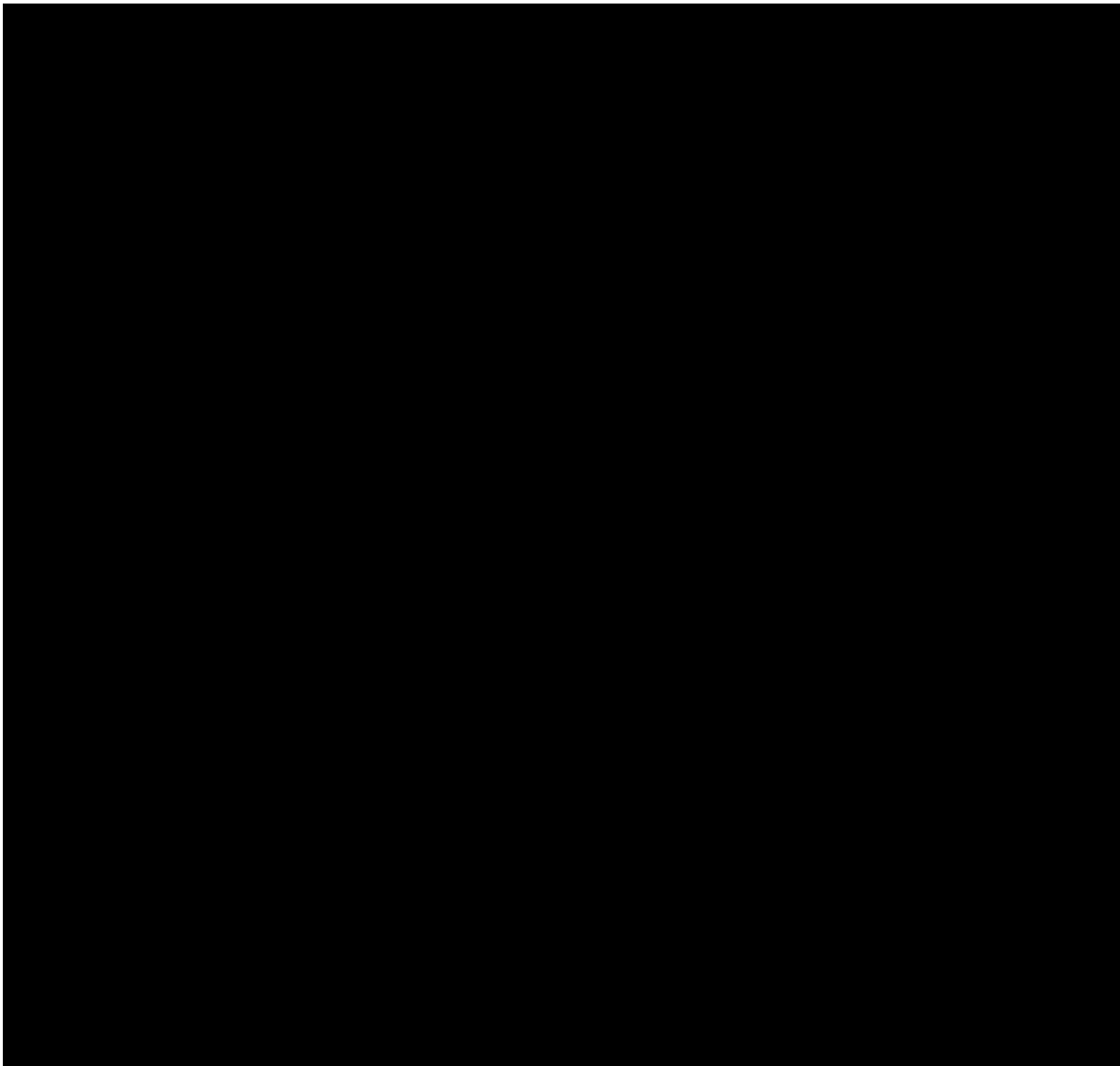

KN-77-1

Copy No. 26

DISTRIBUTION ON LAST PAGE

E. I. DU PONT DE NEMOURS & COMPANY

NEWPORT PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: CONTROLLED SULFATION/HYDROLYSIS OF CPC-BB

PERIOD COVERED: December, 1975 - January, 1977

NOTEBOOKS: E-8369, E-10663, E-12469

PREPARED BY: R. J. GUSCHL R.J. Guschl DATE: AUGUST 5, 1977

APPROVED BY: C. W. ANDERSON

PREVIOUSLY RELATED REPORTS: None

ABSTRACT

Variables in the sulfation and hydrolysis steps of CPC-BB processing have been identified and studied. The reaction of sulfuric acid and pigment (sulfation) influences crude beta phase content whereas the temperature of hydrolysis determines particle size. A low temperature sulfation/hydrolysis of CPC-BB (25°C.) was used to prepare a BBS product without a 6-hour premilling of the crude.

DUP050108899

INTRODUCTION

A fire in late 1975 moved all CPC-BB synthesis to CPC-II (A-200) and created an immediate need for a process for preparing these products in existing equipment. Unfortunately CPC-II had been designed to produce BB via an HT drowning process which had become obsolete due to economic and environmental considerations. An economic evaluation[1] favored a direct transfer of the CPC-I synthesis/sulfation/hydrolysis process to CPC-II. To determine if the process could be so implemented, a laboratory evaluation of the process was undertaken.

