KN-77-4

Copy No. 12

DISTRIBUTION ON LAST PAGE

E. I. DU PONT DE NEMOURS & COMPANY

NEWPORT PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: IMPROVED CPC GREEN PRODUCTS

PERIOD COVERED: August, 1976 - February, 1977

NOTEBOOKS: E-12469, E 12475

PREPARED BY: R. J. Guschl RJG Date: May 3, 1977

APPROVED BY: C. W. Anderson CWA Date: May 3, 1977

PREVIOUSLY RELATED REPORTS: None

ABSTRACT

Experiments directed at CPC green chlorination and breachings have given us several interesting results which could be developed into new or improved green products. A Green G dry toner has been developed which is more transparent than GP-817-D equals Harmon's 5018 in transparency and dark flop. The large aggregates in our GT-820-P, which prevent good textile ink dispersibility, are formed during the final stages of ODCB removal. Acceptable and improved GT-820-P has been prepared from both GEU and GGU by several procedures including high turbulence during distillation. A perclene/AS, solvent/surfactant combination can be used to prepare adequate GT-751-D and more transparent greens.

2-(2-Aminoethylamino) ethanol

A = Aminoethyl ethanolamine $H_2N-CH_2-CH_2-NH-CH_2-CH_2-OH$

S - sulframine 1298 - p-dodecylbenzenesulfonic acid

DUP050108777

TABLE OF CONTENTS

		Page No.
DISCUSSION		
A.	Luwa LC Crude for GE Halogenation	4
B.	A More Transparent Green	6
C.	Green Breaching Studies	12
D.	Perclene for ODCB in Green Breachings	17
E.	An Improved GT-820-P	19
F.	GT-805-D	24
EXPERIMENTAL		
A.	Procedure for GE Chlorination	28
B.	Procedure for GEX Breaching	29
C.	Procedure for GGX Breaching	30
D.	Procedure for Orchem's Breaching	31
APPENDICES		
A.	W. P. VanVliet letter to R. J. Guschl - Experimental Transparent Green CPC	
B.	R. J. Guschl letter on GT-751-D/GT-820-P Quality	
C.	Analytical Method for Determining % ODCB in GT-820-P	
D.	The History of SL0451, GT-820-P	
E.	P. J. Krape letter to J. Jackson (NRD-4-77/ILF-9-77)	
F.	P. J. Krape letter to J. Jackson (G-36-76/ILF-73-76)	

DUP050108778

Introduction

Although CPC green pigments enjoyed large volume production and sales in 1976, quality was variable and it became obvious that new and improved products are needed to maintain these levels. For sometime, R&D has directed programs at producing strong, yellow and intense green pigments from both plants. Marketing has put its emphasis on expanding green pigment sales through the development of a green presscake for textile ink applications. Although GT-820-P was developed two years ago to meet this need[1], it has not been accepted because of poor and variable dispersibility in textile ink applications. Only three lots of plant GT-820-P made to date have been acceptable.

There has also been a steady demand for a more transparent dry green toner for automotive finishes. Initially, R&D developed GP-817-D[2] but it was too expensive. Subsequent work[3] did not improve upon GP-817-D[3].

Currently, all CPC-II green production uses purchased Japanese LC crude (Dianichiseika (Dian)) for chlorination to GEU. Since we could incrementally save 50¢/lb. to use our own LC crude, there is interest in developing a process for making acceptable GT-751-D in CPC-II from our own Luwa dried high purity LC crude (LDHPLC).

Objectives

- To develop a process for consistently producing GT-820-P with strength in textile inks equal to our standard lot 451. To develop a GT-820-P equal to Sun's green presscake (464-6947)
- To develop a dry Green G shade toner equal in strength, hue, intensity and transparency to GP-817-D in automotive products via a practical process.
- To develop an improved understanding of green breaching and restore plant GT-751-D quality to strong, yellow and intense.
- To develop a GT-805-D with improved strength, intensity and transparency.

Summary and Conclusions

We have developed a more transparent Green G dry toner for use in automotive finishes. The product is produced from our crudes (LDHPLC) which havebeen GE chlorinated and routinely breached followed by flash distillation to remove the solvent.

DUP050108779

Summary and Conclusions (Continued)

Either ODCB or perclene can be used. The product is more transparent than our earlier GP-817-D and equals Harmon's 5018. It should be economical to produce.

We have identified the critical step in preparing GT-820-P to be the distillation. By ODCB/AS breaching a good GEU or GGU, GT-820-P equivalent to SL0451 can be prepared by flash distillation, batch distillation with intense agitation or incomplete distillation (50%) followed by solvent washing to remove the residual ODCB. Such press-cakes adequately washed with 2-ethoxy ethanol (2EE) and acetone have quality near that of Sun's 464-6947.

The breaching of green crudes has been extensively studied and we have used this information to help obtain strong, yellow and intense GEX from CPC-II. Fundamentally, the variables of reactant concentration, synthesis by-products, reflux time, batch size and chlorination endpoint affect GEX quality. Several new surfactant/solvent systems have been successfully used to generate acceptable GT-751-D including perclene and Arquad. Substitution of perclene for ODCB in our existing process would give acceptable GT-751-D from both GG and GE crudes.

The implications of these studies on GT-805-D are discussed.

Patent Situation

Much of the work covered in this report is related to current plant processes and is either not patentable or already patented. Our work on a more transparent green or an improved GT-820-P may offer a new twist to an already known process and maybe of interest to Legal if new products result.

Program

Several contributions to our understanding of green CPC pigments have been made and this work should be pursued to benefit the colors business. Specifically, I feel that the following areas should be developed further:

1. A more transparent green pigment should be developed based on a Luwa-dried high purity LC crude (LDHPLC). This crude should be GE halogenated, breached in either ODCB or perclene and flash distilled. Flash distillation is needed to remove the solvent without producing an opaque masstone.

DUP050108780

Program (Continued)

2. An improved GT-820-P should be pursued following our discovery that significant aggregation occurs during the last stages of ODCB removal. Plant samples should be generated from both GE and GG crudes using flash distillation or batch distillation with intense agitation. Furthermore, the two-solvent breaching concept should be further studied and optimized to develop a GT-820-P which equals or exceed Sun's 464-6947. Whether or not sulfonic acid groups are responsible for Sun's improved properties (or could be of value) should be resolved.

3. Serious thought should be given to the use of perclene as the breaching solvent for GT-751-D and the more transparent green product described herein.

4. The differences between our LDHPLC crude and Dian crudes should be resolved and this information should be utilized to make acceptable GT-751-D in CPC-II. Experiments should be completed to determine if there are growth inhibitors in LDHPLC-based GE crudes.

The author has accepted a transfer to Pigments, Chestnut Run and plans no further work in this area.

Acknowledgements

I wish to thank P. J. Krape for many hours of discussion and all textile ink evaluations. It took our joint effort to open up the GT-820-P problem. For many long hours in the laboratory, I thank J. T. Johnston and the technicians at Chestnut Run. Thanks also go to W. E. Miller for many discussions and access to his experience in green pigments.

DUP050108781

DISCUSSION

A. Luwa LC Crude for GE Halogenation

In CPC-II, all greens are produced by GE halogenation and only Japanese crude LC (Dianichiseika, Dian) is chlorinated. Typically, the use of our own LC crude (CPC-I synthesized, tray dried) gave a bluer and duller product through this process, although both this crude and the Dian crudes give acceptable GG crudes in CPC-I. The incentive for making an acceptable GT-751-D via GE halogenation from our own crude is a savings of 50¢/lb. (incremental cost versus the price of Japanese crude) and we have already demonstrated that the additional pounds of LC crude can be so made in CPC-I without new investment[4]. The drying capacity for this additional crude is also available in our new Luwa driers.

In the laboratory, we chlorinated (GE, Experimental A) several LC crudes without complications. Table I is a summary of these experiments. Included were a variety of Luwa-dried LC crude, laboratory synthesized LC, the current Dian crude and several crudes extracted by caustic and acetone before chlorination. Analytical data on the LC crudes appears in Table II.

In tinting properties, the Luwa-dried High Purity (>90% CPC) LC crudes (LDHPLC) of low kerosene content (<0.6%) made acceptable GT-751-D after routine breaching. However, there was a noticeable blueness and dullness versus standard. Please note that this type of crude is standard for CPC-I production since mid-1976[5]. The masstones of all laboratory prepared samples were very dark and will be discussed in Part B of this discussion. There were no discernible differences between GT-751-D pigments made from LDHPLC synthesized in "LOPS" kerosene and that synthesized in Deobase kerosene[6].

Using these laboratory results for guidance, XON-33 was written by W. E. Miller to chlorinate LDHPLC in CPC-II. The XON called for three sets of experiments on

(1) 50% LDHPLC/50% Dian
(2) 75% " /25% "
(3) 100% " /0 "

When part 1 was run, the resulting GT-751-D product was very blue and dull[7]. Since laboratory breachings of these GE crudes also gave very dull products (eg. 103 Y40 D40), we concluded that additional work must be done in this area before the plant would be permitted to use only 100% LDHPLC for GE. Earlier we had observed blueness and dullness, but the effect was not as great as that observed in the plant.

DUP050108782

A. Luwa LC crude for GE Halogenation (Continued)

We strongly suspect fundamental differences between GEU derived from LDHPLC and that produced from Dian crude. Earlier, R. L. Sweet had characterized several such differences between LC crudes synthesized in kerosene and trichlorobenzene (TCB)[8]. He had concluded that kerosene residues and tars are responsible for dull GE breached products and that these impurities can be extracted by acetone (Soxhlet). The darkness of masstone characteristic of GEX made from LDHPLC and the wider x-ray absorptions noted in Table I support this position. Note also that Dian crudes are probably TCB synthesized.

The experiments necessary to determine if our LC crudes (LDHPLC) can be used in the GE process were outlined as follows and need to be completed.

1. All the Luwa crude used in XON-33 must be laboratory chlorinated and breached to confirm the plant results.

2. A 50/50 blend of these crudes and Dian crude must be laboratory chlorinated and breached as well.

3. Laboratory chlorinations and breachings should be run on the following crudes as they are and after they have been caustic and acetone extracted.

   a. Dian crude
   b. A representative LDHPLC
   c. Toyo-Japan crude since these crudes have never been acceptable for GE, GG and BGD use.

The extractions for part 3 have already been run and two chlorinations/breachings have been run side by side. Tested were the extracted Dian crude and one of the LDHPLC crudes used in XON-33. The extracted Dian crude gave a strong, blue and dull product (94 B_{10} D_{10}, E-12475-130A of Table I) and the LDHPLC gave a yellow and intense product (100 Y_{15} I_{15}, 130B). It is interesting to note that when the LDHPLC sample was laboratory chlorinated and hydrolyzed in the presence of 2% Emcol P-10-59, the final GEX was 100 B_{15} D_{15} (130C). Although these experiments only warrant completion of the above proposed study, it is interesting to postulate that the impurities in normal Dian crude help generate more crystal growth possibly by making the GEU more dispersible in the breaching medium. Regardless of the mechanism, these results (blue and dull with Dian) are inconsistent with the accepted belief that there are growth inhibitors generated (or already present) in the chlorination of LDHPLC. Furthermore, these studies invite further experimentaion and suggest that 100% LDHPLC could be used in CPC-II to make GT-751-D. If indeed there are identifiable differences between the crudes, a modified breaching procedure would have to be developed.

DUP050108783

A. Luwa LC Crude for GE Halogenation (Continued)

Reference to Table I shows that the depth and transparency of most of our laboratory chlorinated LDHPLC exceeds the differences demonstrated in Table III. There is an additional darkness associated with using these crudes over Dian crudes. Since several of the breachings in Table I even exceeded Harmon's 5018 in darkness, we concluded that the quality of Harmon's 5018 masstone can be readily matched using a low kerosene LDHPLC which experiences a short distillation time after breaching.

