesis and sulfation, using a suitable control, the yield of LB/CPC (crude extracted) in the former being 89.1% (sulfated) and the latter 90.0% (unsulfated). A check series gave a 93.2% and 93.5% yield for an unsulfated and sulfated run, respectively.

f - Solvent Recovery by Use of Centrifuge

Centrifuge studies indicate that kerosene sulfated slurries can be centrifuged with ease to give cakes of approximately 75% crude CPC sulfate solids.

The acidity of the kerosene decanted or centrifuged from the sulfation slurry was shown to be practically negligible and can probably be attributed to a large extent to dissolved phthalimide. (0.08 to 0.8 pound of NaOH required per 1000 pounds of decanted kerosene).

g - Hydrolysis of LB/CPC Sulfate

In contrast with previous experience where balling of LB/CPC almost invariably accompanied the steam distillation - hydrolysis of LB/CPC sulfate, it has been found that a cold, neutral, or slightly alkaline, hydrolysis of the LB/CPC sulfate, following decantation and drainage of kerosene from the sulfated slurry, produces a well dispersed slurry which can be steam distilled without balling, or which can be alkaline extracted and then filtered with no difficulty. The latter alternative eliminates the steam distillation step from the process. Analysis of the dry, crude extracted pigment for residual kerosene, from each of the above two alternative procedures, indicates kerosene contents within the limits previously established as acceptable for isopropanol grinds.

h - Extraction with Acetone

In an effort to improve the quality of laboratory kerosene-synthesized-sulfated materials, the crude LB/CPC sulfate (after kerosene removal) was washed with a relatively large volume of acetone until the residual kerosene and colored impurities were substantially removed, and was then hydrolyzed and finished as usual. The final product was vvs green and equally intense versus BP-173-D, the first instance where a kerosene-synthesized, solvent-ground product proved essentially equal to BP-173-D as regards quality. The control was red and vs to s. dull against the acetone-washed product. Subsequent experiments indicated that some destruction of the acetone occurs (presumably to mesityl oxide) due to the reaction of acetone with any concentrated sulfuric acid associated with the CPC sulfate. This effect is more pronounced on prolonged contact.

It is expected that the use of an acetone extraction at some point in the process will offer the tinctorial advantage described above. Inasmuch as acetone extraction of the LB/CPC sulfate presents operational difficulties, the following sequence of operations is being considered:

1) "Cold hydrolysis" of LB/CPC sulfate
2) Caustic extraction
3) Acid extraction

4) Ammonia extraction
5) Acetone wash and displacement of water by acetone in the ammonia extracted pulp (enclosed filter press).
6) Acetone grind of LB/CPC acetone pulp

The procedure as outlined eliminates the steam distillation step, and the need for oven-drying of the crude LB/CPC prior tothe grinding operation. The method permits complete kerosene removal with its attendant advantages as regards subsequent grinding, and lake preparation where even traces of kerosene effect the degree of pigment dispersion. Further, the advantage of an acetone extraction may eliminate the need for some of theaqueous extractions of the crude LB/CPC.

5 - Kerosene - Grind Process

The discussion included here concerns the removal of the kerosene grinding medium from kerosene-ground ball-mill slurry. While this information is no longer pertinent to the process as described in Appendix I, some considerations inherent in the use of kerosene as a synthesis medium, rather than as a grinding medium, are described, some of which still play an important role in the present process. (i.e. effect of kerosene residues in 91% isopropanol grinding etc.)

a - Removal of the Kerosene Grinding Medium from Ground Ball-Mill Slurry

The kerosene-grind process imposes several problems as regards the removal of the kerosene grinding medium from the ball mill slurry. The removal of the kerosene, as will be discussed under the section "Preparation of Lakes", is necessary in the interest of optimum dispersion for lake preparation.

a1 - Kerosene Residues

Deo-Base kerosene, marketed by L. Sonneborn, Sons, Inc. is a highly refined, washed, odorless distillate boiling in the range 185° - 265°C, which on extended evaporation leaves a negligible residue. The presence of the higher boiling ends, in addition to the gummy residue produced during the course of the Blue syntheses, however, imposes process problems at the subsequent kerosene removal stage by steam distillation, and, as will be discussed later, also causes difficulty during the 91% isopropanol grinding stage of the revised process.

An indication of the amount of gums formed during the course of the Blue LB synthesis which can be attributed to kerosene has been determined to be approximately 0.02% of the weight of kerosene. Deo-Base heated at 200°C. for 4 hours in the presence of cupric chloride yielded a residue on evaporation amounting to 0.15% of the weight of kerosene. The possibility of controlling excessive gum formation through the use of anti-oxidants did not appear promising. The agents tried are apparently ineffective

at the relatively high temperature of CPC formation and/or in the presence of large quantities of copper salts which are known to catalyze the oxidation of petroleum hydrocarbons.

a2 - Filtration of Kerosene Reactor Slurry
Attempts at the removal of a portion of the kerosene by filtration of the ground kerosene slurry indicated that the slurry filters very slowly to yield a cake containing only 40% of kerosene, corresponding to the removal of approximately 85% of the kerosene initially present. Because of the poor filtration rate, filtration of the ball milled kerosene slurry is not being considered for plant operation.

a3 - Mineral Spirits Replacement of Kerosene
The steam distillation removal of kerosene suggested the displacement of the kerosene with mineral spirits, after completion of the synthesis reaction, and grinding the mineral spirits-wet filter cake in additional mineral spirits, followed by what was expected to be the comparatively easier removal of the mineral spirits by steam distillation. These hopes were not fully realized.