OBJECTIVES

Our objectives at the start of this work were:

1. To determine if CPC-BB could be synthesized, sulfated, hydrolyzed and extracted with caustic in CPC-II
2. To determine if the caustic extraction step of this CPC-BB process is necessary, and
3. To develop a fundamental understanding of the sulfation and hydrolysis of CPC-BB crude.

SUMMARY AND CONCLUSIONS

We have found that the process used for over twenty years in the manufacture of CPC-BB in CPC-I could be readily used in existing equipment in CPC-II. Because of the dangers associated with pumping hot kerosene slurries, it was necessary to reduce the temperature of sulfation from 130+^{6}C. to 95°C. This process is now a standard operating procedure.

The caustic extraction step in CPC-BB crude processing does not add to the quality of finished BBS codes. This step does however, guarantee that no acidic pigment is charged to the mills, a condition which could generate hydrogen gas.

A procedure has been developed to deal with "separated" CPC batches. In "separating", the kerosene and pigment separate from the aqueous phase of the crude slurry making pressing and transfer very difficult if not impossible.

The temperature of hydrolysis is the critical factor in determining the crystallite size of BBU (crude). Higher temperatures generate larger crystals. The temperature of sulfation, the amount of sulfuric acid used and the degree of agitation which accompanies it determine the amount of pigment which is unsulfated and remains as beta contamination of the crude.

DUP050108900

SUMMARY AND CONCLUSIONS (Contd.)

In the laboratory, a low temperature (25°C.) sulfation/hydrolysis has been used (with 25% extra sulfuric acid to ensure complete sulfation) to prepare a BBU of crystallite size comparable to that of normal material which has been premilled six hours (BBZ). This material after acetone milling gave an acceptable BBS (N-8510).

PATENT SITUATION

Much of the material covered in this report is related to current plant processes and is either not patentable or already covered. One concept, the use of low temperature sulfation and hydrolysis to reduce milling cycles is possibly unique and a patent proposal (Appendix A) has been forwarded to G. A. Hapka of the Legal Department.

PROGRAM

The author has accepted a transfer to Chestnut Run and plans no further work in this area. K. M. Kolb has the responsibility for executing XON-32 to completion.

ACKNOWLEDGEMENTS

I wish to thank P. H. Griswold for introducing me to CPC chemistry and for many useful discussions. The contributions of J. T. Johnston are gratefully acknowledged. Thanks also to many plant supervisors and operators for their useful suggestions.

DUP050108901

TABLE OF CONTENTS

		Page No.
DISCUSSION		
A.	History	4
B.	Sulfation/Hydrolysis/Extraction of CPC-BB	5
C.	BBS without Premilling	8
D.	Controlled Sulfation and Hydrolysis of LC Crude	11
E.	The Caustic Extraction of CPC-BB	11
EXPERIMENTAL		
A.	Table II - A Summary of Laboratory Sulfations	13
B.	Procedure to Synthesize, Sulfate, Hydrolyze and Extract CPC-BB as in the Plant	19
C.	Laboratory Procedure for Room Temperature Sulfation/Hydrolysis of CPC-BB	21
D.	Procedure to make BT-284 from N-8510 (CPC-BBS)	22
E.	Laboratory Procedure for Premilling and Acetone Milling CPC-BB to BBS	23
APPENDICES		
A.	Patent Proposal	
B.	XON-17	
C.	SOP-110, BB Crude Syntheis Sulfation	
D.	XON-21	
E.	XOP-451	
F.	XON-32	

DUP050108902

DISCUSSION

A. History

In October of 1975, production of CPC-BB in the old CPC plant (CPC-I) was halted by a fire in a synthesis kettle. The cause of the fire was attributed to the addition of wet 4-CPA (4-chlorophthalic acid) to hot kerosene causing a boilover of kerosene onto hot pipes[2]. In the interest of safety, all BB production moved to the new CPC plant (CPC-II). Synthesis itself presented only minor problems, however, implementation of the sulfation, hydrolysis, extraction, pressing and drying steps of this crude became an active area since CPC-II had been designed to utilize HT drowning. Unfortunately, by 1975 environmental considerations required that all waste acid be neutralized before discharge, a requirement which would have increased mill costs by a full $1.00/lb. of CPC. Hence, HT drowning was no longer practical and R&D was asked to find alternate processes for finishing BB in CPC-II with minimal new investment.

Several alternate processes were developed[3] and all were economically evaluated.[1] For late 1975, it was considered best to simply implement the old CPC-I procedure in CPC-II followed by Luwa drying in CPC-II. Problems accompanied the implementation of each step of the process. I feel it is important to record this history and how the problems were solved since there emerged a new understanding of process variables.

1. Old CPC-I process in CPC-I. Synthesis, sulfation at 130°C., hydrolysis, caustic extraction at 90°C., pressing and tray drying.

2. Fire in CPC-I. End of CPC-BB synthesis in CPC-I (10/75).

3. Synthesis in CPC-II. Transfer of cold kerosene slurry to CPC-II for sulfation (11/75).

4. Discovery that green and dull BBS resulted from Step 3 due to incomplete sulfation (high beta content) (1/76).

5. Sulfation and hydrolysis of BB crude in CPC-II at 95°C. (2/76). Transfer of hydrolyzed slurry to CPC-II for extraction and pressing (Appendix B).

6. Separation of batches during transfer of slurry to CPC-II. Pumping and pressing problems. Interim methods to re-establish slurry developed (Appendix D).