Since a plant process which would utilize this information would require 1) use of our LDHPLC and 2) flash distillation of the breached GEX, we proceeded to evaluate these materials as replacements for GP-817-D. Such a process would not be hampered by the unfavorable economics of GP-817-D[3].

In related work (see part D of this discussion), we prepared very transparent GE products from LDHPLC by a perclene/AS breaching followed by rapid solvent removal. Since we merely substituted perclene for ODCB, this gave us additional flexibility for a proposed plant process since we know perclene can be flash distilled readily (BBX). Table IV is a summary of our breaching with perclene and it is again obvious how the use of our LDHPLC (88A) gives darker masstones than those possible with plant chlorinated lots using Dian crude.

B. A More Transparent Green

The darkness of the masstones observed in Table I was worthy of further study since we have long sought a more transparent green. All laboratory breachings give dark masstones in comparison to GT-751-D and identical laboratory samples of different distillation times demonstrates how opacity can be varied. Compare 70A of Table III with the normal two hour reflux before distillation to 31B with a 20-hour reflux before distillation. With longer reflux periods on Dian based crudes, masstone changes from Dk_{99} to Dk_5 versus GT-751-D, although both are Lt_{99} versus Harmon's 5018.

For the more transparent green products prepared above, paint evaluations versus GT-751-D, GP-817-D and Harmon's 5018 were obtained. In Ford's TSA (Newark evaluation #76-336A), our experimental green (ODCB, WEM #1963) is more transparent than GT-751-D and GP-817-D and equals or exceeds that of Harmon's 5018. It also has a darker flop in metallics than GT-751-D and Harmon's 5018. This evaluation was repeated on another sample (E-12475-61) against standards by W. P. VanVliet of Chestnut Run (see Appendix A) who concluded "Experimental transparent CPC green E12475-61 is significantly more transparent compared to Monstral® Green G,

TABLE I

SUMMARY OF LABORATORY CHLORINATIONS

Chlorination Exp. # (E-12475)	LC Crude	IR[1]	Breaching[2] Exp. # (E-12475)	% CPC	X-Ray[3]	Rubout Tint	Rubout Masstone vs. GT-751-D	Rubout Masstone Harmon's 5018	Textile Ink[4] Min.	Textile Ink[4] Max.	Comments
16	Luwa 1688	0.09	20			103 B_{30} D_{30}	$Dk_{99}+I_{99}+$	Lt_{15} D_{15}	NA	NA	
57	Dian	0	63	92.5		100 B_3 D_3	Dk_{29} I_{29}	Lt_{99} D_{99}	NA	NA	
59	Luwa 1963	0.11	65	93.6	1.06	92 Y_{15} I_3	$Dk_{99}+I_{99}+$	Lt_{19} D_{15}	140	97.5	
WEM[5]-1963	Luwa 1963	0.62	61			94 B_5 D_5	$Dk_{99}+I_{99}+$	Dk_9 I_9	NA	NA	
WEM[5]-1958	Luwa 1958		WEM-1958			100 - D_{29}	$Dk_{99}+I_{99}+$	Dk_9 I_5	NA	NA	
67	Luwa 1963	0.31	70B	92.7		94 Y_7 D_7	Dk_{99}	Lt_{15}	125	97.5	
68	Lab LC#114	0.08	70C	93.7		97 Y_{15} I_{15}	Dk_{29}	Lt_{29}	140	100	
80	Luwa LOPS	0.63	82	93.0	1.40	97 B_5 I_5	Dk_{99}	Dk_5	NA	NA	
			88A		1.50	103 Y_5 D_5	Dk_{99}		NA	NA	Perclene/AS
116	Dian	0.19	118C	94.2	0.80	97 B_{35} D_{35}			120	NA	GY Eutectic
129A	Dian(Ext)	1.03	130A	91.5	1.20	94 B_{10} D_{10}			NA	NA	
129F	Luwa	0.26	130B	93.5	0.84	100 Y_{15} I_{15}			NA	NA	
$129F_1$	Luwa	0.26	130C	91.8	0.96	100 B_{15} D_{15}			NA	NA	Hydrolysis with 2% Emcol P-1059

DUP050108785

TABLE I (Continued)

Chlorination Exp. # (E-12475)	LC Crude	IR[1]	Breaching[2] Exp. # (E-12475)	% CPC	X-Ray[3]	Tint	Masstone vs. GT-751-D	Masstone Harmon's 5018	Textile Ink[4] Min.	Textile Ink[4] Max.	Comments
Plant Lot											
383	Dian	0.11	10A	92.2		100 Y_3 I_5	-	-	NA	NA	
384	"	0.08	10B	92.8		100 Y_3 I_3	-	-	NA	NA	
369	"	0.06	33	82.0	NA	~200 $B_{99+}D_{99+}$	-	-	160	125	
416	"	0.09	70F	93.3		100 Y_8 D_8	-	-	125	95	
432	"	0.14	106A	94.0	0.90	100 Y_{10} D_{10}	-	-	117.5	107.5	
434	"	0.0	106B	93.9	0.80	103 Y_5 D_5	-	-	115	107.5	
451	"	0.09	SL0451	92.5	0.70	101 Y_{17} I_{11}	-	-	100	95	

(1) IR ratio reflecting tetrachlorophthalimides

(2) Standard ODCB/AS breaching

(3) Width at half height (degrees) at 26.8° two theta

(4) Evaluations by P. J. Krape (Pigments, Chestnut Run) using the complete Sherwin-Williams non-ionic master batch with SL0451 as standard

(5) Work by W. E. Miller

DUP050108786

TABLE II

LC Crudes

Lot No.	% Kero	% WSS	% CPC	% H_2O
1688	0.14	2.64	84.7	2.33
1958	0.20	0.58	92.3	NA
1963	1.60	0.46	93.0	NA
Dian	0	1.06	91.8	2.15
Dian (Ext, 113A)	0	-	95.6	-
Lab E10663-114	0.22	0.58	97.5	1.15

DUP050108787

TABLE III

The Effect of Reflux Time on GEX Breaching

Exp. # (E-12475)	GEU Crude	% CPC	X-ray	Rubout Tint	Rubout Masstone (vs.GT-751-D)	Textile Ink Min.	Textile Ink Max.
31B	384	91.5	NA	106 $Y_{11}D_5$	Dk_5	160	125
70A	384 (20 hr. Reflux)	90.9	NA	103 Y_7 D_7	$Dk_{29}I_{29}$	>200	130
70F	416	93.3	NA	100 Y_8 D_8	Dk_{29}	125	95
94B	416 (No Reflux)	93.3	0.70	92 B_7 I_1	Dk_{99+}	112.5	100

DUP050108788

TABLE IV

PERCLENE FOR ODCB; A MORE TRANSPARENT GREEN

Exp. (-12475)	GEU	Breaching Solv./Surf.	% CPC	X-Ray	Rubout Tint	Rubout Masstone 751	Rubout Masstone 5018	Textile Ink Min.	Textile Ink Max.	Comments
70F	416	ODCB/AS	93.3	NA	100 Y_8 D_8	Dk_{29}	Lt_{99}	125	95	Control
81A	416	Perclene/ Emcol P-1059	94.8	0.90	108 B_{20} D_{20}	Dk_{29}	Lt_{29}	175	120	
81B	416	Perclene/AS	93.8	1.00	100 Y_5 D_5	Dk_{99}	Lt_{29}	150	115	
84B	416	Perclene/ Dres. X	95.0	0.94	100 Y_{25} D_{25}	Dk_{99}	Lt_{29}	150	102.5	
85B	416	ODCB/Dres. X	95.5	0.60	103 Y_5 I_5	Dk_5	Lt_{99+}	115	100	
110A	416	Perclene/AS	93.7	0.84	106 B_{11} D_{11}	Dk_{99}	Lt_{29}	NA	NA	5-hr.Perclene reflux
125	GGU-232	Perclene/AS	93.2	0.92	>128	-	-	NA	NA	
88A	E12475-80	Perclene/AS	NA	1.50	100 B_{20} D_{20}	Dk_{99+}	Dk_5	NA	NA	
88B	416	Perclene/AS	92.7	0.90	103 Y_5 D_5	Dk_{99}	Lt_{15}	NA	NA	
88C	384	Perclene/AS	89.3	0.92	108 Y_{15} I_{15}	Dk_{99}	Lt_{13}	NA	NA	
92B	416	Perclene/ Igepal CO-630	93.2	0.80	106 B_5 D_{13}	-	Lt_{29}	125	105	
121A	432	Perclene/AS	94.7	0.90	111 Y_{30} D_{30}	-	-	125	93	2-hr. reflux 50% off
141	432	Perclene/AS	94.1	0.84	106 Y_6 D_6	-	-	120	93	10-hr.reflux 50% off

DUP050108789

B. A More Transparent Green

GT-751-D (standard); slightly more transparent compared to Harmon's Phthalo Green G-5018 and approximately equal in transparency compared to experimental "Ramapo" Green GP-817-D in Ford's TSA enamel". A subsequent evaluation of this material (Newark evaluation #77-401) in TPA gave similar results.

An evaluation of a perclene prepared sample (E-12475-88A) in Ford's TSA (Newark evaluation #77-402) showed the same type of high performance. Outdoor exposures of all these panels are in progress, however at this point it appears that we have generated a long-awaited more transparent green.

It is interesting to note how chlorination of LDHPLC gives a desirable, more transparent green, however in part A of this discussion, we are looking for ways to so modify this crude to give a match to GT-751-D. Fortunately, tint variations can be accepted if the masstone is acceptable for automobile finishes. Although we cannot explain why the masstones are do deep for these materials, the widths at half-height of the x-ray absorptions suggest we are producing aggregates of very small crystallites.

As an additional incentive to develop a more transparent green product, W. E. Miller has recently demonstrated flash distillation of ODCB from a GEX breached crude in Newport's semi-works[9]. The only test remaining is the plant chlorination of LDHPLC followed by routine breaching and flash distillation.

C. Green Breaching Studies

To meet the objectives of our green program, it was obvious that we needed to develop an improved understanding of the green breaching process. We hoped that this information would first restore plant GEX quality to yellow and intense and then be useful in developing our new green products. Accordingly, we ran a series of laboratory breachings to vary the GEX process. Appropriate controls were included and all evaluations were against N8104 (GT-751-D) standard. The applications of these studies to plant production is summarized in Appendix B, a letter written initally to relate plant quality problems to irregularities in the GEX process. A subsequent plant coverage by Quality Control and R&D focused in on those items which were most responsible for poor plant quality[10].

1. Changes in the concentrations of pigment, ODCB and AS in the standard GEX breaching affect quality.

DUP050108790

C. Green Breaching Studies (Continued)

TABLE V

Effect of Concentration

Exp. (E-12475)	GEU	Solv./Surf.	% CPC	Tint	Comment
14A	383	ODCB/AS	91.0	103 Y_3 I_3	Normal conc.
14B	383	ODCB/AS	92.2	100 Y_3 I_3	Half conc.
14C	383	ODCB/AS	91.0	105 B_3 D_5	Double conc.

Based on the data in Table V, some plant quality problems are probably due to changes in batch size and variability. If all the ingredients are scaled properly (water and caustic included) there is only a minimal effect on quality as dictated by changes in distillation times.

2. The presence or absence of salts during breaching has no significant effect on quality. Two lots of plant GEU were breached with and without 20% water soluble salts (Table VI). In textile ink applications, all four samples were equally unacceptable as GT-820-P. The only noticeable shift was a slight blue to yellow shift resulting from removing (or preventing) high salt.

