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CHEMICAL DIVISION - COLORS

BLUE SYNTHESIS: YIELD STUDIES

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NEWARK PLANT
PIGMENTS COLOR RESEARCH REPORT
PROGRESS REPORT

TITLE: BLUE SYNTHESIS: YIELD STUDIES

PERIOD COVERED: JUNE, 1950 - DECEMBER, 1952

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INTRODUCTION:

After a standard process for plant production of CPC was established, it was considered desirable to investigate the synthesis step further with a view to improving yields and/or quality. This report covers the laboratory and associated semi-works studies of CPC synthesis variables carried on intermittently from June, 1950 to December, 1952.

CONCLUSIONS:

Goal yields for CF/CPC and LB/CPC were established for plant synthesis yield comparison as 90.2% and 84.2% of theory respectively.

There were indications that 2 hours is sufficient reaction time for good yields of CPC.

A variable involving delaying the addition of cupric chloride showed some promise of producing a stronger CF/CPC in better yield.

The preferred sources of copper are cupric chloride or cuprous chloride. When used in an amount equal to 110% of the theoretical requirement, a yield increase is realized over the original standard process, wherein only the theoretical quantity was specified.

The minimum of urea which must be used to obtain a good yield of CPC is 14.5 moles per 1 mole of copper and 4 moles of phthalic anhydride.

When phthalic anhydrides, containing more than one chlorine substituent, are employed in standard process to synthesize CPC with chlorine content much higher than 4.1%, the products tend to be weaker, duller and greener than standard LB/CPC.

The best 4-chlorophthalic acid for LB/CPC manufacture is that made by a low temperature chlorination of disodium phthalate. The use of 4-nitro phthalic anhydride in an amount calculated to give the mononitro compound results in a very dull product.

The most effective catalyst is ammonium molybdate or molybdic oxide. Phosphorus oxychloride is as effective as the molybdenum, when used in large quantities. Aluminum chloride or titanium tetrachloride are somewhat effective, if used in molar quantities equal to the source of copper.

DISCUSSION:

Standard CPC Synthesis

A set of six laboratory syntheses of chlorine-free CPC were made to determine the average yield for use in the Newport plant as a goal yield. The average yield of crude having only an alkaline extraction

was 97.7% of theory, based on starting phthalic anhydride. The average extracted solids using a mixed solvent extraction was 92.3%, making the average yield of essentially 100% CPC 90.2% of theory (1403-70).

Nine control LB/CPC laboratory syntheses with a 91.7% of theory yield of crude and an average of 91.8% extracted solids gave a 100% CPC yield of 84.2% of theory.

Variations in Standard CPC Synthesis

Low Urea

When the ratio of urea to cupric chloride was lowered from the usual mole ratio of 14.5:1 to 13.5 or 12.5 for one of cupric chloride a yield decrease of 7-10% resulted (1403-85).

High Urea

Amounts of urea greater than the above standard amount produced no greater yield of CPC (1434-65)

Temperature Variable

CF/CPC syntheses made in the lab. at temperatures of 195°, 210°, 220° and 230°C all produced essentially the same yield of crude and quality of finished product. However, the products from the reactors at the higher temperatures were more granular. Considerable kerosene losses were observed at the higher temperatures. (1367-52).

When these same temperatures were applied to LB/CPC syntheses the yields were equivalent, but weaker products were obtained at higher temperatures, especially at 220° and 230°C. There were no noticeable differences in physical appearance of the kerosene slurries. Again the higher temperatures resulted in considerable loss of kerosene, approaching 50% loss in the case of 230°C reaction temperature (1367-52).

Reaction Time and Temperature Comparisons

In view of evidence that indicated 3-iminophthalimidine is an intermediate in CPC formation, a synthesis was held at a lower temperature (145°-150°C) for two hours (i.e. under conditions to promote formation of intermediate and to minimise decomposition and side reactions) before finally raising the temperature to the usual synthesis reaction temperature (195-200°C). The total time of this reaction was not increased over the usual four hours; therefore, the time at the higher temperature was only two hours. The yield was found to be 4% lower than its control, but the products had slightly better strength (1403-61).

Based on reports by Orchem that their yields of CPC using TCB as diluent were improved if the reaction mass was held at 160°C for a time before heating to the 195-200°C reaction temperature, syntheses were made holding the temperature at 150°, 160°, 170° and 180°C for four hours before maintaining at the usual reaction temperature of 195-200°C four hours. In our kerosene syntheses there was no evidence of yield improvement over a control, but the longer heating did have a tendency toward increasing dullness of the final product (1403-62).