A method for determining the effectiveness of the kerosene replacement by mineral spirits in the crude LB filter cake based upon refractive index measurements of the wash filtrates has been devised. There is an essentially linear function relating refractive index with the composition of the kerosene-mineral spirits mixture.

a4 - Use of A Fractionated Kerosene for Synthesis
In the interest of ease of removal of the synthesis and grinding media by steam distillation the use of a kerosene fractionated so as to remove the higher boiling fractions was investigated. This has been discussed in a previous section devoted to LB synthesis media.

a5 - Acetone Solvent Extraction of Kerosene
The removal of the kerosene grinding medium by means of extraction with a kerosene-miscible solvent has received considerable attention. A continuous Soxhlet extraction of a ground kerosene ball-mill slurry using acetone as extractant effects the complete removal of kerosene and kerosene gums, as well as green acetone-soluble impurities, from the LB/CPC slurry. Replacement of the acetone with water yields a completely water-wet pulp of quality superior to that obtained by the more standard kerosene removal methods (i.e. distillation or drying).

Filtration tests have indicated that a large investment in filtration equipment would be required for the acetone extraction step. Economic studies of the process show it to be unattractive and accordingly it is not being considered further at this time.

6 - Acetone Grinding

a - Acetone Grinding vs 91% Isopropanol Grinding

Acetone grinding of kerosene synthesized LB/CPC yielded a product equal in strength and superior tinctorially to the isopropanol ground counterpart. A similar tinctorial improvement, with a strength advantage of as much as 10%, resulted from the use of acetone, rather than isopropanol, in the grinding of pigment synthesized in TCB. (Samples not "sulfated").

The advantage of grinding in acetone over 91% isopropanol grinding of TCB-synthesized material is apparent only when trichlorbenzene is steam distilled from the pigment instead of being filtered, the former method presumably permitting the accumulation of the higher boiling, more highly chlorinated benzenes on the pigment with consequent poorer wetting of the solids by the 91% isopropanol grinding medium. In the case of "sulfated" materials from which the TCB is removed by filtration, the differences between the two types of grind are slight, with some indication that the alcohol grinds are slightly greener and trace intense versus the acetone grinds.

Likewise, the advantage of acetone over 91% isopropanol grinding of kerosene-synthesized material is apparent only when the quantity of residual kerosene and kerosene "gums" associated with the crude LB/CPC is comparatively great, the use of acetone presumably permitting better wetting of the pigment surface and, therefore, better grinding. Kerosene and kerosene "gums" are relatively more soluble in acetone (99.5%) than in 91% isopropanol. A series of grinds designed to show the effect of residual kerosene on the crude pigment in the grinding operation indicated that in grinding a crude LB/CPC containing approximately 8% residual kerosene, the order of decreasing efficiency of grinding medium was: acetone (99.5%), a 1:1 mixture of acetone (99.5%) and isopropanol (91%), isopropanol (91%). Also, acetone grinding of semi-works crude LB/CPC, or isopropanol (91%) grinding of an acetone-extracted (Soxhlet) semi-works crude, yielded products tinctorially superior to that obtained by isopropanol (91%) grinding of the corresponding untreated semi-works crude. The superiority of the acetone grind is due presumably to better wetting while the improvement resultant from acetone extraction is believed to be due to removal of kerosene and other impurities with consequent better wetting by the isopropanol.

The above facts suggest that in solvent-grinding LB/CPC crudes containing residual synthesis solvent, the use of essentially water-free grinding solvents miscible with the residual synthesis medium will give greater grinding efficiency.

7 - LB/CPC Lakes from Kerosene-Grind Process Material

The preparation of LB/CPC lakes was attempted using as starting material the final extracted pulp derived from the kerosene-grind process which was currently under investigation in the semi-works. The final "water" pulps so obtained contained a considerable quantity of kerosene which was not removed during the kerosene ball-mill slurry steam-distillation step, and which was retained by the pigment during the subsequent aqueous extraction step. The presence of this kerosene in the pulp presented a problem insofar as dispersion and subsequent lake preparation was concerned. This work was undertaken to determine means for utilizing such kerosene-containing water-presscakes for lake preparation.

a - "Ramapo" Lake

When water-wet, acid-pasted copper phthalocyanine is dried, aggregation occurs and, in general, the finer (i.e. small particle size) the water-wet pigment, the weaker the dry pigment. The greater the extent of aggregation, the harder the resulting color. If aggregation on drying is avoided, the tinctorial strength of copper phthalocyanine increased with decreasing particle size in the investigated range. Unfortunately, the strength inherent in fine particle size CPC cannot generally be directly realized due to aggregation. To obtain high strength toners, therefore, aggregation accompanying the drying of the water-wet pigment must be prevented, and laking makes it possible to approach the strength to be expected on the basis of particle size.

Although the ultimate strength of two different toners may be substantially equal, the ease of attaining that strength may vary considerably. "Ramapo" laking permits a rapid rate of strength development and good texture due to the fact that aggregation, is minimized and less work need be done on the lake to realize a given strength.