TABLE VI

Water Soluble Salts

Exp. (E-12475)	GEU	% CPC	X-ray	Tint	Textile Ink (Min./Max.)	% WSS
75A	98	92.2	0.72	99 Y_{11} D_{11}	107.5/102.5	21.0
75B	99	91.7	0.72	98 B_{11} I_{15}	112.5/102.5	24.9
75C	98	91.8	0.76	102 Y_{17} D_{17}	110/102.5	1
75D	99	92.2	0.92	100 Y_{13} I_5	115/102.5	1

3. All variations of GEX breaching used by R&D or Quality Control give comparable products. The variations of pH measurement and additions of surfactants and ODCB do not affect quality. The darkness of masstone is, of course, dependent upon sample size.

DUP050108791

C. Green Breaching Studies (Continued)

4. The amount of reflux time needed for GE breaching appears to significantly affect GT-751-D quality. In the laboratory, quality can be altered by breaching with (100 Y_8 D_8) or without (92 B_7 I_7) the usual 2-hour reflux (see Table III) Recent Control Laboratory studies suggest an extended reflux can improve quality (Lot 434, 2-hr., 106 Y_{20} D_{20}; 4-hr., 100 Y_{15} I_{15}/Lot 435, 2-hr., 104 Y_{15} D_{13}; 4-hr., 99 Y_{15} I_7). W. E. Miller is studying this effect on various types of GEU crudes and his work may re-establish the optimum reflux times needed in GE and GG breachings.

   Apparently the breaching operation must be considered as two discrete processes which occur in sequence. First the agglomerated GEU is broken down into small aggregates or crystallites, then these smaller particles grow to the desired dimensions. Since this growth can go beyond the desired size, extended distillation cycles can lead to very large crystallites and opaque masstones. On the other hand, extended reflux before solvent removal probably aids in breaking down the agglomerates and therefore insures a better crystal growth.

5. Although the level of WSS may not affect breached quality, the levels of residual phthalimide (or non-water soluble salts) can. A lot of plant crude (369) which gave an extremely blue and weak product (~200 B99+ D99+) was washed with caustic and acetone before breaching. The extractions improved product quality to 106 Y_{30} D_{30} and raised CPC purity.

   In this same study, several finished GEX products were extracted by a variety of methods after breaching to remove residual impurities. In this study, we hoped to identify whether residual impurities are responsible for poor tint or presscake quality. All these experiments are summarized in Table VII.

   It is obvious that when Lot 369 was breached with its impurities (33), it gave an unacceptable product but when the crude was extracted before breaching (86B), an acceptable (although still dull) product was obtained. Since this crude was Dian based (hence no residual kerosene), further analysis could shed light on factors which contribute to blueness and dullness.

   The other experiments summarized in Table VII were designed to determine the effects of these impurities on end-use properties. Residual surfactants were also considered in this study. The data show that residual surfactants and impurities are not the cause of poor quality and poor dispersibility in textile ink systems. Furthermore, since there is little or no change in

DUP050108792

TABLE VII

Synthesis By-Products on Pigment Quality

Exp. (E-12475)	GEU	% CPC	X-Ray	Tint	Textile Ink (Min./Max.)	Comments
76	451	91.9	0.70	100 Y_{10} I_{10}	107.5/100	Two distillations[2]
78A	451	98.0	0.60	97 Y_5 I_5	102.5/97.5	Benzene/ Acetone Ext.
78B	452	98.5	0.56	100 Y_{30} D_{15}	112.5/102.5	Benzene/ Acetone Ext.
451-I[3]	451	91.3	0.80	99 Y_{20} I_{20}	102.5/102.5	Control
33	369	82.0	NA	200 $B_{99+}D_{99+}$	160/125	Compare
86B	369[4]	92.3	0.45	106 Y_{29} D_{29}	107.5/100	Compare

(1) All ODCB/AS standard breachings

(2) Laboratory history to match plant history of SL0451

(3) Not SL0451, but from same lot distillation crude

(4) Purified by acetone and caustic extractions before breaching.

DUP050108793

C. Green Breaching Studies (Continued)

5. (Continued)

properties after washing with solvents or caustic, residual surfactants are not responsible for poor dispersibility as well, hence, there is nothing fundamentally wrong with the surfactnts we use. (More on textile ink applications in Part E of this discussion.) Basically, these purifications served only to improve the ultimate tinting strength of the pigments by increasing the percent CPC.

6. The chlorination endpoint (whether a batch has been over or underchlorinated) does not affect GT-751-D quality and has only a minor effect on textile ink properties. In 12/76, Quality Control and R&D monitored the plant GE process and published a list of recommendations to guarantee standard quality[10]. In January (1/77), Six GE batches were halogenated within these guidelines and routinely breached (laboratory). These experiments and other chlorinations are summarized in Table VIII.

TABLE VIII

The Effect of the Chlorination Endpoint[1]

Exp. (E-12475)	GEU	IR	% CPC	X-Ray	Tint	Textile Ink (Min./Max.)	Comments
70A	384	NA	90.9	NA	103 Y_7 D_7	200/130	Control
70F	416	NA	93.3	NA	100 Y_8 D_8	125/95	Control
106A	432	0.14	94.0	0.90	100 $Y_{10}D_{10}$	117.5/107.5	
106B	434	0.10	93.9	0.80	103 Y_5 D_5	115/107.5	
106C	435	0.0	94.0	0.88	100 Y_8 D_8	140/107.5	
110C	110	0.36	93.2	1.00	100 Y_5 I_5	112.5/107.5	
110D	431	0.07	94.0	0.78	100 Y_3 I_0	125/105	
118C	116[2]	0.19	94.2	0.80		120/NA	
SL-0451	-	-	-	-	101 $Y_{17}I_{11}$	100/95	

(1) All ODCB/AS standard breachings
(2) Laboratory prepared crude (E-12475-116A) using a GY eutectic salt (No $FeCl_3$)

In summary, all lots, regardless of IR ratio, made acceptable GT-751-D and GT-820-P using our accepted procedure. By x-ray, all lots but #110 were properly breached, lot 110 showing a broader x-ray pattern indicative of underbreaching. Note also how a crude prepared in a eutectic without $FeCl_3$ (116) gave an acceptable GT-751-D (118C)

DUP050108794

C. Green Breaching Studies (Continued)

7. GE crudes finished by the GEX breaching process are near identical in quality when finished by our GGX process (see examples 70F and 85B of Table IV).

8. Perclene in combination with several surfactant systems can be used to prepare acceptable GT-751-D. See part D of this discussion for more on this subject.

9. The tinting strength of a GEX product can be markedly enhanced by washing the resulting presscake with a solvent such as 2-ethoxy ethanol (2 EE) or acetone. Please note in Table XI how the quality of a routinely breached sample (with only 50% of its ODCB distilled off) after drying was 117 Y_{29} D_{29}, but when the same presscake was washed with 2EE or acetone before drying, the tint was 83 Y_{29} I_{29}. An enhancement of 34 points in strength with an increase in CPC purity of only 3%. Obviously, we have removed some cementing agents which make the pigment more dispersible to achieve its ultimate crystallite strength. Although such plant washings would never be practical, we should determine what causes this enhancement and attempt to utilize this information in all GE, GG and GY grades

10. GE pigments can be readily breached with Arquad surfactants (Cationic) to give acceptable products. Any extension of this result to optimize this effect could lead to a useful cationic breaching. Please note, however, that cationic breaching on the acid side (pH=2, 135) did not give an acceptable product. These experiments are summarized in Table IX as are experiments in which 2-5% CPC-MS (monosulfonic acid) was added to prevent aggregation of the pigment during distillation (see Part E of the discussion). As will be pointed out in this discussion, we have not had success with CPC-MS added.

D. Perclene for ODCB

In Part B of this discussion, it was pointed out that a more transparent green GT-751-D could be made with either ODCB/AS or perclene/AS on GEU from LDHPLC. The critical step was identified as a quick removal of the breaching solvent. Table IV also serves as a summary of our other perclene breachings. In the laboratory, we prepared acceptable GE pigment (GT-751-D) by breaching in perclene instead of ODCB. Perclene in combination with either the AS surfactant combination (81B) or Dresinate X (84B) gave products with acceptable tints, however with Emcol P-10-59 (81A), a weak product resulted. All these presscakes had poor dispersibility in textile ink tests.

DUP050108795

TABLE IX

Green Cationic Breachings

and

Breachings in the Presence of CPC-MS

Exp. (E-12475)	GEU	Solv./Surf.	% CPC	X-Ray	Tint	Tex. Ink (Min./Max.)
114A	432	ODCB/Arquad 16-50	94.9	0.68	106 B_{15} D_{15}	150/105
114B	432	ODCB/Arquad 2C-75	93.8	0.82	100 B_7 D_3	150/100
121C	432	ODCB/AS + 5% CPC-MS	94.2	0.86		NA
123	432	ODCB/Arquad 2C-75 + 5% CPC-MS	92.3	1.06	111 B_{50} D_{50}	NA
135	432	ODCB/Arquad 2C-75	89.4	0.84	115	145/120
112B	432	ODCB/AS + 2% CPC-MS	93.2	0.80	100 B_{15} I_{15}	130/95

DUP050108796

D. Perclene for ODCB

The list of surfactants which can be successfully used with perclene includes the nonionic Igepal CO-630 (92B). The product was somewhat defensive at 106 B_5 D_5 but acceptable. These and the other breachings in Table IV suggest that perclene might readily replace ODCB in both GG and GE breachings and that a return to the use of Dresinate for GE breachings may be feasible. Further testing, including part evaluations would be needed along with a GT-820-P based on perclene to necessitate a plant conversion to perclene. However, if GT-820-P should be the only product which cannot be made with perclene, a partial conversion to perclene may be justifiable.

E. Improved GT-820-P

In developing a better understanding of the GEX process to improve GT-751-D quality, we studied many variations of the process. These studies led to the development of a more transparent green and generated a large number of presscake samples. Since a long-term objective of Colors R&D has been to develop an improved GT-820-P for textile ink applications, most of these presscakes were also evaluated for textile ink properties by P. J. Krape of Chestnut Run. The results of these studies have appeared in all the tables of this text and demonstrate that we never generated a presscake even comparable to SL0451 of GT-820-P. Even in the laboratory under controllable conditions, we could make yellow and intense pigments, but none of them had the dispersibility of SL0451 (our in-house standard). It was obvious that we could not hope for acceptable GT-820-P to come from the plant if we could not even make it in the laboratory. Since only three lots of plant GT-820-P had ever been acceptable (lots 451, 762 and 112A), we began to realize that these lots were unique and that our process as is could not repeatedly give acceptable GT-820-P. Yet since three acceptable lots had come from the plant, some modification of our plant process was our solution.

In Part C of this discussion, we established that there was nothing wrong with ODCB or the AS surfactant since no differences in ink dispersibility were observed with or without residual amounts of these materials present. Related work by J. Jackson of Colors R&D, Newark supported this idea and further demonstrated that no major enhancements were possible by simply changing surfactants. In like manner, the ODCB level of the product did not point to the solution even after these levels were quantitized by an extraction - GC analytical method developed at the Experimental Station (see Appendix C). A careful study of the actual plant history of SL0451 gave us several clues

DUP050108797

E. Improved GT-820-P (Continued)

to its uniqueness and each was tested in the laboratory. (The valuable documents which relate the history of SL0451 have been included in Appendix D to this report.)

1. Lot 451 was chlorinated in a eutectic melt which did not contain $FeCl_3$ (a GY salt instead of a GE salt). Experiment 118C of Table VIII shows this was not an important variable.

2. Lot 451 was a small batch prepared in CPC-I. In Part C, we established that if batch size is properly scaled, it is not a factor, however variations in the distillation cycles are significant.)

3. Lot 451 was initially incompletely distilled, reslurried in caustic and distilled to dryness. In effect, it received an additional caustic extraction and distillation. In Part C, we established that additional extractions do not make a more dispersible GT-820-P, however, they did improve ultimate strength by improving CPC purity. Compare the CPC purity of our products to those of our competitors in Table X. Evaluation in Table VII (76) show that the second distillation did not improve dispersibility. It only removed the residual ODCB in a more dilute system and increased percent CPC purity.