Another experiment along these lines employed preheating at 160°C for varying times with subsequent heating at reaction temperature for varying times, the total time in each case being six hours.

The four hours at 195-200°C appeared to be the optimum time and temperature, with longer heating offering no yield improvement, and shorter heating periods (in spite of longer heating at 160°C) giving indications of slightly lower yields. Limited preheating does not compensate for reaction at high temperature in giving a good yield of CPC (1403-63).

When LB/CPC syntheses were held at 160°C four hours before heating to 195-200°C for four hours, there were no differences observed in yield or quality (1403-64).

Delayed Addition of Copper

The effect of delaying the introduction of cupric chloride in CPC synthesis was examined first with chlorine-free CPC. The theoretical amount of cupric chloride necessary to react with phthalic anhydride present was added at 160°, 180° or 190°C as the mass was heated up to reaction temperature. The yields were a little low due to poor transfer of the $CuCl_2 \cdot 2H_2O$ to the hot reaction mass, for violent dehydration blew some of the copper compound out of the reactor. The quality of the finished products showed that the higher the temperature of addition, the stronger the pigment. All were greener and more intense than the control (1382-19).

Later experiments on delayed addition of copper employed a kerosene slurry of anhydrous copper chloride. In the laboratory the yield of CF/CPC was equal to controls, but LB/CPC yields were low. Some yield advantage was found in each type of synthesis if 110% instead of 100% of the theoretical amount of copper was used. Both the chlorine-free and LB types were stronger than their respective controls with slightly darker masstones (1382-67, 70).

If the copper was added in CF/CPC immediately upon reaching 190°C a good yield was obtained. If addition was made after one hour at 195°C the yield dropped to 66% and the CPC did not form a smooth slurry, but crystallised in large lumps, so that agitation was impossible. Excessively delaying addition of copper chloride led to lower yields and a more granular product or actual solidification into a cake (1382-87).

One semi-works trial of delayed addition of 110% of theory anhydrous $CuCl_2$ in CF/CPC synthesis produced 97% yield with quality 3% strong, vs red versus a control (SW 2545-2551).

One semi-works attempt of LB/CPC synthesis by delayed copper addition failed because the mass crystallised in the reactor to extremely large solid lumps. It was felt that the CF/CPC synthesis may have been fortuitous, so no more syntheses were run until some

assurance could be given that the reaction mass would remain a smooth slurry. This problem has not yet been solved.

One attempt was made in the laboratory to obtain a smooth slurry by using an Orchem product DV-17 (50% kerosene solution of 80/20 "Lorol" methacrylate/"Daktose" B) in the synthesis. The smooth slurry was maintained, but only a 78% yield was obtained (1403-16).

Variations in CPC Synthesis Reactants

Copper or Copper Compounds

Table I shows the average of alkaline extracted crude yields of CF/CPC and LB/CPC with 100% and 110% of theoretical amount of $CuCl_2 \cdot 2H_2O$ necessary to react with the phthalic anhydride present. Numbers in parentheses indicate number of syntheses averaged.

TABLE I

	LABORATORY		SEMI-WORKS	
	CF	LB	CF	LB
100% $CuCl_2 \cdot 2H_2O$	94 (6)	92 (8)	84 (7)	84 (1)
110% $CuCl_2 \cdot 2H_2O$	96 (8)	94 (6)	91 (2)	86 (1)

There is a general increase in yield resulting from increasing the amount of copper in the synthesis. The quality of the products from 110% copper reactions was essentially equal to that in which 100% copper was employed. The laboratory CF/CPC products finished by glass jar, five day grinds averaged vs weak versus standard BT-297-D, lot 373, but the semi-works products milled 48 hrs. in a 58 gallon ball mill were 6% stronger than the same standard. The laboratory LB/CPC products were 6% strong, versus standard BT-304-D, SD 90719, with the semi-works products essentially equal (1382-1 thru 20, 40, 47; 1367-54).

Copper oxychloride (ex. Rohm and Haas, $CuCl_2 \cdot 3Cu(OH)_2$) was evaluated as a possible substitute for $CuCl_2 \cdot 2H_2O$ (ex. Harshaw) in the event of short supply of the latter and also as a cheaper source of copper. Table II shows the average yield obtained when this material was used.