"Ramapo" Blue (BP-173-D) is a barium rosinate lake of copper phthalocyanine (70% CPC, 30% rosinate) prepared by current production from an acid-pasted semi-chlor CPC. The lake is made by precipitating barium rosinate in the presence of an essentially well-dispersed copper phthalocyanine water slurry. The resulting lake exhibits desirable texture properties which would not be obtained by a mere mechanical mixture of the two components. The lake is characterized by soft texture (wedge grit), good rate of strength development, and excellent ultimate strength, soft ink body, and ink length.

The preparation of "Ramapo" lakes was attempted, starting with a water pulp obtained from a kerosene-synthesized-kerosene-ground LB/CPC, rather than from an acid-pasted pulp. As stated previously the major problem inherent in the kerosene process is the completeness of the removal of kerosene from the ball mill slurry. (Footnote 1)

(Footnote 1)
The discussion which follows refers to preparation of lakes from pigment which has been ball-milled in kerosene. In the case of pigment ground in alcohol rather than in kerosene (i.e. current process), no major difficulty has been encountered in obtaining water dispersion adequate for lake preparation.

Whereas steam distillation of kerosene ball-mill slurry appears to be preferable to kerosene removal by drying, the latter method yielding unsatisfactory material tinctorially, neither method for solvent removal makes it possible to free completely the pigment of kerosene, or kerosene gums formed in the course of synthesis, in the sense that a completely water-wet, water-dispersible pigment is produced. Some final kerosene-process (i.e. ball milled in kerosene) pulps obtained from semi-works operation have contained from 5-30% of kerosene by weight of pigment, and, despite vigorous agitation, disperse to a negligible extent in water due to poor wetting.

The preparation of lakes, including lakes other than "Ramapo", from phthalocyanines, presumes a relatively easy dispersion of the pigment pulp in water so that optimum distribution of pigment in the substratum can be accomplished. The kerosene normally associated with the final pulp produced by the kerosene-grind process (kerosene removal by steam-distillation) precludes easy water dispersion by the standard methods currently used for the lakes under consideration and the lakes prepared by the standard methods, therefore, do not exhibit the desirable properties normally associated with these lakes. The kerosene present during the final stages of drying of the "Ramapo" does, however, contribute to the production of a superior-textured product (wedge grit).

b - Preparation of Lakes from Pastes Containing Kerosene

"Ramapo" lakes prepared from semi-works alkaline-extracted filter cake by the usual type procedure were objectionably weak as compared to BP-173-D. The samples were essentially equal in wedge grit to the standard, however, and exhibited rate of strength development not greatly inferior to the standard. The cause of the weakness is due to a strength deficiency of the toner used, together with improper dispersion during the laking procedure.

c - Rosin-Flush Dispersion

Dilute aqueous sodium or ammonium rosinates, as used in the standard Ramapo process, do not appear to disperse steam distilled, alkaline extracted LB/CPC (containing some kerosene) to any great extent. Good dispersion of this pigment containing considerable kerosene can be effected by mixing (Baker-Perkins mixer) the filter cake with free powdered rosin so as to flush the major portion of the water and to assure intimate and vigorous contact between the rosin and the kerosene-coated pigment. The viscous mass so produced disperses readily in alkaline solutions to yield dispersions of outstanding quality.

d - Ammonium Rosinate Dispersion Technique

As stated previously, dilute aqueous ammonium rosinate as employed in the standard "Ramapo" process does not have much dispersive effect on the typical LB/CPC pulps obtained from the kerosene grinding process. However, it has been shown that a filter cake containing approximately 30% of kerosene by weight of LB/CPC, can be dispersed in a hot concentrated ammonium rosinate solution, containing excess ammonia, to a degree adequate for preparation of "Ramapo" lakes. Sodium rosinate solutions are not equally effective. Although dispersion of all the pigment is not effected, it appears that a major portion of the kerosene is effectively removed from the pigment particles so that a "balling" effect is not experienced in the subsequent Ramapo process. A portion of the kerosene so

displaced apparently forms an oil-in-water emulsion, the excess kerosene rising to the surface as a thin film. Inasmuch as semi-works kerosene-ground LB/CPC contains 8-10% of diluents (naphthenates etc.) less than the usual quantity of rosin need be mixed with it to obtain a lake of the desired CPC content. The strength of the lake obtained is that which would be predicted from its CPC content (as calculated from copper analyses). Lakes equal in strength to BP-173-D (for the same CPC content) have been obtained. (Appendix IV)

The kerosene associated with the pigment in the course of "Ramapo" preparation, and ultimately appearing with the final Ramapo to a degree dependent upon drying conditions, serves admirably as a soft-texture agent, as evidenced by the production by this process of Ramapo considerably superior in wedge grit to BP-173-D. "Ramapo" prepared from semi-works material were vvs dull, and vs green vs BP-173-D, much superior in wedge grit and slightly inferior to BP-173-D in rate of strength development on loose passes (but equal on tight passes). The dullness reported here is that to be expected on the basis of the starting toner that was used. Unsulfated pigment was used in this study, which accounts for at least some of the dullness observed.

e - Napthenic Acid as an Aid in Dispersion of LB/CPC

In the preparation of Ramapo lakes from pigment ground in kerosene, it has been observed that the extent of the dispersion obtained by the ammonium rosinate technique varied appreciably from one semi-works lot to another, and this variation was reflected in the quality of the resulting lake. Dispersion appears to be related to the amount of naphthenic acid associated with the pigment during the various finishing steps, especially the grinding step. Better dispersion is obtained with the samples containing naphthenic acid, and the extent to which this acid is removed in the alkaline extraction step is critical for the subsequent dispersion step. It appears that the hot concentrated ammonium rosinate serves to emulsify the kerosene associated with the pigment and subsequently acts as a wetting and dispersing agent. The excess ammonia in the ammonium rosinate solution dissolves out the naphthenic acid, which has been brought into intimate contact with the pigment during the course of grinding, and gives rise to further dispersion.