7. Implementation of caustic extraction and filtration in CPC-II. Transfer of wet presscake to CPC-I for drying (6/76).[4]

8. Luwa drying of CPC-BB in CPC-II (2/77?)[5].

DUP050108903

A. History (Continued)

This report will deal with steps 4-6 of this history. Step 7 has already been presented by R. D. Nelson[4]. We will also discuss future work which could eliminate premilling steps from BBS finishing by a low temperature sulfation/hydrolysis of CPC-BBU (XON-32 in Appendix F).

B. Sulfation/Hydrolysis/Extraction of CPC-BB

Immediately after the fire, synthesis of BB began in CPC-II and sulfation remained in CPC-I until it could be moved to CPC-II as well. Adequate agitation in the South Development Tank of CPC-II was considered essential to good sulfation. Since no sulfations had ever been run in CPC-II, laboratory sulfations were run on plant crudes to simulate plant conditions. We attempted to model the equipment and agitation of both plants. Resin kettles were employed with propeller-type agitators. Rates of agitation were calculated to match the tip velocities of laboratory equipment to that of the plant agitators. These experiments are summarized in Part I of Table II in the Experimental Section. The conclusion was that there is sufficient agitation in CPC-II for sulfation.

At this point, we had noticed that our laboratory products were greener and stronger in tint than comparable plant standards (N-8520). Studies by x-ray showed our products had a higher beta content (8-13% vs. 0-1% for N-8520), and smaller valley parameters (10-20 vs. 48-55 for N-8520). The only differences we could determine were temperatures of sulfation and agitation. A series of sulfations at different temperatures (Part IV of Table II) soon established that the temperature of sulfation in conjunction with adequate agitation could determine residual beta content (the unsulfated pigment remained as beta contamination). It was also noticed that sulfation at 90°C. gave a product more like N-8520 standard (VP 25 and beta content near zero). Subsequent work of the type in Part V of Table II established that excess acid could be used to guarantee complete sulfation even at temperatures below 90°C.

Simultaneously customer complaints pointed out that our BB products were "green and dull in automotive enamels and resulting batches could not be shaded to meet specifications".[6] It was soon recognized that these pigments had been synthesized in CPC-II and transferred in a kerosene slurry to CPC-I for sulfation. In the interest of safety, the slurries had been cooled before transfer, hence sulfations in CPC-I were performed near room temperature. Analysis of fifteen plant lots verified that these cold sulfations were indeed giving the greener products of higher beta content (5-15% vs. a standard 0.3%). Based on

DUP050108904

B. Sulfation/Hydrolysis/Extraction of CPC-BB (Continued)

these data and the inability of CPC-I to heat kerosene slurries before sulfation, XON-14 was written for sulfation of CPC-BB in CPC-II at 90°C. This XON was rewritten once before implementation to XON-17 (Appendix B) to reflect our more complete understanding of the sulfation/hydrolysis process.

The XON was run from 2/28/76 to 3/2/76 under the guidance of K. M. Kolb, P. H.Griswold, W. E. Miller and the author. The actual lot followed was #400 and despite numerous equipment problems, the sulfation and hydrolysis were relatively successful. Sulfation began at 67°C (goal 95°C.) and 50% more acid than normal was used to guarantee complete sulfation. Agitation was sufficient and the final product had 1% beta but only 1.17% Cl (goal 4.1% Cl, problem not related to this XON).

Six more lots of CPC-BB were successfully sulfated (1% beta, proper chlorine) with R&D coverage. As predicted from laboratory work, the particle size of the product BBU was slightly smaller (valley parameter = 35-50) than the previous standard (VP = 50-55) due to sulfation and hydrolysis at 80°C. The XON was modified to include necessary changes to become SOP-110A (Appendix C).

Further work in the laboratory established that the temperature of sulfation coupled with agitation determines the completeness of sulfation. Incomplete sulfation leads to unreacted pigment as beta contamination. Sulfation without agitation (Part III of Table II) leaves 10-15% beta even at elevated temperatures. At room temperature, agitated sulfation with 25% less acid leaves 5-10% beta (Part V of Table II) whereas agitated sulfation with 25% extra acid is beta free. At the standard 2.20 ratio of acid to pigment, beta contamination at lower temperatures depends too much on agitation, hence we recommend that any sulfation below 60°C. include 25% extra acid.

Finally, we found that the temperature of hydrolysis (closely related to the temperature of sulfation plus heat generated during sulfation) is the critical factor in determining the particle size of the product. Hydrolysis at high temperatures (95-100°C.) gives large crystallites (VP = 50), whereas a room temperature (25-30°.) hydrolysis yields smaller crystals (VP = 0-10). The relationship is not linear or without complications but it is basically supported by the temperature experiments listed in Part IV of Table II. Please note how a 25°C. sulfation followed by a hot water hydrolysis at 90°C. gives a valley parameter of 30 to support this concept. At the lowest temperature studied (0°C. with ice water) the sulfate agglomerated into large ball which retained the heat of hydrolysis to change the experiment to a higher temperature hydrolysis. Such an effect could make low temperature hydrolysis difficult whenever large quantities of pigment are so treated unless heat dissipation is possible.

DUP050108905

B. Sulfation/Hydrolysis/Extraction of CPC-BB (Continued)

In other experiments listed in Table II, we learned more about these processes.