TABLE II

	LABORATORY		SEMI-WORKS	
	CF	LB	CF	LB
100% $CuCl_2 \cdot 3Cu(OH)_2$	92 (3)	90 (8)	91 (2)	76 (2)
110% " " "	93 (6)	90 (8)	90 (2)	----

These yields are poorer than those of Table I where the $CuCl_2 \cdot 2H_2O$ was used. Quality of pigment obtained with the oxychloride was essentially equal to that of the corresponding $CuCl_2 2H_2O$ products

(1382-3 thru 15, 35 thru 40, 47, 57, & 58).

Synthesis with $CuSO_4 \cdot 5H_2O$ produced a low yield of CF/CPC (84%), with ultimate quality of the product being strong, v green, v dull, versus controls (1382-1).

A DuPont-Grasselli compound referred to as "Copper A" (tetracopper calcium oxychloride - 45% Cu) gave a low yield (76%) of CF/CPC (1382-8).

Cuprous chloride (ex Millmaster Chemical Corp.) was found to give yields and quality entirely equal to that of cupric chloride dihydrate (1382-8).

Finely powdered copper metal was used with an oxidizing agent, ammonium perchlorate, in TCB according to U.S. Pat. 2,469,663 (Standard Ultramarine). The yield and quality of this CF/CPC was found to be entirely equal to that from standard type synthesis from cupric chloride dihydrate (1403-6, 7).

A Harshaw product "Black Copper Oxide"
(Ref. Letters: J deL Moomaw to F. C. Evans "Copper Materials"-4/18/51
J. H. Cooper to P. H. Griswold, "Substitutes for $CuCl_2$ 4/26/51)

when employed to synthesize CF or LB/CPC gave reaction masses which solidified upon reaching reaction temperature of 195-200°C. Another Harshaw product "Copper Hydrate" gave the same result. However, if the copper compound was first dissolved in the urea to be used for synthesis, and this followed by the addition of the other reactants, then the difficulty was overcome sufficiently to permit the reaction. A low yield (75%) was obtained, with ultimate quality of the product being dull and green.

When the copper hydrate was mixed with $CuCl_2 \cdot 2H_2O$ in a 3/1 molar ratio as is found in the oxychloride the yield of 88.6% was slightly lower than that obtained when the complex compound itself was used (92%). The ultimate pigment quality was equal (1367-74 & 75).

When copper acetyl acetonate was employed as a copper source no CPC was obtained (1434-21).

Solvents or Diluents

Table III lists the diluents used in standard syntheses with corresponding yields of CPC.

TABLE III

Diluent	% Of Theoretical Yield
Kerosene, Bayol D	94.0 CF/CPC

TABLE III (Cont)

Diluent	% OF Theoretical Yield	
n-Hexyl ether (1365-58)	87.4	CF/CPC
ODCB (1403-25B)	69.3	LB/CPC
α-Cl Naphthalene (1403-26)	55.4	CF/CPC
Diethyl Carbitol (1365-58, 1403-27)	None	
Dichloroisopropyl ether (1365-58)5	None	
Dimethyl formamide (1403-26)	None	
Tetramethyl urea (1403 - 71)	None	

Bayol D is only satisfactory if it has not been subjected to air oxidation. A considerable amount of work was done in an attempt to determine the factors which may inhibit synthesis of CPC. Some interesting observations were made from this work.

The yields of syntheses with varied amounts of fresh kerosene and kerosene which had been treated with air at 195-200°C show that the yield of CPC is directly dependent upon the relative proportions of such kerosene used. Peroxide in the kerosene does not per se inhibit CPC formation. (1403-75, 78).

There are several unusual occurrences especially noticeable when synthesis is carried out with a relatively large proportion of "oxidized" kerosene. The initial reaction of phthalic anhydride with urea wherein gases are evolved is accompanied by serious foaming. In the range 140±5°C a considerably larger amount of water distills than normal. At 170°C a reaction occurs with excessive foaming yielding predominately a red-brown mass. Continued heating to reaction temperature produces some CPC with the total mass appearing very dark green. Treatment with caustic soda and acid removes considerable impurities and copper salts. The resulting finished CPC is excessively dull (20% yield of CPC with 35% deteriorated kerosene).

Simple reflux of deteriorated kerosene showed it to produce five times as much water as fresh kerosene. When this reflux of deteriorated kerosene was carried out in the presence of anhydrous copper chloride in the same proportion as is used in the synthesis the amount of water produced was twenty times that of fresh kerosene and four times that from the bad kerosene alone. Ammonium molybdate in the normal catalytic amount produces the same result. The kerosene turned very dark brown during the reflux with cupric chloride.