A "Ramapo" prepared from kerosene process material having no naphthenic acid in the ball mill or steam still was inferior in wedge grit texture to standard on the loose passes and essentially equal on the tight passes. In rate of strength development, the product was greatly inferior to standard on the loose passes and achieved full strengh only after 3 tight passes. The product is regarded as wholly unsatisfactory. A "Ramapo" prepared from kerosene process material having 5% naphthenic acid in the mill, but none in the steam still was in no way better than the "Ramapo" described above. Kerosene process material having 5% naphthenic acid in the mill, and 5% naphthenic acid in the still continued to give consistently good "Ramapo" (superior texture, rate of strength development inferior on loose passes, equal on tight passes, softer and longer inks.)

An increase in the range 0-50% in the quantity of naphthenic acid used in the kerosene grinding step results in increase in the degree of dispersion obtained on subsequent application of the ammonium rosinate technique to the material in the preparation of lakes. However, the use of naphthenic acid as a grinding aid is undesirable in that the tendency to "balling" during steam distillation, following grinding, increases with increase in the quantity of this

g - Quality of Toner for Lake Preparation

It is of interest to note at this point that a comparison of current standard BT-172-D with BP-173-D ("Ramapo" Blue) reveals that BP-173-D is appreciably more intense than BT-172-D, and the available information indicates that a toner must be superior to BT-172-D in this respect if a standard quality Ramapo lake is to be obtained with use of the toner. A similar situation apparently also exists in the case of other LB/CPC lakes. A possible cause for the observed difference in intensity between BT-172-D and BP-173-D has been discussed elsewhere. Suffice it to say that the tinctorial quality of a "Ramapo" or other lake of LB/CPC will be essentially equal to that of the toner pigment material from which it is produced and a starting toner at least equal in tinctorial properties to BP-173-D is, therefore, necessary.

8 - Miscellaneous

a - Flushing (Preliminary Studies)

Semi-works kerosene-process material was flushed in #1 transparent varnish with use of the laboratory B-P mixer, using heat alone (no vacuum) for water removal. In this way it was possible to prepare a flushed ink containing 55% total solids as contrasted to a maximum LB/CPC content of approximately 30% in the case of flushed inks from acid-pasted CPC. This effect is presumably associated with the generally observed lesser "body" and greater flow of inks from kerosene-ground material. No strength advantage was evident from preparation of the ink by flushing rather than by dry grinding; in fact, the "as is" flushed ink was quite poor in wedge grit rating and possessed only 87% of the strength which could be realized by subsequent grinding on an ink mill, and even after such grinding was no stronger (on equal pigment basis) than a BT-172-D ink. However, the rate of strength development on grinding of the flushed ink was much superior to that of ink prepared from BT-172-D.

Preliminary studies indicate that kerosene process materials can be readily flushed into an alkyd vehicle.

b - LB/CPC Vinyl Plastic Tests

Four experimental LB/CPC toners were evaluated in vinyl plastic. Lab-kerosene ground material showed the best dispersion, being better than standard BT-172-D, and better to slightly better than semi-works kerosene material. Lab-isopropanol material exhibited vs better dispersion than the semi-works kerosene product. Salt-milled material was rated inferior in disperion to BT-172-D standard. All samples are greener in tint vs BT-172-D and all except the salt-milled are inferior in strength to BT-172-D, semi-works kerosene material being the weakest and dullest. All samples showed excellent resistance to light (144 hours, fadeometer).

c - Soft Texture LB/CPC Toners

Application to semi-works isopropanol ground toner of the soft texture treatment currently used for BT-172-D, results in a product of wedge grit rating appreciably better than that of BP-173-D. However, the improvement in rate of strength development resultant from the treatment is much less than the change in wedge grit, so that the treated product is much inferior to BP-173-D in this respect.

acid present. Presumably, this increased "balling" increases the difficulty of kerosene removal and also decreases the effectiveness of subsequent extraction steps.

A Ramapo lake prepared from kerosene process pulp by the ammonium rosinate dispersion method was found to be green and vs dull relative to BP-173-D on evaluation in alkyd enamel and in lacquer. The material was equal to the standard in strength in lacquer but was weak, as well as somewhat poorer in gloss, in alkyd. The product was superior to BP-173-D in flocculation behavior. The experimental sample yielded a less "puffy" enamel than did the standard which permitted formulation at higher solids. Except for the differences in the strength results of the lacquer and alkyd tests, for which no explanation is immediately evident, the properties of the Ramapo are those predicted from the nature of the toner used in its preparation, and it appears that the aforementioned dullness is related to the dullness of the starting pigment.