- o A minimum temperature of complete sulfation at the 2.20 ratio with agitation appears to be 60-70°C. Below this temperature, more acid must be used for a beta-free product.

- o Excess times of addition for the acid do not influence product. The sulfation is complete at the end of the addition and the settling time is only used to aid in kerosene decantation.

- o The presence of 2% Emcol PT-10-59 surfactant during routine sulfation/hydrolysis (as in BBF) does not alter the beta content or valley parameter of the product. Rubout properties are also unaffected. The main effect is a more difficult decantation of the kerosene from the sulfate. We also noted a lower percent CPC purity of the crude, probably the result of poor kerosene removal.

- o Duplicate sulfations at 25°C. were followed by 25°C. hydrolyses with and without agitation (during hydrolysis). The products were identical by x-ray (beta-free, VP = 0) showing that agitation during hydrolysis is not a critical variable in the laboratory. In the plant, it might be useful in dissipating heat but the agitator would not reach the slurry until considerable water has been added.

- o The sulfation process raises the temperature of the kerosene slurry by 15-20°C. in the laboratory.

Despite our growing knowledge of the BB process, plant problems continued to call for R&D attention. For several months (2/76 to 6/76) CPC-BB was successfully sulfated and hydrolyzed in CPC-II and transferred to CPC-I by trailer for extraction and pressing. Initially, contamination from LC synthesis was a problem. At times, the plant experienced handling problems caused by the separation of a pigment/kerosene phase from the aqueous phase making trailer-transfer or pressing after extraction impossible.

The cause of these separations was found to be over-agitation of the CPC-BB batches after sulfation/hydrolysis. Excessive periods of high speed agitation in both plants led to agglomeration of the pigment into pellets, slime or cakes which could not be pressed. In the laboratory, several slurries of CPC-BB/kerosene/water "separated" with sufficient agitation. In controlled studies on several plant lots, intense agitation (220 RPM) caused separation after 5-15 hours as compared to a

DUP050108906

B. Sulfation/Hydrolysis/Extraction of CPC-BB (Continued)

control of mild agitation (80 RPM) which did not separate even after 24 hours. High pigment content led to earlier separation. The addition of 1.50% Triton X-100 surfactant before agitation prevents separation under normal agitation but contaminates the pigment.

To eliminate this problem without resorting to Triton in each batch, we recommended sulfation/hydrolysis/transfer/extraction and pressing without delays. When delays are encountered, batch agitation must be minimized. A procedure to salvage separated batches based on recirculation through a centrifugal pump was provided (XON-21, see Appendix D). It was not until steps up to and including caustic extraction were in Plant II (6/76) that CPC-BB production became routine.

C. BBS Without Premilling

One obvious outgrowth of our sulfation/hydrolysis study is that particles the size of our current BBZ crude (6 hour premilled, valley parameter = o) can be generated during hydrolysis. In the laboratory, we sulfated and hydrolyzed CPC-BB at 25°C. to prepare a BBU which is equivalent in size and phase to BBZ (91.7% CPC, 4.04% Cl, 0% beta, VP = 15). Half of this material was premilled and acetone milled (E-10663-93B of Table II) and the other half was directly acetone milled (E-10663-93A). As a control, a sample of plant sulfated and hydrolyzed crude BBU (95°C.) was also treated (E-10663-95A premilled and acetone milled, 95B only acetone milled). Quality data versus N-8510 standard are given in Table I.

TABLE I

	Masstone			Tint		
	Value	Hue	Chroma	Str.	Hue	Chroma
E-10663-93A	Dk_4	G_5	I_{15}	97	G_{10}	I_{10}
93B	Dk_{10}	G_5	I_{10}	94	G_{11}	I_{15}
95A	Dk_{10}	G_5	I_{10}	97	G_{12}	I_{12}
95B	Dk_2	G_7	I_5	97	G_{20}	D_{25}

In comparing these four experiments, several conclusions can be made:

- o Premilling definitely enhances BBS quality (strong, green and intense)

DUP050108907

C. BBS Without Premilling (Continued)

- To maintain our current N-8510 standard with 95°C. sulfation/hydrolysis, premilling is desirable although "just acceptable" material could be produced without premilling
- With 25°C. sulfation/hydrolysis, it should be possible to either eliminate premilling and maintain current N-8510 standard or consistently exceed N-8510 standard.

Five BT-284 samples were prepared from these four samples and standard N-8510. All used 8% $BaSO_4$ as an extender and samples were evaluated in 30-J alkyd, Ford's TSA and acrylic lacquer 927 (Newark evaluations 76-232A, 233A and 231A respectively).

A. E-10663-93A + 8% $BaSO_4$
B. E-10663-93B + 8% $BaSO_4$
C. E-10663-95A + 8% $BaSO_4$
D. E-10663-95B + 8% $BaSO_4$
E. Plant standard N-8510 + 8% $BaSO_4$

In Ford's TSA, all samples flocculated but C, D and E were more flocculated than A, B and 284 standard. In tint and metallics (10/90 and 50/50) A, B, C, D were stronger than E and standard although B and D were slightly green and dull. In 927 lacquer, the same orders were observed. In both Ford's TSA and 927 lacquer, whitening was barely discernible for all samples.

In 30-J alkyd, all six samples flocculated equally and again, A, B and C were stronger than standard in tints and metallics. Sample E was slightly stronger than standard and D was noticeably green and dull. Viscosities in 927 lacquer and Ford's TSA were all slightly greater than or equal to standard in the order A > BD > CE = standard. In 30-J alkyd, the order was E = standard > AB > CD.