To determine whether this water evolved was consuming urea in the synthesis and thereby decreasing yield, syntheses in deteriorated kerosene were run with increased urea. Only a trace improvement in yield was observed (1403-84).

Syntheses with lower than the normal amounts of urea were made in good kerosene to observe whether the same effects occured

as with normal urea in deteriorated kerosene. None were observed. The behavior was entirely normal except that a lower yield was obtained (1403-85).

Treating air exposed kerosene with caustic at 110°C prior to CPC synthesis improved yield only very slightly (16 to 21%), but the resulting CPC was very much improved in intensity (1403-78).

To determine whether the oxidizing power resident in deteriorated kerosene was specifically the cause of low CPC yield, such kerosene with peroxide no. 45 was heated under N_2 gas to 195-200°C until the final peroxide number was only 2.4. This kerosene, when used in a synthesis, gave exactly the same yield of CPC as before destruction of the oxidizing ability. This indicates that the by-products of the oxidation are probably the principal inhibitors of CPC production (1403-79).

An attempt to remove the oxidizing ability of a treated kerosene by washing with acidified potassium iodide was not very successful. Ten washings reduced the peroxide number from 45 to 31 (1403-79).

All the above experiments involved kerosene which was exposed to air in contact only with glass equipment. Metals are known to catalyze oxidation of hydrocarbons with air. To test this, CPC syntheses were made with kerosene treated with air at room temperature and then also in the presence of cupric chloride solution. The initial peroxide numbers (0.10) showed no essential difference. The yield of CPC with kerosene treated with air in absence of copper ion was good (94%), whereas the yield from the kerosene treated with air in the presence of copper was very poor (71%) (1403-84).

The copper compound formed in the reactions with air treated kerosene was not isolated. It was present along with CPC, and no promising physical means of separation were found due to extreme insolubility of both substances. The red brown material formed in a 20 hour standard reaction at 125-130°C was purified by washing with organic solvents and analysed. It had a high percentage of copper (28%) and considerable nitrogen (7.8%). Treatment with strong acids decomposed it leaving a phthalimide residue. Beyond these facts, that the compound contains copper and phthalimide or an analogue, the structure is unknown.

Production of such a substance was shown to be dependent upon use of air exposed kerosene. A reaction with fresh kerosene under N_2 gas gave no such substance as that when a similar reaction was allowed to breathe air. Another reaction with an exposed kerosene produced this same red-brown product.

Phthalic Anhydride Substitutes

Varying amounts of dichlorophthalic anhydride (ex Niagara Alkali Co.) were employed in CPC synthesis in an attempt to

approach the hue of BT-297-D. Products were obtained in good yield, but they were weak and dull as ultimate pigments. The amount of greenness increased with increasing chlorine content. It required 75/25 mole percent ratio of dichlorophthalic anhydride to phthalic anhydride to obtain a product as green as BT-297-D (1357-3, 9).

A special process for manufacture of 4-chlorophthalic acid (4-CPA), developed by W. R. Remington of Jackson Laboratory, was examined. This process involved chlorination of disodium phthalate solution, with frequent pH adjustments as chlorination proceeded to maintain pH above 5, all at a temperature of 50°C. (Ref. JLR-59-1, No. 99 Serial No. 20847). When 4-CPA made by this process at Orchem or Newport was used on the basis of analysed organic chlorine content, the finished LB/CPC was found to be weak and green versus standard BT-304-D. (Ref. Letter, Blue LB, P.H.G. to J.H.C. 1/24/51) (1367-66, 67; 1382-34).

When 4-CPA was introduced into LB/CPC synthesis as a monosodium, disodium or cupric salt the yields were found to be equal to a standard control synthesis. Quality of ultimate pigment was fully equal to the control. (1382-43).

Phthalocyanine synthesis from a 2/2 mole ratio of 4-nitrophthalimide to phthalic anhydride produced a good yield of a weak, green dull pigment versus BT-284-D, SD-444 (1348-83).

Formation of a mononitro CPC by reaction of a 1/3 mole ratio of the same anhydrides gave an 83% yield of crude pigment. When finished by the usual acetone shot milling, the pigment was found to be very dull and green in rubout versus BT-304-D, SD90719 and strong dull and red versus BT-297-D, lot 373. The flocculation resistance of this finished pigment in alkyd was exceptionally good. Alkyd grinds of 5% and 10% mixes of the mononitro CPC with BT-304-D showed slight and proportionate improvement in flocculation, but not enough to be of interest as a flocculation inhibiting component (1403-4).