   With all other leads eliminated and the distillation suspect, we proceeded to sample a routine green distillation and determine if dispersibility is affected by the distillation step. Perhaps the unique distillation history of SL0451 could account for its unique properties. As the data in Table XI shows, it is the distillation which affects dispersibility properties. Specifically, we feel that significant aggregation occurs during the last stages of ODCB removal and it is this aggregation which must be prevented to make a good GT-820-P. Although we could simply break up these aggregates after distillation (as suggested by J. Jackson), it would be better to simply prevent their formation. The experiments summarized in Table XI show how this aggregation was detected and our attempts to date to prevent their formation. Several concepts were tested to prevent this aggregation and from these studies viable processes are possible for routinely producing GT-820-P equivalent to SL0451.

DUP050108798

E. Improved GT-820-P (Continued)

- Three batches of GE were normally breached and distilled to remove varied amounts of ODCB. As reported in the data taken from Table XI, GE which is not distilled free of ODCB is more acceptable as GT-820-P

Exp. #	% ODCB Nom.	% ODCB Actual	Tint	Textile Ink Min./Max.
106A	0	0.06	100 Y_{10} D_{10}	120/92
111B	25	5.62	103 Y_{11} D_{11}	102.5/95
111A	50	16.10	110 Y_{29} D_{29}	97.5/92
Sun	0	0	94 Y_{15} I_{15}	92.5/90
SL0451	0	0	101 Y_{17} I_{11}	100/95

- In experiment 121B, we repeated this incomplete distillation and washed off the residual ODCB with large quantities of 2EE and acetone (121B). It is obvious that the ODCB can be washed off without hurting minimum work dispersibility. In fact, the washing so increased CPC purity to give even a stronger presscake, approaching the strength of Sun's product. It is interesting to note that the tint enhancement was significantly more (see Part C).

  In experiments 133I and 133II, this procedure was repeated and the acetone and 2EE washes were tried separately at lower levels (500 ml/50 g CPC). In both cases, products comparable to SL0451 were obtained but strengths (both tint and textile ink) did not equal 121B. Apparently fewer impurities were removed and the combined effect of two solvents is somewhat greater than each by itself.

  The solvent 2EE was selected because Orchem once used a mixed ODCB/2EE breaching medium (see Experimental D and experiment 132 of Table XI). Although this process gave good GT-751-D, its presscake was difficult to disperse. We had hoped that a 2-solvent system would prevent aggregation during distillation by preventing wetting of the pigment by water from ODCB. In experiment 139, we added a large excess of 2EE during distillation (50% point) and obtained a product free of ODCB and slightly stronger than SL0451. Such a two-solvent approach, although less practical than others, could be the key to a GT-820-P

DUP050108799

E. Improved GT-820-P (Continued)

equal to Sun's product since in one process aggregation is prevented and the extraction properties of 2EE are realized during filtration. In the plant, this filtration may require additional equipment, however, the two-solvent approach should not be limited to 2EE. Another water soluble solvent might do as well and be acceptable to our plant as is.

- o Acid extraction before (to remove residual $FeCl_3$) and after breaching (to remove cementing agents or other interfering impurities) did not improve GT-820-P properties.

- o A semi-works flash distillation gave a GEX comparable to SL0451 in minimum work dispersions (WEM 1-4 in Table XI). Apparently there is enough turbulence during flash distillation to prevent severe aggregation.

- o High speed agitation during distillation (137) gives a more dispersible product than normal agitation. In the laboratory, this variable can be used to obtain weak and strong dispersion strength from the same lot of crude GEU. Apparently the troublesome aggregates reduce dispersibility in ink systems but can be easily prevented with proper shear during distillation. Lot SL0451 with its unique history, was made from a good crude which probably experienced an incomplete distillation with good agitation.

- o A perclene/AS breaching followed by an incomplete distillation gave a v weak product (121A). The same crude with a 10 hr. reflux (vs. 2 hr. normal) increased minimum work dispersion to 110 (141).

- o Attempts at utilizing Arquad (Cationic) surfactants or adding CPC-MS to give more dispersibility to our press-cakes were unsuccessful.

- o Experiment 118B shows that both GG and GE crudes can be used to generate acceptable GT-820-P by incomplete distillation to prevent aggregation.

In summarizing these experiments, it appears that there are several practical processes for making SL0451-quality GT-820-P. Preferably, we would either use flash distillation or batch distillation with high agitation. Although the exact experiments have not yet been run, it also appears that GG crudes can be used and that such products (either GE or GG) may also be useful in other end uses, eg. aqueous paint applications.

DUP050108800

E. Improved GT-820-P (Continued)

To exceed SL0451 and approach or exceed the quality of Sun's 464-6947, we may need only to optimize breachings or distillations. We know already that additional strength can be achieved by using a two-solvent breaching as described above ($121B_1/139$).

The formation of aggregates at the end of distillation is consistent with electronmicrographs of our GT-820-P products which show large football-shaped aggregates (see Appendix E). Although Sun's product does not show a full dispersion of discrete crystallites, there are no large clumps of crystallites. In earlier work on developing a new finishing process for BB grades[11], a process was studied in which TCB was steam distilled from the pigment and very large aggregates were found at the end of the distillation. In this case, the aggregates did not break up into a filterable presscake and the final product was very lumpy and difficult to wash. At that time, Professor W. Tiller of Stanford University, a consultant to our department suggested that such aggregation is the result of sudden changes in the solvent medium during the distillation. In effect, the pigment goes from an organic phase of low dielectric constant to a highly aqueous solution of high dielectric and such a shock could cause aggregation.

Such aggregation during distillation has been known for years, but it is unfortunate that it was not recognized that it is this aggregation which makes a good pigment into a poorly dispersing presscake for the low work applications such as textile inks.

The lack of lumps in Sun's product explains why the masstone of Sun's product is so dark (Dk_{99+} I_{99+}) versus our SL0451. Earlier we had made this observation and assumed we wanted a dark masstone green such as our new more transparent green product (Part B). Unfortunately these materials did not make good presscakes because the source of their dark masstones is underbreached small crystallites.

It is interesting to note that GEX from which 50% of the ODCB has been removed, when dried gives a darker masstone rubout than if allowed to distill to completion. This concept to darkening a masstone (incomplete distillation) must not be forgotten, especially in a system like GT-805-D which is already "underbreached" versus competition (see Table X and Part F).

One final approach which could generate a product which is not highly aggregated could come from a study of our competitors. Sun's product analyzes for 0.2% sulfur and

DUP050108801

E. Improved GT-820-P (Continued)

our knowledge of the related Color King process suggests that chlorination in chlorosulfonic acid generates a green with enough sulfonic acid groups present to act as anti-flocculating agents. Our few attempts at using CPC-MS for this purpose (see Table IV) were not successful but should be explored further if our current approaches do not give us a viable process. R. D. Nelson of Newark has yet to resolve the chemical nature of the 0.2% S found in Sun's 464-6947.

F. GT-805-D

In our program, we had hoped also to develop a GT-805-D with improved strength and transparency. An initial evaluation of our current product versus strong competition in this area revealed several weaknesses in our product (see Table X). Harmon's G-5400 is the most crystalline product with all competitors (including our GT-805) appearing "under-breached". In CPC purity, most competitors have $\geq$ 95% CPC whereas GT-805 standard is only 90.6%, hence a strength gain is possible if we could reduce the amount of aluminum benzoate used as extender.

Although we have not actually tried to apply our new GEX knowledge to GY products, W. E. Miller will have this opportunity and has already studied the effects of other surfactant systems on the breaching of GYU made from both Japanese LC crudes and LDHPLC[7]. In future work, a more transparent GY should be possible by either using crudes from LDHPLC or by applying that which we are learning about aggregation during distillation.

DUP050108802

TABLE X

Competitive Green Products

	% CPC	% WSS	X-Ray	% Br/% Cl[8]	
GT-820-P					
SL0451 GT-820-P	92.5	1.47	0.70	NA	
Sun 464-6947 (C#76298)	95.2	0.45	0.54	NA	
GT-805-D					
GT-805-D Std.	90.6	0.27	2.6	63.0	3.0
BASF 9140	98.8	0.11	2.6	40.0	21.0
Harmon's G5400	95.1	0.37	1.3	47.0	16.0
Harmon 5018	92.8	0.67	1.6	NA	
Fastolux Green 264-8137	94.0	0.45	1.0		
Chemetron GT-4818	94.8	0.54	3.8		
ICI Green GY	95.3	0.62	3.2		
BASF 9360	97.1	0.26	3.4		

DUP050108803

TABLE XI

An Improved GT-820-P - Distillation Studies

Exp. # (E-12475)	GEU	Solv./Surf.	% CPC	X-Ray	Tint	Tex. Ink Min./Max.	Comments
451-I	451	ODCB/AS	91.3	0.80	99 Y_{20} I_{20}	102.5/102.5	
SL0451	451	ODCB/AS	92.5	0.70	101 Y_{17} I_{11}	100/95	
452-I	452	ODCB/AS	94.9	0.60	105 Y_{24} I_{0}	107.5/100	
Sun (464-6947)	NA	NA	95.2	0.54	94 Y_{15} I_{15}	97.5/95	
111A	432	ODCB/AS	94.7	0.68	110 Y_{29} D_{29}	97.5/95	ID (50)[1]
111B	432	ODCB/AS	94.8	0.80	103 Y_{11} D_{11}	107/100	ID (25)[1]
111C	416	ODCB (2EE)/AS	92.5	0.78	103 Y_{11} D_{11}	125/95	
118A	GGU-232	ODCB/AS	95.0	0.80	97 Y_{17} I_{17}	125/97.5	
118B	GGU 232	ODCB/AS	96.0	0.72	111 B_{20} I_{20}	97.5/92.5	
118C	116	ODCB/AS	94.2	0.80	97 B_{35} D_{35}	120/	GY[2]
121A	432	Perclene/AS	94.7	0.90	111 Y_{30} D_{30}	125/93	ID (50)
121B	434	ODCB/AS	94.8	0.78	117 Y_{29} D_{29}	97.5/95	ID (50)
$121B_1$	434	ODCB/AS	97.7	1.00	83 Y_{29} I_{29}	96/93	ID (50)[3]
132	432	ODCB (2EE)/ "Staybelite"	89.9	0.82	97 B_{20} D_{20}	135/98	Orchem

DUP050108804

TABLE XI (Continued)

Exp. # (E-12475)	GEU	Solv./Surf.	% CPC	X-Ray	Tint	Tex. Ink Min./Max.	Comments
133I	432	ODCB/AS	97.7	0.78	100 Y_8 D_8	100/94	ID (50)[4]
133II	432	ODCB/AS	97.7	0.80	100 Y_8 D_8	102/93	ID (50)[5]
137	434	ODCB/AS	93.6	0.80	103 Y_8 D_8	102/94	Super agitation
139	434	ODCB (2EE)[6]/AS	94.9	1.10	100 Y_{15} I_{15}	95/95	
141	432	Perclene/AS	94.1	0.84	106 Y_6 D_6	120/93	ID (50)[7]
WEM-1(3268-1A)[8]	434	ODCB/AS			104 Y_4 D_{11}	115/100	
-2(3268-1B)	434	ODCB/AS			104 Y_{11} D_6	100/95	
-3(3268-1C)	434	ODCB/AS			104 Y_{14} D_3	102/97	
-4(3268-1D)	434	ODCB/AS			103 Y_{15} -	102/95	

1 - ID (50) means incomplete distillation with only 50% ODCB recovered.
2 - GY eutectic salt for halogenation
3 - ID (50) plus 2EE/acetone wash
4 - ID (50) plus acetone wash
5 - ID (50) plus 2EE wash
6 - 2EE added at 50% ODCB off
7 - 10-hr. perclene reflux before distillation
8 - Flash distillation

DUP050108805

EXPERIMENTAL

A. Procedure for GE Chlorination
(See notebook E-12475-101)

Equipment: 1-liter resin kettle fitted with a chimney vent, overhead stirrer, a Teflon® dip tube, thermometer and heating mantle. Also a tank of Cl_2, rotometer calibrated to about 50 gm/hr. and Cl_2 scrubber with concentrated sulfuric acid.