In summary, all four laboratory samples are good 284 with a preferred order of A > B = C > D. As for E (our proposed new standard BT-284), we may encounter minor flocculation difficulties in Ford's TSA and 927 lacquer.

Since all premilling/acetone millings were in the laboratory, XOP-451 (Appendix E) was written to test the quality of BBS prepared from plant BBU (95°C.) without premilling. In August, 1976, the XOP was run ahead of additional laboratory work to avoid leaving three solvent mills idle for 24 hours due to a shortage of premilled feed. Current BBU crude (95°C. sulfation/hydrolysis) was charged directly to the acetone mills and the product was somewhat weak (108 and 106), green (G_{11}) and dull (D_{11}) but blendable. Unfortunately, there was some contamination from substandard crudes.

DUP050108908

C. BBS Without Premilling (Continued)

The next and final test of this concept was a plant sulfation/hydrolysis at reduced temperatures. We had anticipated that such a BBU would be comparable to 6-hour BBZ and could be acetone milled without premilling to acceptable N-8510. XON-32 (Appendix F) was written and implemented in part on 2/3/77 on Lot 713. The original XON is designed to find optimum combinations of

1. The temperature of sulfation and hydrolysis
2. Premilling time
e. Acetone milling time

However, time and cost factors restricted the XON to a single test batch at 40°C. Lot 713 was cooled in the cooling tank to 30°C. and dropped to the South Development Tank. Addition of the 393 gal. of sulfuric acid (25% excess) raised the batch temperature to 65°C. and 1100 gal. of cold kerosene was used to cool this to 50°C. Hydrolysis and filtration went without problems. Analysis by x-ray gave a valley parameter of 44 and no beta phase establishing that the sulfation was complete, but the hydrolysis did not occur as expected. Apparently, the large cake of sulfated pigment readily absorbs the heat generated from early hydrolysis and creates in effect a high temperature hydrolysis. Unless this sulfate can be cooled during hydrolysis or spread out to a thin film which will not retain the heat, this procedure is not viable for our existing equipment.

In the laboratory, BB sulfated and hydrolyzed at 25°C. filters roughly 2 to 3 times slower than that treated at 95°C. Recent work by K. M. Kolb suggests even slower rates of filtration would have occurred if the BBU had a smaller particle size.

Although we have prepared acceptable BBS in the laboratory without premilling, we did not succeed in preparing BBX without premilling (Part VI, Table II). BBU prepared from a room temperature sulfation/hydrolysis was breached with perclene but the products were always weak and dull. In repeated experiments, our best product was obtained using an excess of perclene and Dresinate X surfactant, but it was still weak (109) and dull. Although excess Dresinate and perclene improve strength, it appears that a more drastic change in surfactant, breaching solvent or procedure would be needed to eliminate premilling completely from the BBX process. It does seem possible to develop shorter premilling cycles for BBX if a lower temperature sulfation/hydrolysis of BB is demonstrated.

DUP050108909

C. BBS Without Premilling (Continued)

The use of a controlled sulfation hydrolysis process is still of great interest to CPC production. It may be possible to eliminate or at least reduce premilling cycles of BB grades. No significant effort has been directed at understanding why the temperatures of sulfation and hydrolysis are so important, however, a few thoughts seem appropriate.

Mechanistically, we are simply applying basic principles to the CPC-BB process. If one looks upon sulfuric acid as a solvent for CPC, we are simply recrystallizing from sulfuric acid. To aid in recovery, we are introducing water as a second solvent to cause crystallization. Typically the temperature of such a process determines crystal size and morphology. In our case, a lower temperature gives a smaller crystal size.

Granted, this is not a perfect analogy since CPC is not really "soluble" in 2.20 times its weight in sulfuric acid. In fact, the green tetrahydrosulfate is suspended in the excess acid and the process is more of a crystal ripening, where the limited solubility of the solute prevents complete dissolution.

D. Controlled Sulfation and Hydrolysis of LC Crude

A logical extension of this work (preparing BBZ size pigments directly from hydrolysis) was to try to directly prepare an LCZ by this process. To our surprise, a controlled room temperature sulfation/hydrolysis of LC crude yields an alpha I-phase CPC of large particle size (Valley Parameter 62) and very good tinctorial properties (see Part VI of Table II). In comparison to finished LC codes, the pigment is extremely red shade and dull versus BT-297, 383 and 487. Against BT-401, the hue is similar but weak (110) and dull.

This result is very interesting in that BB crude subjected to the same process is converted to alpha I of small particle size (VP = 0 to 10). Accordingly, controlled sulfation/hydrolysis offers little hope of eliminating premilling for LC codes by directly generating a material of premilled particle size. It may, however, be possible to develop this technique as an alternate to acid swelling. Since the kerosene crude would be sulfated directly, this could, in effect, eliminate premilling.

E. The Caustic Extraction of CPC-BB

At one point in developing a CPC-BB process for CPC-II, R&D was asked to assess the need for caustic extraction of BB crudes. Laboratory experiments established that the caustic extraction in BB finishing is not necessary to produce N-8510 quality. Four experiments were run and are summarized in Part II of Table II.