Attempts to produce a "Ramapo" from conventional type semi-chlor pulp (BK Paste) using the ammonium rosinate dispersion method yielded superficially hard products. A satisfactory product, texture wise, was obtained, however, if kerosene was added to the slurry after the dispersion step. This finding confirms the belief that the presence of kerosene with solvent-ground material contributes to improved texture.

f - Preparation of Other LB/CPC Lakes

A BL-263-D linoleum lake prepared from kerosene grind process material using the standard formula, dispersed satisfactorily in linoleum, despite poor initial water dispersion observed in the course of manufacture. The product was a green vs standard and equal in strength. The product was found by analysis to contain 19.1% CPC as compared to 17.6% for the standard.

Some color change was observed on curing the linoleum sample containing the experimental lake whereas the standard product was little effected.

The preparation of a water-dispersible lake (BL-220-D) from kerosene process material using the standard BL-220-D formula, was not successful. Little coloring of the China Clay substratum was observed due to poor dispersion of the color. A satisfactory lake was prepared however, using the aforementioned ammonium rosinate dispersion method. The product is 100% stronger in extension (paper coatings - brushouts) than standard BL-220-D despite the fact that the CPC content of the two are essentially equal. The material is equal to standard in lightfastness, working properties, wetting, and is superior in dispersion. The product is s. green vs standard.

Work on the preparation of LB/CPC lakes from kerosene process pulps was discontinued due to a decision to employ isopropanol as the solvent-grinding medium, the use of which assures a more easily water-dispersible pulp comparatively free of residual kerosene.

d - Comparison of Solvent and Salt-Milling

A grinding series designed to compare solvent-milling versus salt-milling suggests the following conclusions. (Duplicate runs were consistent.)

Kerosene grind appears to be very slightly superior to mineral spirits grind.

9/1 Na_2SO_4/CPC salt-milling appears to be superior to 9/1 NaCl milling (Orchem), which, in turn is superior to 4/1 Na_2SO_4 and 4/1 Na_2SO_4 plus oleic acid.

9/1 Na_2SO_4/CPC salt milling produced the best results of the series. The best solvent-milled sample appears essentially equal to the 9/1 NaCl salt-milled sample but is slightly (±5%) weaker than the 9/1 Na_2SO_4 sample.

Steam-distillation of a solvent milled sample in the presence of alkali yields pigment slightly inferior in strength (±5%) and very slightly dull compared to the 9/1 Na_2SO_4 salt-milled color.

Inks prepared from salt-milled pigment are muchheavier in body than thoseof comparable strength made from solvent-ground pigment. The difference in body is such as to raise serious objection to the use of salt milling in this instance.

e - Consistency of Finishing Process

A series of experiments designed to determine the extent of the variation in tinctorial properties to be expected in pigments prepared from a particular sample of crude LB/CPC indicate that except for slight differences in strength, the properties of the several finished samples were essentially identical. The finishing process studied consisted of the following successive steps:

a) replacement of kerosene in the crude kerosene filter cake with mineral spirits.
b) grinding of the pigment in mineral spirits.
c) steam distillation of the grinding medium.
d) sulfuric acid extraction.
e) ammonia extraction.
f) drying.

IV. APPENDIX I

1 - Laboratory Synthesis and Finishing of LB/CPC

The procedures as outlined here represents the best conditions for synthesis in kerosene devised for laboratory preparation to date, consistent with the use of a solvent-milling process for particle-size reduction. The finishing procedures are adapted for use with a kerosene-synthesized crude. Major alternative procedures within the kerosene process are listed as well as process differences involved in the use of trichlorbenzene as synthesis medium.

a - Equipment Used in Laboratory Synthesis Studies

The reactor is a glass, 2000 ml resin reaction flask provided with four necks and a removable top, (Scientific Glass Apparatus Co., Bloomfield, New Jersey, Catalogue #7977) designed to facilitate the removal of solid materials from the flask and to permit the use of a large and efficient anchor-type glass stirrer which would not fit through the opening in the ordinary three-neck flask. The anchor-type agitator rotates at 200-230 rpm, and clears the bottom and sides of the reactor by approximately 1/4 - 3/8". The arms and crossbars of the agitator are 3/8" wide, and the height of the anchor, 3". The reaction vessel is heated by means of a Glas-Col heater (Variac-controlled) especially designed for this assembly. The assembly is provided with a thermometer and an air condenser. One neck on the assembly top is used for the introduction of sulfuric acid during the "sulfation" procedure.

b - Synthesis Charge

	M.W. -	Grams
(Dec-Base Kerosene or	-	702
(Trichlobbenzene	-	1413
Cupric Chloride (anhydrous)	134.48	37.8
Urea	60.06	250.1
Ammonium Molybdate	-	0.34
Phthalic Anhydride	148.11	136.4
Crude 4-chlorphthalic Acid	-	54.6

Materials specifications: The following substances were used in the laboratory preparations:

Phthalic Anhydride - Supplied by National Aniline Co.

Urea - Supplied by DuPont

Copper Chloride - ($CuCl_2$) Anhydrous Powder, J.T. Baker's "CP Analyzed". Copper Chloride Dihydrate ($CuCl_2.2H_2O$) Technical, supplied by Harshaw Chemical Co. is satisfactory (use 47.9 grams in the above formulation).

Ammonium Molybdate (contains 82.2% MoO_3) J.T. Baker's "CP Analyzed".