Procedure:

Halogenation:

1. Be sure rotometer is clean and calibrated
2. Mix and add to resin kettle

   300 gm $AlCl_3$ (anhydrous)
   51 gm NaCl
   34 gm $FeCl_3$

3. Heat to 175°C. to melt, cool to 150°C.
4. Add 60 gm of LC pigment at a rate so as not to exceed 165°C. Adjust temp. to 165-175°C.
5. Add chlorine at 50 gm/hr. below eutectic surface until chlorination is complete as judged by permanganate test or IR test.

Hydrolysis: (5-liter or larger battery jar)

1. Dilute 260 ml H_2SO_4 (conc.) into 3000 ml H_2O
2. Add charge from halogenation. Be careful -- hot from reaction and violent reaction
3. Stir 30 minutes
4. Filter and wash to 2500 ohms.
5. Save presscake and obtain % solids, % WSS and % CPC purity on solids.

DUP050108806

B. Procedure for GEX Breaching (100 g CPC) (E-12469-105)

Equipment: 1 liter beaker, 150 ml beaker, magnetic stirrers
2 liter RBF with condenser, mantle and stirrer

Procedure:

1. In the 1 liter beaker add in order with moderate stirring, the following:

   a. 100 g CPC content of green presscake
   b. 280 ml water
   c. 10 ml 50% caustic
   d. Agitate 15 minutes
   e. Check pH, adjust to 12.4-12.6

2. In smaller beaker, add

   a. 84 ml ODCB
   b. 4.4 g aminoethylethanolamine
   c. 4.4 g Sulframin 1298 (lin.)
   d. Stir 15 minutes on magnetic stirrer
   e. Add to 2 liter RBF
   f. Flush out beaker with 80 ml water and add to 2 liter RBF

3. Agitate 2 liter RBF 15 minutes (with ODCB/surfactant) and add contents of 1 liter beaker, Rinse out 1 liter beaker with 120 ml water and add this flush also to the 2 liter RBF

4. Breaching

   a. Heat to reflux
   b. Hold at reflux 2 hours
   c. Begin distillation. Distill off all ODCB. Add water if necessary and distill until no more water collects in the Dean-Stark trap

5. Filter and wash to 3000 ohms and if desired, dry presscake at 80°C.

6. Obtain from analytical % solids, % CPC purity, % WSS and rubout product against N-8104 standard.

DUP050108807

C. Procedure for GGX Breaching (100 g CPC) (E-12469-107)

Equipment: 2 liter RBF with mantle, overhead stirrer and set up for distillation

Procedure:

1. Add 260 ml water to 2 liter RBF, agitator on
2. Add 28 ml 50% caustic
3. Add 3.4 g Dresinate X
4. Check pH, adjust to over 10
5. Mix until all Dresinate X dissolves
6. Add 100 g. CPC content of presscake
7. Add dropwise over 15 minutes 82 ml ODCB
8. Adjust volume to 720 ml with water
9. Heat to reflux and distill off ODCB. Distillation complete when no more ODCB comes over to Dean-Stark trap.
10. Filter and wash to 3000 ohms.
11. If desired, dry at 80°C.
12. Obtain from analytical % solids, % CPC purity, % WSS and rubout product against N-8104 standard. (Pilot GGX

DUP050108808

D. Procedure for Orchem's Breaching (E-12475-104 and Ref. #8)

Equipment: 1 liter RBF for reflux and distillation

Procedure:

1. Weigh out 125 g. CPC content of green presscake
2. Add water (only if presscake is higher than 33% solids)
   Amount of water
   = 380 - (g. presscake)
3. Add 105 ml 2-ethoxyethanol (d = 0.931)
4. Add 36 ml 50% caustic (10 ml of 30% soln)
5. Stir 10 minutes
6. Make up a solution of 4.5 g. "Staybelite" with ODCB

   $$\text{ml ODCB} = 65 \left(\frac{\text{g presscake} - 125}{2 \times 125}\right)$$

7. Add "Staybelite"/ODCB solution in 5 minutes to flask
8. Quickly heat to reflux and hold 20 hours
9. Add 80 ml water
10. Adjust pH to over 12
11. Quickly distill off ODCB
12. Filter and wash to 5000 ohms
13. If desired, dry at 80°C.
14. On dried product, obtain % CPC purity, % WSS and rubout against N-8104 standard.

DUP050108809

K-13004

APPENDIX A

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

PIGMENTS DEPARTMENT

cc: E.W.Stewart,Pigm.C.R.
H.W.Ling,Pigm.C.R.
R.H.Zabel,Pigm.C.R.
E.E.Jaffe,Pigm.Newport
W.S.Struve,Pigm.Newark
C.W.Anderson,Pigm.Newport
C.F.Rolle,Pigm.Wilm.
D.E.Yonker,Pigm.C.R.
F.C.Dzielak,Pigm.C.R./File

FIRST & FINAL - ANRD-29-76
Initial Report - S-76227

Chestnut Run
December 14, 1976

TO: R. J. GUSCHL
PIGMENTS-NEWPORT

FROM: W. P. VAN VLIET
PIGMENTS-CHESTNUT RUN

EXPTL. TRANSPARENT CPC GREEN (INTERMEDIATE SHADE)
E-12476-61 COMPARED TO MONASTRAL® GREEN G, GT-751-D
IN FORD'S THERMOSETTING ACRYLIC TSA ENAMEL

OBJECT:

To determine if process modification used in making Experimental Transparent Green, E-12476-61 can significantly improve transparency of CPC greens.

INTRODUCTION:

E-12476-61 was lab prepared in the shade range of GT-751-D. The experimental was made with Luwa dried high purity LC crude, breached in ODCB and "flash" distilled. R&D feels these process modifications will improve transparency of CPC greens, without significantly altering tinctorial properties.

The chlorinated CPC green was choosen for initial evaluation; however, the technology should be applicable to brominated CPC greens as well.

Also included were Harmon's Phthalo Green G-5018 and Experimental "Ramapo" Green GP-817-D for comparative transparency purposes.

CONCLUSIONS:

Experimental Transparent CPC Green E-12476-61 is significantly more transparent compared to Monastral® Green G, GT-751-D (standard); slightly more transparent compared to Harmon's Phthalo Green G-5018 and approximately equal in transparency compared to Experimental "Ramapo" Green GT-817-D in Ford's TSA enamel.

SUMMARY:

Tinctorial

The tinctorial difference of E-12476-61 compared to GT-751-D (standard) was not a major concern. The experimental, however, is dull and slightly bluer at approximately equal strength compared to the GT-751-D (standard). All samples were steel shot milled because of very limited

DUP050108810

SUMMARY: (cont.)

Tinctorial (cont.)

quantity and the need for greater recovery than could be obtained by Jiffy sandmill. Earlier work(1)(2) suggests the blueness and possible dullness may be caused by iron reduction. Therefore, future work, with larger quantities, evaluating the tinctorial characteristics of the experimental should be dispersed by sandmill.

Transparency

The relative order of transparency from best to worst is:

E-12476-21 $\cong$ GT-817-D $>$ G-5018 $>$ GT-751-D

Flocculation

All pigments exhibited equally good flocculation resistance.

Exposure Durability

Exposure series S-76227 will be exposed @ 5°S in Florida and recalled every six (6) months for a total of eighteen (18) months.

EXPERIMENTAL DETAILS:

1) All paints prepared, according to TF-1040-4 in Ford's TSA enamel by ballmill (1 pt.).

2) All paints sprayed with automatic spraymation according to TF-8613-1.

3) Paints prepared:

Metallic:	90/10 toner/Al
	50/50 toner/Al
Tints:	5/95 toner/TiO_2

PIGMENTS EVALUATED:

Monastral® Green G, GT-751-D (PS-89040)
Experimental Transparent CPC Green E-12476-61 (sample depleted)
Experimental "Ramapo" Green GT-817-D (CS# 121376A)

REFERENCES:

1) Monthly Summary, Newark, 10/28/75, A.R.H.
2) Letter to C.F.Rolle from R.C.Horr, 1/16/76 - Color Shift (Blueness) & Dulling Problems with Monastral® Green G, GT-751-D in 30J Alkyd

LAB WORK BY: C. W. BUEMLER

LAB REFERENCE: CWB-76-11-07

WPV:lb

DUP050108811

EXPOSURE SERIES S-76227
5° South Florida

Panel #	Pigment	Ratio	Initial 20° Gloss	P/B
1	GT-751-D/Al	90/10	78	0.09
2	G-5018/Al	"	75	0.09
3	GT-817-D/Al	"	72	0.09
4	E-12476-61/Al	"	70	0.09
5	GT-751-D/Al	50/50	55	0.07
6	G-5018/Al	"	62	0.07
7	GT-817-D/Al	"	41	0.07
8	E-12476-61/Al	"	51	0.07
9	GT-751-D/TiO_2	5/95	70	0.5
10	G-5018/TiO_2	"	61	0.5
11	GT-817-D/TiO_2	"	73	0.5
12	E-12476-61/TiO_2	"	74	0.5

WPV:mal

APPENDIX B

E. I. du Pont de Nemours & Company
INCORPORATED
NEWPORT, DELAWARE 19804

PIGMENTS DEPARTMENT

R J Gunkel

CC:
C. F. Rolle*	-	Wilmington
E. W. Stewart	-	Chestnut Run
J. R. Webster*	-	"
P. J. Krape*	-	"
C. G. Hubbard*	-	"
W. S. Struve	-	Newark
R. L. Sweet*	-	"
J. Jackson*	-	"
G. M. Loughran	-	Newport
D. M. Strouss	-	"
V. J. Lewis*	-	"
J. W. Ignace*	-	"
J. J. Adams	-	"
A. F. Lewis	-	"
I. A. Berkemeier	-	"
S. W. Severance	-	"
W. H. Hoffman	-	"
C. E. Woodruff	-	"
E. E. Jaffe*	-	"
C. W. Anderson*	-	"
W. E. Miller*	-	"

September 7, 1976

SUMMARY

GT-751-D/GT-820-P MEETING

On September 2, 1976, a meeting of Newport R&D, Chestnut Run and Newport Quality Control was held to relate the latest in 820 presscake testing and to discuss current GEX quality. Our goal is to develop a coordinated program between members of these groups and Newark R&D to develop an adequate 820 product and to consistently get standard quality GEX from the plant.

From our meeting, we concluded that

- R&D will have full responsibility for developing an improved quality GEX presscake, suitable for both aqueous and oil emulsion ink systems. The product will be comparable to Sun's 464-6947.

- Chestnut Run is responsible for developing a non-proprietary test for green presscakes which will identify products which will be suitable for all our customers. Until such a test is developed, Chestnut Run will supply Newport R&D and Quality Control with the Sherwin-Williams non-ionic aqueous test, which appears adequate for this purpose.

DUP050108813

- The current quality of GEX products is too variable to be acceptable to R&D and Quality Control. Many plant practices must be corrected and innovations added before GEX will consistently be of 451 quality (as it should be). R&D will assist Quality Control in developing meaningful procedures.