DUP050108910

E. The Caustic Extraction of CPC-BB (Continued)

1. Normal BB finishing as per N-8510

2. Same as #1, no caustic extraction

3. Same as #1, a neutralization to pH 7-8 instead of caustic extraction

4. Same as #1, an additional acid extraction (pH 0.6-0.8) instead of a caustic extraction

Paint evaluations were run of all four pigments in thermo-setting acrylic (TSA) versus BBS (N-8510) and BT-284. A tint (5/95) and metallics (10/90 and 50/50) were prepared for each (Newark code 75-363). In all cases, the paints equalled or exceeded standards in appearance, flocculation resistance and viscosity. No differences could be observed between laboratory samples finished with and without the caustic extraction.

It appears that the main reason for this extraction is safety. To guarantee that no acid gets into a shot-filled mill (which would of course generate hydrogen gas), such an extraction has been justified.

DUP050108911

TABLE I

A SUMMARY OF LABORATORY SULFATIONS

Notebook[1] Pages	Temp. Sulf. (°C.)	Temp. Hydrolysis (°C.)	Ratio (Acid) (Pigment)	Analytical Results % CPC	% Cl	% Beta	Valley Parameter	Remarks
III. Experiments to Determine Value of Agitation								
A. With Sulfation								
E-10663-44 (-8369-86)	25	25[2]	1.82	86.8	3.39	11.0	0	No agitation during acid addition.
B. With Hydrolysis								
E-10663-80 (E-12469-5/6)	25	25[2]	2.20	89.5	4.01	0	0	No agitation during hydrolysis
E-10663-82 (E-12469-7)	25	25[2]	2.20	89.9	4.00	0	0	Full agitation during sulfation and hydrolysis
IV. Effect of Sulfation/Hydrolysis Temperature								
E-10663-43 (E-8369-85)	200	100[2]	1.82	85.0	3.56	0	33	
E-10663-46 (E-8369-88)	150	100[2]	1.82	NA	NA	0	42	
E-10663-47 (E-8369-116)	70	70[2]	1.82	87.5	3.54	0	27	
E-10663-60 (E-8369-127)	25	25[2]	2.20	89.2	4.10	0	0	Control
E-10663-83 (E-12469-8)	25	90	2.20	89.9	4.00	0	30	Hot water hydrolysis

DUP050108912

Notebook[1] Pages	Temp. Sulf. (°C.)	Temp. Hydrolysis (°C.)	Ratio (Acid) (Pigment)	Analytical Results % CPC	% Cl	% Beta	Valley Parameter	Remarks
V. Acid Ratio								
E-10663-66 (E-8369-130)	25	25[2]	1.65	87.0	4.11	7.7	0	25% less acid than needed
E-10663-57 (E-8369-131)	25	25[2]	2.74	86.2	4.12	0	0	25% more acid than needed
E-10663-93A (E-12469-33A)	25	25[2]	2.20	95.7	4.06	0	51	Values for acetone milled end product
E-10663-93B (E-12469-33B)	25	25[2]	2.20	96.1	4.11	0	48	
E-10663-95A (E-12469-37A)	95	95[2]	2.20	96.8	4.59	0	43	Values for acetone milled end products
E-10663-95B (E-12469-37B)	95[3]	95[3]	2.20	95.6	4.69	0	41	

Footnotes:

(1) E-10663 Notebook for experimental procedures, E-8369 and E-12469 for results and interpretation

(2) Actual hydrolysis temperature not recorded but probably 10-15°C. higher than sulfation due to heat

(3) Plant performed sulfation/hydrolysis

DUP050108913

TABLE II

A SUMMARY OF LABORATORY SULFATIONS

Notebook[1] Pages	Temp. Sulf. (°C.)	Temp. Hydrolysis (°C.)	Ratio (Acid) (Pigment)	Analytical Results % CPC	% Cl	% Beta	Valley Parameter	Comments
I. Experiments to Test Agitation of CPC-II								
E-10663-1 (E-8369-31)	25	25[2]	2.20	76.4	3.59	14.0	0	Typical lab equipment
E-10663-4 (E-8369-33)	25	25[2]	2.20	79.9	3.60	13.3	13	Agitation to simulate CPC-II
E-10663-12	25	25[2]	2.20	86.7	3.58	10.7	10	Agitation to simulate CPC-I
II. Experiments to Test Value of Caustic Extraction Step								
E-10663-22 (E-8369-73)	25	25[2]	2.20	97.1	3.60	0	55	No caustic extraction
E-10663-73 (E-8369-74)	25	25[2]	2.20	96.5	3.58	0	51.3	No caustic extraction; acid neutralized
E-10663-16 (E-8369-72)	25	25[2]	2.20	97.2	3.56	7.6	47	Control with caustic extraction
E-10663-17 (E-8369-75)	25	25[2]	2.20	98.1	3.47	8.8	64	Second acid extraction
III. Experiments to Determine Value of Agitation								
A. With Sulfation								
E-10663-44 (E-8369-86)	25	25[2]	1.82	86.8	3.39	11.0	0	No agitation during acid addition