Kerosene - "Dec-Base" a deodorized kerosene supplied by L. Sonneborn Sons, Inc. or Esso "Bayol" D supplied by the Standard Oil Co. of New Jersey

Trichlorbenzene, technical - supplied by Dow Chemical.

Crude 4-chlorphthalic acid - Newark Laboratory synthesized (Notebook 1261-31).

Analyses: 12.65% organic chlorine
15.57% inorganic chlorine

This corresponds to: 4-chlorphthalic acid 71.6%
sodium chloride 25.7%
phthalic acid (by difference) 2.7%

Sufficient crude 4-chlorphthalic acid is used so as to insure a reaction mixture containing 17.3 mol percent of 4-chlorphthalic acid and 82.7 mol percent of phthalic anhydride and phthalic acid. The quantity of unchlorinated phthalic acid present in the crude-4-chlorphthalic acid is taken into account in determining the charge of phthalic anhydride. The quantity of sodium chloride present is taken into account in calculating the quantity of sulfuric acid to be used in the subsequent "sulfation" procedure.

c - Procedure

Charge the kerosene and reactants in the amounts listed. Heat by means of the Glas-Col heater to 195°C. over a period of 2-2-1/2 hours, the charge being well agitated throughout (200-230 RPM) this and the subsequent heating period. Maintain the temperature of the charge at 195° ±3°C for 4 hours.

d - Sulfation

Continue the agitation and allow the reaction mixture to cool to 150°C. Add 116.6 ml. of 98% sulfuric acid, dropwise, to the agitated slurry over a period of 3/4-1 hour. Some agitation difficulty may be experienced during the addition of the last 10% of the acid. 1.25 parts of 98% sulfuric acid are used per part of LB/CPC assuming a 90% yield, plus that quantity of acid required to convert the sodium chloride originally associated with crude 4-chlorphthalic acid and now present in the final reaction mixture, to sodium hydrogen sulfate.

Allow the sulfated reaction mixture to cool to room temperature (Note 1) Decant the major portion of the kerosene from the sulfated mass and suck the crude LB/CPC sulfate as free as possible from residual kerosene (Note 2), (Note 3).

e - Hydrolysis of the "Sulfate"

The green LB/CPC sulfate crude is hydrolysed by steam distillation in the presence of 10% sodium hydroxide solution until the kerosene odor is no longer evident. (Note 4). The hot slurry is filtered and washed free of alkali.

f - Acid Extraction

Extract the washed filter cake by slurrying it in 2% sulfuric acid at the boil for 1 - 1-1/2 hours. Filter hot and wash free of acid.

g - Ammonia Wash

Wash the acid-extracted crude cake on the filter with a solution of 500 ml. concentrated ammonia in 500 ml. of water. Wash free of ammonia.

h - Drying of the Crude

The crude, extracted LB/CPC is dried in the oven at 150°C. for 48 hours. (Note 5).

i - Grinding Crude LB/CPC

Grinds are run in 1/2 pint glass jars using 5/32" steel balls.

Grinding Charge (Note 6): 12.0 gr. crude extracted pigment
100 ml. 91% isopropanol
600 gr. 5/32" steel balls
5 ml conc. aqueous ammonia

Grind for 120 hours.

j - Final Extractions

The ground slurry is strained and water-washed from the steel grinding balls. Steam distill the ground slurry, until free of grinding solvent (odor no longer evident).

Add sufficient dilute sulfuric acid to insure a final acid concentration of 2%. Extract at the boil for 1 hour. Filter hot and wash free of acid (litmus). Reslurry in 3% ammonia solution and extract at 75°-90°C for 1/2 hour. Filter hot and wash free of ammonia.

The final finished presscake may be retained as a pulp, or oven-dried at 180°F. for 24 hours.

k - Rubouts

Masstone: 0.5 gr. dried pigment mulled (Hoover Muller) with 1.0 gr. varnish drier (5 x 50).
Extension: 0.180 gram masstone ink, 10 gr. zinc oxide.
All comparisons are adjusted strengthwise.

a - Kerosene product (not acetone-washed) - v.v.s. dull, and v.v.s. red vs. BP-173-D standard.
b - Kerosene product (acetone-washed) - v.v.s. red, and equally intense vs BP-173-D standard.
c - Trichlorbenzene product (not-acetone washed) v.s. red and equally intense vs BP-173-D standard.

Acetone grinds give somewhat redder products than do kerosene grinds.

NOTE 1 - Inasmuch as the effectiveness of the "sulfation" process depends to a large extent on the degree of conversion of the LB/CPC to its "sulfate", it is advisable to permit some extended time of contact between the acid and the pigment after all the acid has been added. In laboratory practice, the sulfated, kerosene-slurry has been permitted to remain over night "as is", at room temperature.