A more detailed summary follows:

I. Current 820-P quality for textile ink uses

- P. J. Krape presented several textile ink test results of our 820-P product versus Sun's product (attached)
  - In all tests, the aqueous tests are most discriminating; the best being Sherwin-Williams non-ionic aqueous test.
  - Quality Control's current textile ink test (results attached) is an oil/H_2O emulsion test and not good for current screening for aqueous uses.
  - Initially, it was felt 0451 batch of 820-P equalled Sun; now it appears to be 20% weak. Chestnut Run will clarify this although we recognize that our 820-P is suitable for oil/H_2O systems but not adequate for aqueous. (Please note that 820 was designed for oil/H_2O systems)
- Residual ODCB traces could be making the pigment hydrophobic. ODCB levels need to be defined and correctly analyzed.

II. Current GEX finishing

- Current process
  - Halogenation endpoint only by permanganate
  - Hydrolysis with acid recycle
  - Filtration with inadequate washing (WSS of 26% have been observed)
  - Poor sampling of repulp tank to determine batch size for breaching
  - A breaching procedure which processes from 1800 to 4800#/batch (ODCB and surfactant levels are adjusted, but not water).
  - GEX finished in CPC-II is not much better than that finished in CPC-I (still needs to improve).

II. (Continued)

- o The GEX process must be changed! (The writer gratefully acknowledges that Julius Jackson and Ron Sweet of Newark R&D have long noted major shortcomings of our plant procedure.)
  - Halogenation endpoint must be determined by both permanganate and IR until we are confident of observing the true endpoint. Production must supply the necessary samples.
  - Reasonable crude filtration times must be established (5-7 hours) to limit batch overlap in the hydrolysis tank.
  - The crude filter must include adequate washing of crude.
  - The acid recycle process must be modified to include checks on both specific gravity and strength.
  - A recirculating line must be installed in the repulp tank to guarantee a meaningful sample. The alternative is to pack out all slurry in tote bins before charging the breaching tank. Production must wait for testing of this sample before charging the breaching tank.
  - GEX samples for both CPC-I and CPC-II must be analyzed identically.
  - The GEX batch size during breaching must be standardized (3000±100 lbs.). Perhaps the repulp tank will be used to regulate batch size if level probes are updated.

III. Blue presscakes (401 and 502)

- o Both of our products are weak versus Chemetron PK 4504 and are finding variable acceptance.
  - Surfactant variations and incompatibility with customer systems
  - LC purity

IV. Other items

- o To coordinate future efforts, copies of 820/751 related correspondence will be sent to all people concerned with these problems (* names on cc).

IV. Other items (Continued)

o Samples to be exchanged

- V. J. Lewis

1. 1 gal. 451 grade 820-P to RJG and PJK
2. 2 (5 gal.) pails 762 to PJK
3. Samples of 109-B, 110-B, 112-A, 762 and 764 (820-P) to RJG and PJK plus two bad batches of 820P to RJG
4. Will rubout 451 (820-P) versus Sun and run both in his oil/H_2O test.

- P. J. Krape

1. Sample of Sun 464-6947 to RJG and VJL
2. Chemicals for Sherwin Williams nonionic test to RJG and VJL
3. A new non-proprietary test for screening presscakes to RJG and VJL (when available)
4. Chemetron's PK 4505 to RJG

- R. J. Guschl

1. Will send samples of Sun 464-6947 and Chemetron PK 4504 to Newark for surfactant testing
2. Will develop better ODCB test for 820-P for Quality Control.

Randolph J Guschl

R. J. GUSCHL - R&D
Research Chemist

/tmj

DUP050108816

GT-820-P
IN
TEXTILE INKS

APPENDIX B (Contd.)

NEWPORT OIL/H_2O TEST		100	100	105	98	100	102					
			GT-820-P					↙	SUN		GT-822-P	GT-820-P LO451 ETHANOL WASHED
		0451	1098	1108	112A	762	764	C#76084	C#72336	L156974	SL33932	
		Current 820 standard	GEX	finished CPC II		GEX	finished CPC I					
SHERWIN-WILLIAMS												
ANIONIC	LITE CUT	100	105	115	100	100	120	82.5	90	85	—	100
	DARK CUT	CONTROL	SW	SW	VSW	=	W	ST	SST	SST		SST
NON-IONIC	LITE	100	115	120	95	100	120	80	—	85	—	—
	DARK	C	W	VW	VSW	SW	VW	VST	-	VST	-	—
BLACKMAN-UHLER												
ANIONIC	LITE	100	100	100	100	100	105	80	—	85	—	—
NON-IONIC	LITE	100	105	110	100	97.5	113	82.5	—	87.5	—	—
SPECTRACHEM												
ANIONIC	LITE	100	100	105	100	97.5	105	85	90	95	—	—
	DARK	C	WSW	=	=	=	SW	ST	SST	SST	—	—
NON-IONIC	LITE	100	105	110	100	97.5	110	85	92.5	90	98	—
	DARK	C	=	=	W	=	SW	VSST	ST	VSST	VSST	—
INMONT												
NON-IONIC	LITE	100	100	120	97.5	95	115	75	—	85	—	—
	DARK	C	=	W	=	=	W	VST	-	VST	-	—
VIVITONE												
NON-IONIC	LITE	100	103	108	100	92.5	115	80	—	87.5	—	—
MEAN μ			104	111	99	97.5	113	81.3	90.8	87.5		
95% CONF. INTERVAL			±3	±4.5	±1	±1.7	±3.4	±2.1	±1.3	±2.3		

C = CONTROL W = WEAK ST = STRONG

DUP050108817

G-29-76
ILF-43-76
9/15/76
PJK

GT-820-P SETTLING IN TEXTILE INKS

APPENDIX B (Contd.)

	GT-820-P 0451	GT-820-P 1098	GT-820-P 1108	GT-820-P 112A	GT-820-P 762	GT-820-P 764	SUN c#76084	SUN c#72336	SUN LI56974	GT-822-P SL33982	GT-820-P LO451 ETHANOL WASHED	DATE OF GRIND
SHERWIN-WILLIAMS ANIONIC	MOD. HARD SETTLE	V.SL. MOD. HARD SETTLE	V.SL. MOD HARD SETTLE	MOD. HARD SETTLE	SL. GOOEY SETTLE	CON. V. HARD SETTLE	SL. GOOEY SETTLE	SL. GOOEY SETTLE	SL. GOOEY SETTLE	—	MOD. HARD SETTLE	8/27/76
NON-IONIC	SL. SOFT SETTLE EASY STIR-IN	SEVERE SOFT SETTLE CURDLIKE	SEVERE SOFT SETTLE CURDLIKE	SOFT SETTLE EASY STIR-IN	SL. SOFT SETTLE EASY STIR-IN	SEVERE MOD. HARD SETTLE	SL. MOD. HARD SETTLE	—	SETTLED PUTRIFIED	—	—	7/29/76
BLACKMAN-UHLER ANIONIC	MOD. HARD SETTLE	NO SETTLE	NO SETTLE	SL. MOD HARD SETTLE	MOD. HARD SETTLE	CON. MOD HARD SETTLE	SL. MOD. HARD SETTLE	—	V.SL. MOD. HARD SETTLE	—	—	7/29/76
NON-IONIC	CON. MOD. HARD SETTLE	〃	〃	MOD. HARD SETTLE	MOD. HARD SETTLE	MOD HARD SETTLE	MOD. HARD SETTLE 1	—	〃 1	—	—	
SPECTRACHEM ANIONIC	V.SL. SOFT SETTLE	NO SETTLE GRITTY SUSPENSION	SAME AS 109	SL. SOFT SETTLE	SL. HARD SETTLE	SL. GOOEY SETTLE	V. SL. SOFT SETTLE 2	V.SL SOFT SETTLE 2	SL. SOFT SETTLE 2	—	—	8/20/76
NON-IONIC	CON MOD HARD SETTLE	NO SETTLE	NO SETTLE	MOD. HARD SETTLE	MOD. HARD SETTLE	CON MOD HARD SETTLE	V.SL. MOD. HARD SETTLE	V.SL. MOD. HARD SETTLE	V.SL. MOD HARD SETTLE	CON. MOD. HARD SETTLE	—	8/20/76
INMONT NON-IONIC	MOD. HARD SETTLE	NO SETTLE	NO SETTLE	MOD. HARD SETTLE	MOD HARD SETTLE	CON. HARD SETTLE	V. SL. MOD HARD SETTLE 1	—	V. SL. HARD SETTLE 1	—	—	8/10/76
VIVITONE NON-IONIC	LUMPY GEL SCUM	LUMPY GEL	LUMPY GEL	LUMPY GEL SCUM	LUMPY GEL	LUMPY GEL SCUM	SMOOTH GEL	—	CREAMY	—	—	8/11/76

1 CRYSTALS FLOATING ON SURFACE
2. SCUM 〃 〃 〃

DUP05010818

APPENDIX C

DON'T SAY IT–WRITE IT

DATE 11/12/76

TO R. J. GUSCHL

AT NEWPORT

FROM L. J. MATIENZO

cc: T. D. McKinley
C. S. Haas-Newport
O. E. Ringwald
File

DETERMINATION OF RESIDUAL ODCB IN CPC CAKE

Please find attached a method for the quantitative determination of ODCB (O-dichlorobenzone) in CPC cake. The procedure is simple, straightforward and existing equipment at Newport can be used for the analysis.

The results obtained by this method for the samples you submitted were:

Sample Number	% (w/w) ODCB in CPC Cake
762	1.32
764	0.39
451	0

If you have any further questions, do not hesitate and give me a call.

QUANTITATIVE DETERMINATION OF ODCB IN CPC CAKE

The analysis is carried out by gas chromatography on hexane solutions used to extract ODCB from the CPC cake.

Sample Preparation

Weigh exactly 5.00g of sample into a 125 ml Erlenmeyer flask. Add 50.00 ml of high purity hexane. Cap the flask with a rubber stopper and shake the mixture at room temperature for ten minutes.

Prepare some glass funnels for filtration. Use Whatman 1PS paper. Filter the mixtures into clean bottles until the whole volume of the organic phase is collected. Remove the filtrate, cap and label the solutions.

Analysis

The analysis is performed with a gas chromatograph under the following conditions:

Column: A six foot stainless steel tube with Dexsil-300
Carrier: Helium

DUP050108819

APPENDIX C (Contd.)

DON'T SAY IT–WRITE IT DATE 11/12/76

TO R. J. GUSCHL

AT NEWPORT

FROM L. J. MATIENZO

Rotameter: 0.5
Inlet Pressure: 50 psig
Rate: 20 ml/min.
Chart Seed: 1 inch/min.
Detector: Thermal Conductivity
Detector Temperature: 300°
Injection Temperature: 270°
Column: 50° - 140°
Rate: 15°/min.

Place a 10.0µl sample in the injection port, run the instrument at the specified heating rate. Use a scale attenuation of 512 for hexane. After three minutes, switch to a scale attenuation of 2. Integrate and measure the area under both peaks.

Calculation

The weight percentage of ODCB in CPC cake is given by:

$$\% \text{ ODCB(w/w)} = \frac{660 \times A_{ODCB}}{A_{ODCB} + 1.17 \times A_{HEX}}$$

Where:

A_{ODCB} = Peak Area for ODCB Peak

A_{HEX} = Peak Area for Hexane

Notes: (1) Whatman 1-PS paper is the only type of filter paper that can be used to separate the water present in the mixture.
(2) The area obtained for ODCB at attenuation X-512 must be divided by 256 to be used on the above given equation.

For example, if A_{HEX} = 832 (at attenuation X-2) and A_{ODCB} = 530 (at attenuation X-512), the percentage of ODCB in the pigment is:

$$\%ODCB = \frac{(660)\left(\frac{530}{256}\right)}{\left(\frac{530}{256}\right) + (1.17)(832)} = 1.40$$

LJM:ghh *STOP ACCIDENTS BEFORE THEY STOP YOU*

CPC AREA III

Lot 451

APPENDIX D

North Halo

Add 1 bin GY Salt to Salt hopper Done DAG 1/22/15 2/22/15

Add to halo kettle as though it was all the salt for entire batch. Done DAG

0.09

Add about 1/2 bin of GY salt to crude hopper - charge 400# crude to hopper - charge ± 1/2 bin on top of crude - charge 400# crude on top. Repeat above charge procedure for a second GY bin and 700# crude. [redacted]

Total charge 3 Bins GY Salt
1500# Crude

Cl_2 Addition - Follow mylar to 4000#
add Cl_2 at 150-200#/HR rate to 4500# then sample. Use endpoint procedure as on test batches.