DUP050108914

Notebook[1] Pages	Temp. Sulf. (°C.)	Temp. Hydrolysis (°C.)	Ratio (Acid) (Pigment)	Analytical Results % CPC	% Cl	% Beta	Valley Parameter	Comments
III. (Continued)								
B. With Hydrolysis								
E-10663-80 (E-12469-5/6)	25	25[2]	2.20	89.5	4.01	0	0	No agitation during hydrolysis
E-10663-82 (E-12469-7)	25	25[2]	2.20	89.9	4.00	0	0	Full agitation during sulfation and hydrolysis
IV. Effect of Sulfation/Hydrolysis Temperature								
E-10663-43 (E-8369-85)	200	100[2]	1.82	85.0	3.56	0	33	
E-10663-46 (E-8369-88)	150	100[2]	1.82	NA	NA	0	42	
E-10663-47 (E-8369-116)	70	70[2]	1.82	87.5	3.54	0	27	
E-10663-58 (E-8369-125)	95	0	2.20	91.8	4.06	0	33	Sulfate balled up during hydrolysis (ice H_2O hydrolysis)
E-10663-60 (E-8369-127)	25	25[2]	2.20	89.2	4.10	0	0	Control
E-10663-83 (E-12469-8)	25	90	2.20	89.9	4.00	0	30	Hot water hydrolysis
V. Acid Ratio								
E-10663-66 (E-8369-130)	25	25[2]	1.65	87.0	4.11	7.7	0	25% less acid than normal
E-10663-57 (E-8369-131)	25	25[2]	2.74	86.2	4.12	0	0	25% more acid than normal

DUP050108915

Notebook[1] Pages	Temp. Sulf. (°C.)	Temp. Hydrolysis (°C.)	Ratio (Acid) (Pigment)	Analytical Results % CPC	% Cl	% Beta	Valley Parameter	Comments
VI, Misc, E-10663-61 (E-8369-128)	25	25[2]	2.20	90.2	4.01	0	0	No 1-hr. settle before hydrolysis
E-10663-62 (E-8369-129)	25	25[2]	2.20	89.2	4.08	0	0	Acid addition over 4 hrs.
E-10663-67 (E-8369-132)	95	95[2]	2.20	79.5	4.04	0	38	2% Emcol P-10-59 present
E-10663-59 (E-8369-126)	25	25[2]	2.20	89.0	4.07	0	0	Material breached per BBX without premilling
E-10663-93A (E-12469-33A)	25	25[2]	2.20	95.7	4.06	0	51	Values for acetone milled N-8510; 93A without premilling/93B with premilling
E-10663-93B (E-12469-33B)	25	25[2]	2.20	96.1	4.11	0	48	
E-10663-95A (E-12469-37A)	95[3]	95[3]	2.20	96.8	4.59	0	43	Values for acetone milled N-8510; 95A with premilling/95B without
E-1063-95B (E-12469-37B)	95[3]	95[3]	2.20	95.6	4.69	0	41	
XOP-451 (E-10663-153/E-12469-92)	95[3]	95[3]	2.20	NA NA NA	NA NA NA	2.0 5.5 0	44 43 35	These 3 crudes were acetone milled directly (without premilling) into N-8510. Quality results vs. N-8510 standard were: Lot 796: Lt_{99} R_{99} D_{99} 108 G_{11} D_{11} Lot 797: Lt_{99} R_{99+} D_{99+} 106 G_{11} D_{11}
E-10663-121 (E-12469-27)	25	25[2]	2.20	NA	NA	0	62	On LC crude

DUP050108916

Footnotes:

(1) E-10663 Notebook for experimental procedures, E-8369 and E12469 for results and interpretation

(2) Actual hydrolysis temperature not recorded but probably 10-15°C. higher than sulfation due to heat of sulfation

(3) Plant performed sulfation/hydrolysis

DUP050108917

EXPERIMENTAL

B. Procedure to synthesize, sulfate, hydrolyze and extract CPC-BB as in CPC Plant II (see Notebooks E-8369-103/ E-10663-51)

Equipment: 5-liter RBF fitted with chimney of glass joints (optional)[8] overhead stirrer, heating mantle and thermometer (1/4000 plant scale as per SOP-110A)

Procedure:

1. Check kerosene for water and peroxides
2. Add 950 ml kerosene. Start agitation
3. Add 0.11 g DBPC (di(t-butyl) paracresol)
4. Add 4-CPA. For this scale, determine the number of grams by the formula

$$\left(\text{grams 4-CPA} = \frac{630}{\%\ \text{organic Cl in 4-CPA (whole numbers)}}\right)$$

Example: Lot 113 is 12% organic Cl, therefore use 52.5 g 4-CPA

5. Heat flask to 125°C. over 1/2 hour. When 125°C. is reached, turn off heat.
6. Add in order listed
   a. 227 g urea (3.78 m)
   b. 26 g CuCl (cuprous chloride) (0.263 m)
   c. 0.68 g molybdic oxide (MoO_4)
7. Stir 10 minutes. Check temperature. If below 110°C., proceed and add 125 g phthalic anhydride carefully (watch out for boilover) (0.844m)
8. Immediately after Step 7, start heating over 1/2 hour to 195°C. Decrease heating rate only if foaming is a problem.
9. Hold at 195°C. for 2 hours.
10. After hold, turn off heat and add 150 ml kerosene (optional)
11. Stir 25 minutes and add a second dilution of 100 ml kerosene (optional)
12. Add dropwise over 90 minutes 156 ml (287 g.) conc. sulfuric acid (2.20 ratio of H_2SO_4 to CPC if 83% yield in synthesis)
13. Stop agitation after acid addition and allow flask contents to settle for one hour.
14. Decant off liquids (mostly kerosene). Return any solids which come over with the kerosene.
15. With no agitation, add dropwise but rapidly over 15 minutes 1000 ml distilled water. At the end of this addition, allow contents to settle for an additional 1/2 hour. Remove any floating kerosene.
16. Start mild agitation and stir 15 minutes. Check and record temperature. If above 45°C., wait until it cools below 45°C.