Catalyst

Standard CF/CPC synthesis with the ammonium molybdate catalyst omitted produced only a 15.2% yield of CPC (1434-24A).

When molybdic oxide (N-418) was used in place of ammonium molybdate in LB/CPC synthesis, it was found to give equivalent yields and quality of pigment (1382-89).

Anhydrous aluminum chloride has some efficacy in promoting CPC synthesis. A large amount was necessary to obtain a reasonable yield. When used in a mole ratio of 0.7/1 of phthalic anhydride, an 80% yield of CPC was obtained (1367-78).

Use of $TiCl_4$ (in place of ammonium molybdate) in an amount proportionate to that used in direct synthesis of polychlor CPC from tetrachlorophthalic anhydride (U.S. Pat. 2,549,842 to Standard

UltraMarine Co.) produced CF or LB/CPC in about 63% yield. The solvent milled LB product with titanium hydrate present was 55-60% weak versus a control synthesis, but only 14% weak after removal of the hydrate. The solvent milled CF product was 45% weak with hydrate present and 10% weak after its removal (1367-79;1403-1,8).

With benzoyl chloride in large amount, a CF/CPC yield of 65% of theory was obtained (1403-5). When phosphorus oxychloride was used, a standard yield of standard quality CF/CPC was obtained (1403-5). Both benzoyl chloride and phosphorus oxychloride were used in a 1/2 mole ratio with phthalic anhydride.

When As_2O_3 was used in a 1/4 mole ratio with phthalic anhydride, a slightly poor yield (80% of theory) of good quality CF/CPC resulted. Sb_2O_3 gave such severe foaming that the reaction mass could not be contained in the reactor. (1403-9).

Alkaline Agents

When alkaline materials such as trisodium phosphate, quinoline or formamide were present in CF/CPC syntheses (10% of phthalic anhydride weight) the yields were lowered, seriously in the case of trisodium phosphate. There was no pigment quality deterioration when the organic bases were employed. (1382-6,7).

With sodium hydroxide (5 or 10% of phthalic weight) present in laboratory CF/CPC syntheses no yield or pigment quality improvements were observed (1382-6, 11, 18, 19, 30), In semi-works syntheses of CF/CPC with 3% caustic present one showed an 81.2% yield as compared with 78.3% for the control. When 110% of theoretical amount of copper was used equivalent yields were obtained with or without caustic. Based on this limited evidence, it appears that practically no yield increase is effected by addition of caustic. The ultimate pigment quality was poorer when sodium hydroxide was used along with the excess copper because the phase change in acetone shot milling was slower than in the control, producing a red hue in the final mill sample versus the control. This same phenomenon of redness was observed in another CF/CPC synthesis from 110% of theoretical copper oxychloride with 3% caustic (SW 2473, 4, 6, 7 and 2502). In view of the lack of definite conclusions from the laboratory and SW studies, the final decision on the merit of addition of caustic soda to the synthesis will depend on actual plant experience.

Oxidising Agents

A mild oxidising agent, nitrobenzene, was added to CF/CPC syntheses in small amounts and found to lower yields slightly, but gave quality essentially equal to the control. (1382-88).

Special Agents

A commercial product referred to as DV-17 (formerly PL-161) manufactured by Orchem (50% kerosene solution of a copolymer of 80/20 "Lorol" metacrylate/"Daktose" B; the latter is diethylamino ethyl methacrylate) was suggested by I.F.Walker of the Experimental Station and by Jackson Laboratory for better dispersion of CPC in the kerosene synthesis slurry, as well as for good yield at lower temperatures with less kerosene. These possibilities were investigated in laboratory and semi-works syntheses, to which was added DV-17 in an amount of 2% on weight basis of pigment yield.

In the laboratory variable study it was found that good slurries were obtained with less kerosene. The ultimate quality of pigments was equal to the control. When the reaction temperature was lowered to 185°-190°C, a yield was obtained equal to that at 195-200°C. There was a tendency toward weakness in the ultimate pigment.

Better data were obtained in the semi-works trials with this agent. Examination of the kerosene synthesis slurries indicated they were thinner because the pigment was more granular than usual and settled out of the slurry faster. Consequently, viscosity measurements were actually made on kerosene containing a smaller concentration of suspended pigment and were, therefore, misleading.