Do not take special samples or measurements. Drown batch in hydro same as GT 826 (just H_2O) Faced
Drum lot from crude filter. Obtain 5 drum composites from crude filter and leave samples in my office.

DUP050108821

HALOGENATION-HYDROLYSIS-REPULP

N-8104 GEX

BATCH 451

See attached sheet for procedure North Little

STEP #	INGREDIENTS			OPERATING CONDITIONS		DATE	TIME	OPR.	REMARKS
Halog.	E. M.	Standard	Actual	Standard	Actual				4500# Cl2 - 15 ml
10	Evt. Salt	2 bins		Init. Salt					4600 12.5
23	Evt. Salt	6212 lbs.		Final Salt					4700 15.6
36	Blue Crude	1117 lbs.							4750 13.0
42	Chlorine	350 lb/hr		4 hrs.					4800 16.0
42	Chlorine	260 lb/hr		7 hrs.					4850 16.0
42	Chlorine	50 lb/hr		As needed					4900 18.0
									5000 12.0
									5100 8.0
						3/24	1129p	EFC	5221 .8
Hydro.						2/24	1159p	EFC	1/2 .5
7	Water	7770 gal.							
11	H_2SO_4	675 gal.							
15	Emcol	12 lbs.							
15	CBSB	50 gal.							
10	ODCB	50 gal.							
23	Product			Drop Batch					
36				Begin Filt.					
				End Filt.					
Repulp									
5-7-9	Water	300 gal ea							
12	NaOH	70 gal.							
17	GE Crude			Filtration					
20				Check ph 11 min.					
43	Water	300 gal		Flush					
51	Water	300 gal		Flush					
				Check repulp empty					

DUP050108822

CPC AREA II

GT-820-P

XOP 439

Refer to XOP

451

TIME	OPR.	INSTRUCTIONS	QUANTITY STD.	QUANTITY RECORD
		Preliminary Preperations		
		1. Drain 225 Still small decanter to ODCB storage.		
		2. Flush 225 Still vapor and condensing system including small decanter.		225, 28
		3. Fill 225 Still small decanter with water.		still
		4. Check 225 Still reflux lines open.		v'kd
		5. Flush out 28 Still and line to 225 Still via recurculation line.		clean
		6. Flush out 225 Still and line to press.		lines
		7. Blank line - 225 Still to press at 1st floor flange near elevator.		flushed
		Breaching - 225 Still		
4/14 730 p	33	1. Check 225 Still empty and clean.		
		2. Add 700 gallons water to 225 Still		
		3. Turn on agitator.		1 pot
		4. Add full pot of caustic (50%) 15 gallons.	15 gal.	15 ga
415		5. Add Green GE Crude (GT-820-P)		
		LOT 451 LBS 3640		364
6/14 430		28 Still TAKE 1 gal CRUDE SAMPLE	sample T	
		1. Check 28 Still empty and clean.	pH V	12.6
445		2. Add 150 gallons of water.		
5/14 530 p		3. Turn on agitator		
		4. Add 65 lbs. Amino Ethyl Ethanol Amine through manhole.		65
545		5. Add 67 lbs. Sulframin 1298 through manhole.		67
6-14 615		6. Add 150 gallons (3 drums) virgin ODCB through mix tank.	1800 lbs	3 du
625		7. Agitate for 10-15 minutes.		
6-14 645		Dump Emulsion Into Pigment Slurry In 225 Still		
		1. While agitating both tanks, pump emulsion from 28 Still into pigment slurry in 225 Still.	Level	80
6-14 700		2. Add 150 gallons water flush to 28 Still and pump to 225 Still.		
		3. Agitate 45 minutes.		
6-14 715		4. Sample Still slurry and check pH using Beckman Blue Tip Electrode pH should be 12.4-12.6.	12.4-12.5	
		If low adjust pH using caustic		
		[illegible] still SAMPLE	yes	

DUP050108823

GT-820-P
XOP 439

TIME	OPR.	INSTRUCTIONS	QUANTITY STD.	QUANTITY RECOR
		HEAT-UP Reflux		
		1. Close Still manhole		
1019	AA	2. Set condensate lines for reflux.		
		3. Heat Still to 98-100°C.		
1124	AA	4. Reflux for 1 3/4 hours.		
		5. Begin distillation of ODCB.		

DUP050108824

Batch No. 451

		INSTRUCTIONS	QUANTITY STD.	QUANTITY RECORD
		27. Increase steam during 1st hour distillation to obtain max. distillation rate without color carry over in distillate.		
		28. Record distillation data every 60 min. after 5 hrs. distillation below.		
		Check pH of distillate at 1st hr. distillation. Notify supv. if below pH 10 - Record start of boil-up.	pH 10min	125

Hours After Boil-Up	Still Level	Still Press"	Temp. °C	GPM Flow	Color	Ml ODCB in 500 Ml Sample
1	75	15	101		Yes No	200/300
2	70	5	101	47	Yes No	200/300
3	70	5	101	47	Yes No	200/300
4	69	5	102	47	Yes No	200/300
5	65	5	102	47	Yes No	[illegible]
6	65	5	102	47	Yes No	0/500
7	65	5	102	47	Yes No	0/500
8	65	5	102	47	Yes No	0/500
9	65	5	102	47	Yes No	0/500
10					Yes No	
11					Yes No	
12					Yes No	
13					Yes No	
14					Yes No	
15					Yes No	

		29. If still level drops below 40" add water to 45".		
		30. When distillate samples show 5cc ODCB in 500cc total sample, continue for 15 min. more then resample. If the resample is the same, the distillation is completed. Distill 1/2 hr. by passing small decanter.		
		31. Check A-120 press. If using 244 press use N992 card. Set up 29 frames. Set up recovery system. Install blast gate.		
		32. If temp. of still is below 95°C, heat charge to 95°C before pressout.	95°C min.	102
		33. Start pumping still charge. TAKE 2 qt. SPECIAL SAMPLE (Done 8 a) Observe press-out & return any bleeds to recovery press.		
		34. Check for odor of ODCB. If strong, notify Supv.		
		35. Finish still with 220.		
		36. Start press washing. Wash for 10 hours. Maintain 20 psi pressure.	10 hrs	

-3- SOP 17N

ORR	INSTRUCTIONS	QUANTITY STD.	QUANTITY RECORD
	37. Record filtrate OHMS.		
	Notify supv. if below 2500 OHMS	2500 OHMS	3859 OH
	38. Check ribbon mixer MT		
	39. Prep press.		
	40. Presscake fill (yes-no) Firm or Sloppy		
	41. If presscake smells of ODCB inform Supv		
	Smell: strong weak none		
	42. Flush press chute with min amount of water		
	Close press replace blast gate.		
	Pressure test press.		
	43. If necessary, add water to mixer to facilitate		
	pumping of slurry (12" from top)		
7:10	44. Start mix for 2 1/2 hrs.		
	45. Start recirculating after one hr. of mixing	1 hr.	
	with air jet on fill		
	46. End 1 & 1/2 hr. recirculation - record pH	1 1/2 hr	
		pH 7 min	9
	47. Inspect slurry - must be creamy. If not, continue		
	recirculation with air jet until creamy.		
	48. Start drumming from mixer.		
	49. Take 1 qt. sample, file packing out. Collect		
	1 dipper from feed of each drum when drum is approx.		
	1/2 full or each 440 lbs. while filling tote bin.		
	50. Record Lot No. 451 Samples by SP		
	51. Stencil: Code-Lot-Net & Tare Weights on each		
	Code 6T-8707 MARK OUT PACKOUT CARD		
	52. Flush mixer & recirculating line with water		
	Remove 1 Air tool		
	MAKE-UP OF DRESINATE SOLUTION PO# 281 or 225 STILL)		
	1. To mix-rm on 3rd floor add 10" of ODCB	10"	
	(Observe all safety rules in handling of ODCB)		
	Sample for water Water Yes No		
	2. Start agitator		
	3. Then add 155 lbs	155 lbs	
	Dresinate resin		
	4. Stir until rosin has been dissolved		
	5. Make unto 16" level with ODCB.	16"	
	6. Travel Weight reading or addition no. 111		
	SPECIAL SAMPLES - CRUDE PRESCAKE COMP. - 1 qt		
	STICK JUST BELOW HEATUP - (		
	MAKE PH ADJUSTMENT 2 gal.		
	(Phone 6/DAY-BR)		
	(NOTE) ALL IN SUPV OFFICE.		
	PRESSCAKE 455 gal.		

DUP050108826

E. I. DU PONT DE NEMOURS AND COMPANY
Pigments Department

(1) W. E. Miller

CC: W. S. Struve, Pigm., Newark
(2) B. H. Perkins, Pigm., Newark
E. E. Jaffe, Pigm., Newport
A. P. Smith, Jr., Pigm., Newport
A. J. Lewis, Pigm., Newport
V. J. Lewis, Pigm., Newport
C. F. Rolle, Pigm., Wilmington

Newark, New Jersey
July 1, 1975

J. R. WEBSTER
PIGMENTS
CHESTNUT RUN

MODIFIED EUTECTIC GREEN PRESSCAKE GT-820-P LOT 451

Ref. 1 JJ - A.P.Smith, Jr. Eutectic Green Presscake GT-820-P 4-30-74
Ref. 2 JJ - W.E.Miller, Eutectic Green Presscake 4-10-75
Ref. 3 JJ - W.E.Miller CPC Grit 6-19-75

As has been known for some time, GT-822-P has not been considered as the ultimate solution for penetration into textile ink sales versus products such as A.S. 464-6947 since it is inadequate in strength and excessively blue in hue.

Eutectic green ex the new plant was supposed to be our basic source of presscake for this type product.

As yet, we have not been given a chance to develop this product in that unit. We have conducted limited experiments in the laboratory and recently in the old plant with this type crude.

These studies lead to a prototype laboratory product (1991-34C) which was examined as dry color and in oil in water type textile ink formulations and considered adequate for plant trial (1973) since it gave an excellent dry product and good presscake quantity.

Recently two lots of crude 451, 452 were made available for use in this type operation, which requires a different set of conditions for hydrolysis and breaching than are currently used. The lots were made with Japanese crude and have been found to contain large amounts of non-pigmentary impurities (Ref. 3). Laboratory examination showed the products to be defensive in quality (Ref. 2) versus previous eutectic crudes examined by me.

We recently were given an opportunity to breach these inadequate crudes in the old plant. XOP 439 - Lot 451, 452. The plant breachings were inadequate; lot 451 being high in ODCB, and 452 unexpectedly weak (possible because of process interruption caused by the recent Newport plant explosion).

However, laboratory breaching of lot 451 crude gave a presscake which was very close to ODCB free plant press of lot 451.

DUP050108827

I am submitting to you for your appraisal in typical all aqueous systems a sample of this lab breached material for evaluation. This type of test application was not considered in the prototype studies since the system was not in use at that time.

The conclusions of this study can only be considered tentative, for the above mentioned reasons but are considered necessary since they will provide guidance as to the suitability of the basic system (i.e. surfactant - crude quality).