DUP050108918

B. (Continued)

17. In a separate 5 l. flask with agitation, dissolve 213 ml 50% NaOH solution into 1230 ml distilled water. To this caustic solution, add the cooled solution from Step 16.
18. Check pH. Adjust to pH 10
19. Heat to 90°C. and hold at 90°C. for one hour
20. Filter and wash until alkaline free to Brilliant Yellow Paper.
21. Dry product at 100°C. and weigh (or save part of press-cake and determine yield in % solids). Theoretical yield 157.9 g.
22. Obtain from Analytical Group - % CPC, % Cl in pure CPC, full scan x-ray and rubout product against N-8520 standard.

DUP050108919

C. Laboratory Procedure for room temperature sulfation hydrolysis of plant kerosene slurry (See Notebooks E-12469-33 and E-10663-91)

Equipment: 5-liter RBF fitted with addition funnel, condenser, overhead stirrer, heating mantle and thermometer.

Procedure:

1. Reslurry BB synthesis slurry and remove sample which will contain 193 g. CPC-BB

   Record Batch # CPC-BB _____
   % Pure CPC in Crude _____
   # g. crude used _____
   (# g. crude x % pure CPC should = 193 g.)

2. Record the temperature of the slurry _____°C. and turn agitator on (at this point, one can adjust temperature to any desired value).
3. Add dropwise over 90 minutes 522 g. concentrated H_2SO_4
4. After acid addition, stop agitation and allow flask contents to settle one hour.
5. Decant off kerosene recovering any sulfate. Note consistency of sulfate; grainy, pasty or balled.
6. One hour after settling of step #4 has ended, proceed with hydrolysis. Try to measure temperature of sulfate before adding water.
7. Hydrolysis - With no agitation, add dropwise but rapidly, over 15 minutes 1375 ml of cold water (25°C. or less). At the end of this addition, agitate for 30 minutes (Note: agitator may be on during this addition, but seems not to effect product)
8. Add an additional 1800 ml of cold distilled water over 15 minutes and stir an additional 15 minutes.
9. Add over 30 minute peiod, 505 g. 50% NaOH solution.
10. Check pH and adjust to 10.
11. Heat solution to 90°C. and hold at 90°C. for one hour.
12. Cool, filter and wash until alkaline free to Brilliant Yellow paper.
13. Dry any part of presscake at 100°C.
14. Obtain from Analytical Group: % CPC, % Cl in pure CPC, full scan x-ray and rubout product against N-8520 standard.

D. Laboratory Procedure to make BT-284 from N-8510 (CPC-BBS) (See Notebooks E-12469-51 and E-10663-105) Actual procedure given comes from E-10663-105.

1. Reslurry 55 g. of E-10663-72E into 460 ml. water
2. Add slowly with agitation 4.40 g. $BaSO_4$ (8% extender)
3. Allow to stir one hour
4. Check pH. Adjust to range 8.0-10.0
5. If additional NaOH (50%) was added, stir an additional 30 minutes.
6. Filter and wash until alkaline free to B.Y.
7. Dry 24 hours at 100°C. in vac. oven
8. Grind powder
   7 LSP
   3/32" RP
   1750 RPM (Max. temp. 210°F.)
9. Rubout against BT-284 standard. This material is ready for paint evaluations.

DUP050108921

E. Laboratory Procedure for premilling and acetone milling CPC-BB to BBS
(Based on information from E. W. Gillow - Notebook E-8369-76)

Premilling:

To a one quart mill (steel container) charge
1500 g. 1/8" steel shot
150 g. #10D steel nails
100 g. CPC
and mill 40 hours at maximum noise level (~300 RPM) on 2" diameter rollers.

Milling with Acetone

To a 2/3 gal. mill charg
4500 g. 1/8" steel shot
120-150 g. CPC
1000 ml acetone
2 drops Triton X-100
and mill 70 hours (68-72 acceptable) at maximum noise level (260 RPM) on 2" diameter rollers.

Finishing

1. Separate shot from pigment slurry
2. Transfer acetone slurry to proper size RBF. Wash out mill and shot with limited water. Add to acetone slurry.
3. Begin steam sparge (do not use a heating mantle to heat acetone) and distill off acetone. Distillation will occur at 55-60°C. and shoot up to 80°C. when all recoverable acetone is off. Hold at 100°C. for 20 minutes.
4. Dilute volume with distilled water to 4 liters.
5. Heat at 95°C. for 1/2 hour.
6. Add 49.3 g. sulfuric acid (27.4 ml conc.)
7. Adjust pH to 1.5
8. Heat at 95°C. for 1/2 hour
9. Filter and wash with warm (40-60°C.) water (2 liters)
10. Wash with solution of 5 ml NH_4OH (conc.) in 50 ml H_2O
11. Wash again with 2 liters warm water
12. Wash with enough cold water to reach> 2000 ohms.
13. Reslurry with enough water to make easily stirrable
14. Adjust pH to 7 to 10.5 with more of the above mentioned NH_4OH solution
15. Filter and dry
16. Obtain from Analytical full scan x-ray, % CPC and % Cl on pure CPC and rubout product against N-8510 standard.

APPENDIX A

PATENT PROPOSAL