APPENDIX IV — FORMULA SHEET

COLOR CODE — LAB. — DATE — NAME "Lanapo" Blue. Blue LB reprinted

OBJECT Hampo Lake (BP-173-D type) from kerosene ground, alkaline - extracted filter cake. CBP-173

BASED ON 1242-22

BATCH SIZE-MOLE 250 gr. starting LB/CPC BATCH NO. OF "G" CALLED 2 (2539)

LBS. OR GMS.	MATERIAL	100% WT.	GAL.	c. c.	MANIPULATION	MS
					Screen into a 4-liter beaker, through a	
					20 mesh sieve	
846	Semi-works lot #20	250				
	alkaline - extracted					
	filter cake (32.12%					
	solids, ±28% kerosene)					
					Add	
450	Conc. NH_4OH (28% NH_3)			500		
					Screen in through a 10 mesh - sieve	
50	K wood rosin					
					Heat to 180°F. plus, without an increase	
					in volume (see notes) and continue heating	
					until all the rosin is dissolved (+30 minutes)	
					"Lightning" agitation is maintained through-	
					out the dispersion step. Occasionally	
					wash down sides of vessel with a minimum	
					amount of water (see notes)	
					Run dispersion into an 8-liter jar	
					Make up volume to	
				5000	with water. Heat with steam to 150°F.	
					(wood-paddle agitation)	
					Strike with a solution of	
25	$BaCl_2 \cdot 2H_2O$ (+98%)				in	
				500	water over a period of 20 minutes.	
					Heat to a boil (steam) and continue heating	
					for 1/2 hour.	
					Filter hot and wash free of ammonia (litmus)	
					and chlorides.	
					Dry at +120° - 140°F. for 48 hrs.	
					Analysis: 72.8% LB/CPC	

PACKAGE LBS. PER COST GROUP SIGNATURE J J Elrick

GOAL YIELD 365 grams

NOTE 2 - An acetone wash of the "sulfated" filter cake on the Buchner funnel at this point to remove residual kerosene and green impurities gives a final pigment which is more intense than the unwashed counterpart. The use of an acetone wash step at this point or at some later point in the process in plant operation presumes that suitable equipment is available for its operation.

NOTE 3 - If trichlorbenzene is used as the reaction medium, the LB/CPC sulfate formed does not settle, as in the case of the kerosene process material and filtration is necessary to effect the separation of the LB/CPC sulfate from the major portion of the trichlorbenzene. Extended agitation of the LB/CPC sulfate slurry in trichlorbenzene appears, however, to give rise to some "balling" of the sulfate, which effect may permit easier separation of the trichlorbenzene, possibly by decantation. This fact has not been definitely established.

NOTE 4 - In semi-works operation, the steam distillation (with or without sodium hydroxide) of the LB/CPC sulfate which is, of necessity, hot after the kerosene decantation, invariably gives rise to serious "balling" effect and hindered steam distillation of the kerosene. In laboratory, this effect is not at all pronounced, due to more complete kerosene removal and rapid cooling of the LB/CPC filter cake to room temperature. This objectionable "balling" can be avoided in semi-works by a "cold-hydrolysis" procedure which employs ice and a quantity of sodium hydroxide sufficient to neutralise the sulfuric acid liberated during the regeneration of the LB/CPC from its "sulfate". A reasonably well dispersed slurry is obtained which can then be steam-distilled without any difficulty to give a final blue slurry of good dispersion.

NOTE 5 - The effectiveness of the subsequent grinding process in 91% isopropanol depends to a considerable extent on the degree of kerosene removal from the crude. In semi-works operation, temperature and time of drying, and thickness of the filter cake are important factors in the drying step.

NOTE 6 - As stated in the discussion, the use of acetone as grinding medium, permits good grinding of crudes containing larger quantities of residual kerosene or kerosene gums. If acetone is used, the concentrated ammonia may be omitted from the grind formula.

NOTES

1) The quantity of conc. NH_4OH specified is in great excess of that required (theor.) to dissolve the rosin. Ammonia losses during the course of laboratory heating cannot be predicted. Excessive loss of ammonia will cause the precipitation of free rosin, and the laboratory scale formula is written to insure a constant excess.

2) Dilution with water during the course of the dispersion step is to be avoided. The maximum dispersion effect is obtained using an essentially concentrated ammonium rosinate solution in excess ammonia. The mixture, however, must be sufficiently fluid to insure rapid and effective agitation. For large-scale operation, internal open-steam heating in an insulated vessel is suggested so as to prevent excessive dilution.

3) If the ammonium rosinate dispersion is permitted to cool, an ammonium rosinate gel forms. The gel can be readily "liquified" for pumping purposes, by agitation and heating. The gel subsequently dissolves. Whether gelling of the ammonium rosinate prior to the strike affects Ramapo quality, has not been determined.

4) The volume specified prior to the barium chloride strike is arbitrary at this stage of the development. Excess ammonia must be present, however, to prevent free rosin precipitation.