Syntheses made at temperatures below the usual 195-200°C gave lower yields. All semi-works finished products made with DV-17 were on the defensive in strength. Added to this deficiency was a slower than normal shade conversion. The use of this agent was not recommended. (1403-13, 14, 77).

EXPERIMENTAL:

Standard CF/CPC Synthesis

The following ingredients are placed in a 2 liter resin flask equipped with anchor type agitator, thermometer and large diameter air cooled gas exit tube.

A. Designed to produce a theoretical yield of 0.28125 moles CPC or 162.03 gms (1382-3A).

166.6	grams	phthalic anhydride	(1.125 moles)
250.1	"	urea	(4.17 ")
0.34	"	ammonium molybdate	
48.0	"	cupric chloride dihydrate	(0.2813 moles)
900	ml.	Bayol D (specially purified kerosene ex Esso)	

B. Designed to produce a theoretical yield of 0.25 moles CPC or 144.0 gm (1403-70)

148.1	gm	phthalic anhydride	(1.0 mole)
222.0	"	urea	(3.7 moles)
0.3	"	ammonium molybdate	-----
42.6	"	cupric chloride dihydrate	(0.25 mole)
800	ml	Bayol D	

The reaction mass is heated within 90 minutes to 195-200°C and held at this temperature four hours. Special care is taken from 105-125°C because the conversion of the anhydride to imide is accompanied by very rapid gas evolution which has a tendency to foam out of the reactor.

After the four hour reaction time the mass is cooled to 150°C and sulfated by dropwise addition of 100 ml. (90 ml. in example B) of 98% sulfuric acid with good agitation. The reaction mass is then allowed to cool to room temperature and filtered as free from Bayol D as is possible. The CPC sulfate is steam distilled free of kerosene in the presence of 200 gms sodium hydroxide (180 gm in ex. B), filtered hot, washed free of caustic and dried at 180°F for 48 hours. The product obtained here represents the crude yield. Extraction by tentative method 3/27/52 (A. H. Oberle) with the solvents acetic acid, ethanol (23A), HCl (conc.) and benzene in the volume ratio 40:45:10:5 removes considerable impurities to give a truer yield of CPC.

Standard LB/CPC Synthesis

The following ingredients are placed in a two liter resin flask:

A. Designed to produce a theoretical yield of 0.28125 moles or 168.75 gms (1382-12A).

137.8 gms phthalic anhydride (0.938 moles) mole ratio (0.827)
50.5 gms 4-chlorphthalic acid Lot #2 (0.196 moles) " (0.173)

Analysis of Lot #2 showed 27.86% total Cl
14.20% inorganic Cl
therefore 13.66% organic chlorine

Assuming all organic Cl to be present as 4-chlorphthalic then 77.29% of Lot #2 is 4-CPA; since 39.04 gms of 4-CPA is necessary 50.5 gms of Lot #2 contains this amount.

250.1 gms urea (4.17 moles)
0.34 " ammonium molybdate
48.0 " cupric chloride dihydrate (0.2813 mole)
900 ml Bayol D kerosene

B. Designed to produce a theoretical yield of 0.25 moles or 150.0 gms (1403-64A)

122.5 gms phthalic anhydride (0.827 mole)
38.5 gms 4-chlorphthalic acid Lot #419 (0.173 moles) (15.93% organic Cl)
222.0 gms urea (3.7 moles)
0.3 gms ammonium molybdate
42.6 " cupric chloride dihydrate (0.25 mole)
800 ml Bayol D, kerosene

Remainder of the procedure is the similar to that for CF/CPC synthesis with the exception that more sulfuric acid is necessary for sulfation due to sodium chloride present in the 4-CPA.

A requires 110 ml of 98% sulfuric acid; B, 100 ml.

Proportionately more caustic is used in the steam distillation of kerosene.

Acetone Shot Milling and Extraction

In 1/2 pint jar are placed 600 gms 1/8 inch steel shot, 12 gms of alkaline extracted crude and 100 ml acetone. This is milled three days, then diluted with water and screened to remove the steel shot. The volume of slurry is made up to one liter and the acetone distilled off with steam. 25 ml of conc. sulfuric acid is added to the slurry and boiling continued for 30 minutes. The slurry is filtered, washed free of sulfate ion, then washed on the funnel with 500 ml of 5% ammonium hydroxide solution. This pigment is dried at 60°C and evaluated by rubout.

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