Julius Jackson

J. Jackson
R and D Division

JJ/cjg

Under Separate Cover -

1 qt. GT-820-P Lot 451 LB (Lab Breached) % Solids 36
1 qt. GT-820-P Lot 451 RD (Plant Breached-redistilled to remove ODCB)
% Solids 36

DUP050108828

1. ~~A. F. Smith~~

2. ~~E. E. Jaffe~~

3. W. E. Miller

cc. A.F. Lewis
T. A. Berkeheier
V. J. Lewis
W. E. Miller
8/12/75

C. E. Woodruff is completely familiar with CPC II

We should insure ODCB

GT 820-P Lot 451

This lot was packed in totes, as slurry, and coded N8101. This lot also has an excessive ODCB content. Tests indicate that once this excess ODCB is removed, the material is suitable as GT-820-P.

Marketing has requested that this lot be reworked in the plant to distill the remaining ODCB, and repacked as GT-820-P.

Batch card is provided; please note following.

① ph adjustment (Step 20). Desired ph is 12.5 (practical range 12.3 - 12.7) If initial ph check is less than 12, add 2 gal NaOH and recheck. If ph is between 12.0 - 12.3 add 1 gal caustic and recheck. If above 12.7 do not adjust back down.

② Distillation - Distill until distillate sample shows 2 mls in a 500 ml sample. (min time 2 hrs.) Then sample from bottom of still. Smell to odor of ODCB.

DUP050108829

If none detected send sample to lab for % ODCB. If results show less than 0.5 % distillation is complete.

(3) Packout - Use #1 filter. Pack out as presscake into new drums.
Stencil CT 820-P
bT 451.
Take 5-5 gal kits of presscake during packout.

J N Ignace

APPENDIX E

K-13004

DUPONT
ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

PIGMENTS DEPARTMENT

cc: W.S.Struve, Pigm., Newark
E.E.Jaffe, Pigm., Newport
C.W.Anderson/R.J.Guschl, Pigm., Newport
P.G.Linsen/C.F.Rolle, Pigm., Wilm.
E.W.Stewart, Pigm., C.R.
H.W.Ling/J.R.Webster, Pigm., C.R.
C.G.Hubbard, Pigm., C.R.

Chestnut Run
February 2, 1977

FIRST REPORT

NRD-4-77
ILF-9-77

TO: J. JACKSON
Pigments - Newark

FROM: P. J. KRAPE
Pigments - Chestnut Run

NEWARK EXPERIMENTAL GREEN
PRESSCAKE FOR TEXTILE PRINTING

CONCLUSIONS

Experimental E-6161-12B had strength equal to Sun's 464-6947 textile grade presscake under low and high shear dispersion in a modified Sherwin-Williams ink. E-6161-12B was ~2.5% stronger (sensitivity of test is ± 2.5%) than GT-820-P, SL-0451 under low shear.

The sample was prepared with a homogenization step which apparently disperses agglomerates formed during the present process. Making such a product at Newport would require installing new equipment.

EXPERIMENTAL DETAILS

- Low Shear - 20 minutes polyethylene "Jiffy" mill with 1/2" Porox balls. Results on several presscakes have repeatedly correlated with Eppenbach grinds but, since millbase rheology is a significant factor in an Eppenbach dispersion, Chestnut Run considers the "Jiffy" method a screening test and will Eppenbach disperse promising experimental samples if they are large enough. Jiffy test requires <15 g. dry weight, Eppenbach ~150 g. dry weight.

- High shear - 45 minutes polyethylene "Jiffy" mill with 1/4" steel shot. The difference in strength between 20 minute and 45 minute grinds is considered a measure of dispersability. Sun's strength increases only ~2.5%; GT-820-P, SL-0451 ~5%; GT-820-P production ≥10%.

DUP050108831

- Formula - Sherwin-Williams latest general anionic formula for green, blue, etc. Presscake is added to a masterbatch mixture of all the ingredients.

ELECTRON MICROGRAPHS

- Sun - clearly visible, separate crystallites of ~.04 um are extensively flocculated throughout the dispersion. Aspect ratio is ~1. Flocculation is continuous - there are no distinct clumps of crystallites. No other material is visible.

- GT-820-P, SL-0451 - very few distinct crystallites are visible. They are all clumped into football shaped agglomerates broadly ranging from 0.4 um to 2 um along the longer axis. Aspect ratio of footballs is ~ 4/3 - crystallites ~ ~3/1. Background is extensively littered with small translucent needle-like crystals.

- Experimental - fewer footballs are visible with many more, flocculates and aggregates of crystallites. Sizes and shapes vary over a very broad range. Individual crystallites appear to be more acicular than Sun's.

SHERWIN-WILLIAMS ANIONIC MASTERBATCH

	GT-820-P SL-0451	Sun C# 76298	E-6161-12B
45 Minute Steel Shot	95	95	95
20 Minute Porox Balls	100	97.5	97.5

PJK:mal
Attachments

DUP050108832

APPENDIX F

K-13004

E. I. du Pont de Nemours & Company
INCORPORATED

PIGMENTS DEPARTMENT

cc: P.G.Linsen, Pigm., Wilm.
W.S.Struve/J.Jackson, Pigm., Newark
E.P.Jaffe/C.W.Anderson/R.J. Guschl, Pigm., Newport
E.W.Stewart, Pigm., C.R.
H.W.Ling/J.R.Webster, Pigm., C.R.
C.G.Hubbard/J.A.Mackiewicz, Pigm., C.R.
L.A.Schlapfer, Pigm., C.R.
F.C.Dzielak, Pigm., C.R. (File)
M.A.Larson, Pigm., C.R. (File)
R.I.McLaren/M.D.Wright, Pigm, Chicago

FIRST & FINAL

G-36-76
ILF-73-76

TO: C. F. ROLLE
Pigments - Wilmington

FROM: P. J. KRAPE
Pigments - Chestnut Run

GREEN PRESSCAKE FOR 3M
ROOFING GRANULES

CONCLUSIONS:

3M's standard presscake (probably from Sun) is inherantly stronger than GT-820-P. Rubout masstone is very dark, intense, and transparent vs. GT-820-P, suggesting the competitive may have a smaller, more nearly optimal particle size and therefore, higher light absorption with less scattering. In tint, the competitive was ~ 5% strong and sl blue.

Earlier work (G-104-72, reported 2/21/73 by V.J.Lewis) showed that GAF's green for roofing granules, 66-3803, could be matched with GT-822-P, BT-436-P, and carbon black. Adding absorption to our green equaled the competitive presscake.

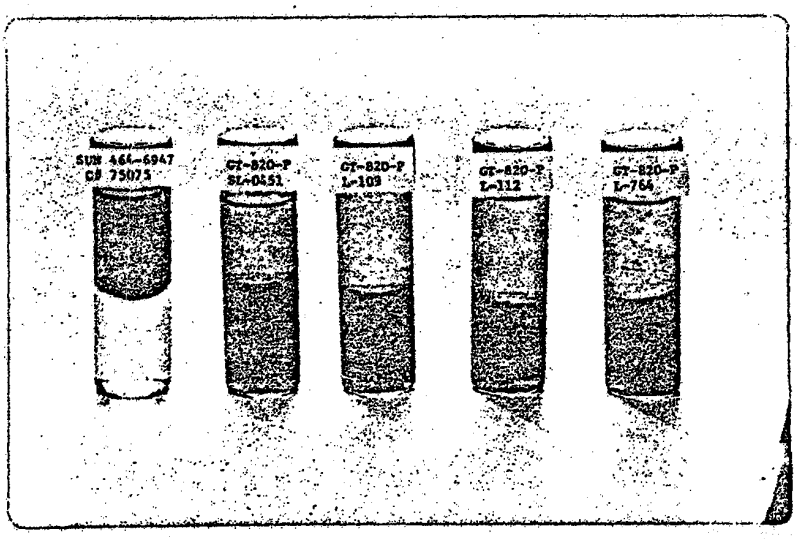
The surface of the 3M standard was also much more hydrophobic than GT-820-D and may be more receptive to surfactants thereby yielding a better dispersion and higher strength. Recent work in textile inks support these hypotheses (results to be issued early '77). Surfaces were characterized by shaking presscake in a vial containing half water and half Varsol mineral spirits (see attached photos). Varsol floats above the water. Our presscakes either float in an emulsion layer or fill the water phase.

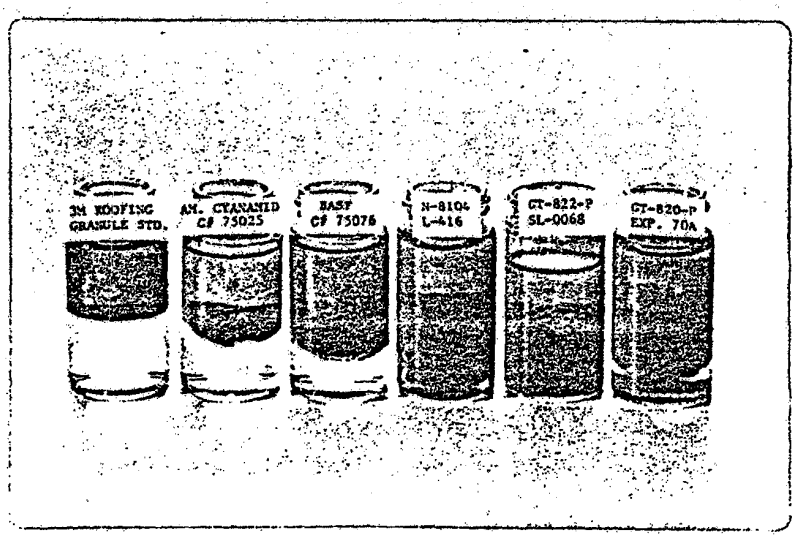
RECOMMENDATIONS:

When a new presscake is developed for textile printing, we recommend sampling 3M. They still refuse to supply a test method for development work.

PJK:mal
Attachments

DUP050108833





DUP050108834

REFERENCES

1. J. Jackson, KN-76-9, "GT-820-P - Presscake Ex Eutectic Green Process"

2. H. Matrick, KN-73-12

3. E. W. Gillow, KN-75-3, "High Transparency Ramapo Green Pigments GP-817-D and GP-818-D"

4. R. J. Guschl, KN-77-3, "Increased CPC Crude Capacity"

5. For more details, see reference 4 and references cited therein

6. E. W. Gillow, KN 76-11, "Kerosene Recycle in the Synthesis of Low Chlorine Content Copper Phthalocyanine"

7. W. E. Miller, January, 1977 Monthly Summary

8. R. L. Sweet, KN-73-2

9. W. E. Miller - To be published

10. This study was summarized in January 1977 by W. E. Miller and published as a letter to Manufacturing

11. R. J. Guschl, KN-77-2, "A New Process for Finishing CPC-BB, the Active Solvent Effect"

DUP050108835

DATE ISSUED:

DISTRIBUTION:

1. E. Gonick - Wilmington
2. W. S. Struve - Newark
3. H. B. Clark - Wilmington
4. J. G. Ishikawa - Wilmington
5. E. J. Mead - Experimental Station
6. J. E. Romano - Newport
7. G. W. Hapka - Wilmington
8. C. F. Rolle - Wilmington
9. E. E. Jaffe/Circ./File - Newport
10. E. W. Stewart - Chestnut Run
11. B. H. Perkins/J. P. Galvin/A. P. Smith/Newark Library
12. C. W. Anderson - Newport
13. N. J. Kane/Newport Library - Newport
14. P. H. Griswold - Newport
15. W. E. Miller - Newport
16. P. J. Krape - Chestnut Run
17. W. P. VanVliet - Chestnut Run
18. H. Matrick/R. L. Sweet/J. Jackson - Newark
19. R. Z. Fortney/J. F. Kane - Newport
20. S. W. Severance/I. A. Berkemeier/W. G. Hoffman/C. E. Woodruff
21. R. D. Nelson - Newark
22. R. J. Guschl - Chestnut Run

23 & 24 - Central Report Index - Chestnut Run

25. Newark Research File - Newark
26. Numerical File - Newark
27. C. Hubbard - Chestnut Run
28. "

DUP050108836