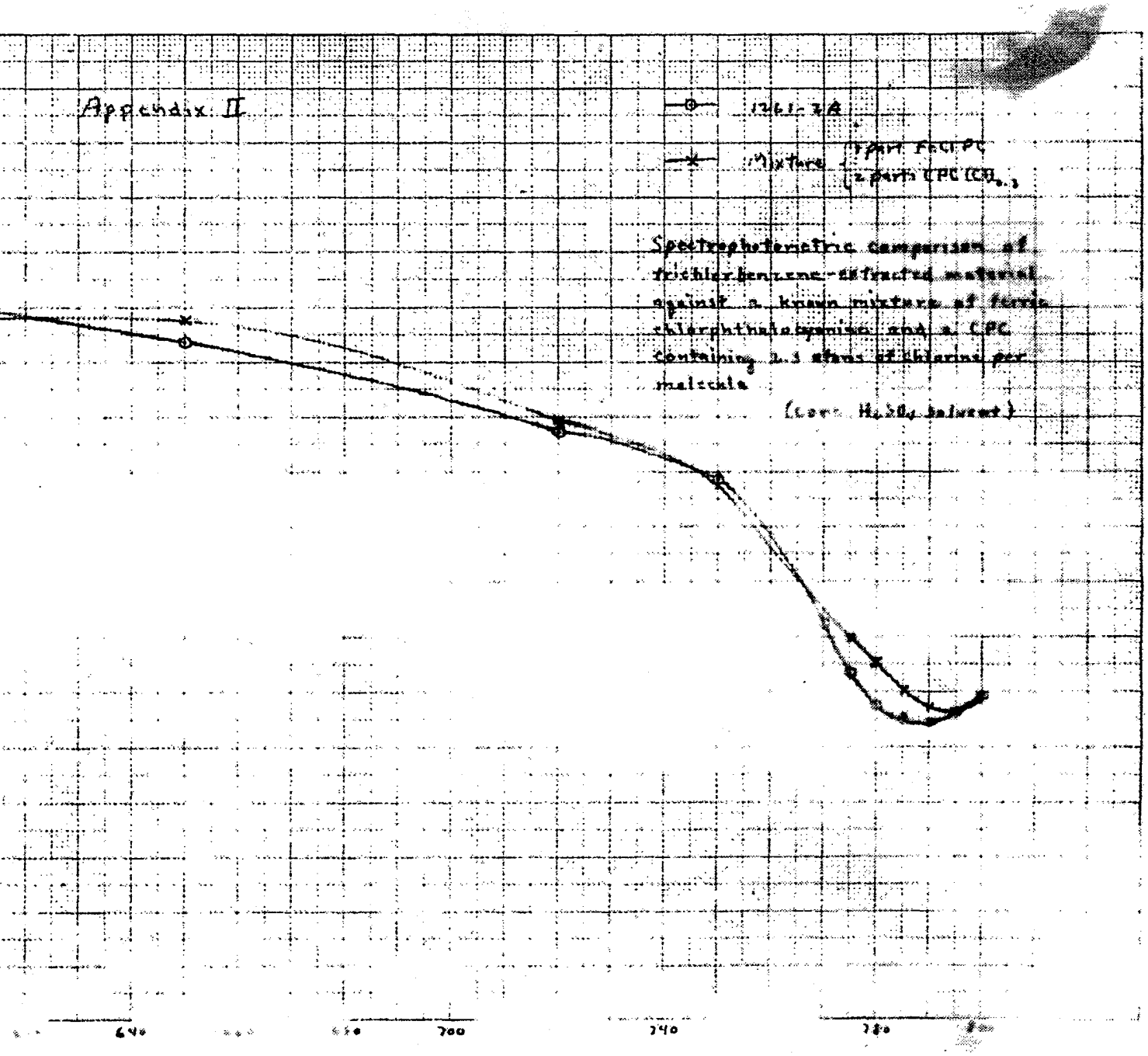
5) No attempt is made to neutralize the final slurry prior to filtration. The procedure presumably serves as an ammonia extraction step. (Standard BP-173-D formula neutralizes with acetic acid. The alkalinity in that process, however, is due to NaOH which cannot be effectivly removed by washing and adversely affects the finished product).

6) The formula, as written, employs 50% less rosin and 50% less $BaCl_2$ than the standard BP-173-D formula. Advantage is taken of the impurities (naphthenates etc.) originally associated with the starting pigment ($\pm$8% based on 100% LB/CPC).

7) Drying at $\pm$200°F. produces a stronger through inferior product from the point of view of rate of strength development.

8) The final product is superior in texture (wedge grit) to standard BP-173-D made from acid-pasted pulp. The soft texture is attributed to the treating-agent effect of the kerosene originally present with the pigment. The product is inferior to standard BP-173-D as regards rate of strength development in the loose passes, but is equal to the standard on the tight pass tests. The inks are softer and longer than BP-173-D standard.

Appendix II



Spectrophotometric comparison of trichlorbenzene-extracted material against a known mixture of ferric chlorphthalocyanine and a CPC containing 4.3 atoms of chlorine per molecule

(conc. H_2SO_4 solvent)

Appendix III

V - REFERENCES

1 - KN-46-7 - "Review of I.C.I. Phthalocyanine Art. A Digest of I.C.I. Reports in Company Files." March, 1946, Newark File 223.4

2 - I.C.I. Report K-598, "Monastral Fast Blue LBS: Manufacture from 4-Chlorphthalic Acid and Phthalic Anhydride". June 10, 1942.

3 - KN-47-5 "Chlorine-Free" CPC: Synthesis by Phthalic Anhydride/ Urea/Kerosene Method." February, 1947, Newark File 223.4.

4 - I.C.I. Report H-3984, "Monastral Fast Blue B: Preparation of Material Satisfactory for Use in Certain Finishes", April 4, 1939.

5 - KN-46-19 "The Finishing of Phthalocyanine Pigments I: Wet Grinding Studies" June 3, 1946, Newark File 223.4.

6 - KN-46-55 "The Finishing of Phthalocyanine Pigments II: Wet Grinding Studies". August 12, 1946, Newark File 223.4.

7 - KN-47-48 -"Laboratory Preparation of Crude 4-Chlorphthalic Acid For Use in "Monastral" Fast Blue LB Synthesis". December 22, 1947, Newark File 223.4.

Notebook References

1195, 1218, 1242, 1261