KW-69-17 IMPROVED BT-383-D AND PROCESS STUDIES By: R. L. Sweet 9/66 - 2/69

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

IMPROVED BT-383-D AND PROCESS STUDIES

Period Covered September, 1966 - February, 1969 (part time)

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SUBJECT: IMPROVED BT-383-D AND PROCESS STUDIES

PERIOD COVERED: September, 1966 - February, 1969 (part time)

SUBMITTED BY: R. L. Sweet RLS Date Submitted: 10/17/69

APPROVED BY: F. F. Ehrich Date Issued: 11/11/69

ABSTRACT

The dispersion mill powder extraction process for BT-383-D has been improved by the use of a surfactant and Na_2CO_3 wash, giving better dispersibility and slightly increased strength. A strength-milling time curve has been obtained which shows that strength increases with milling time to a plateau at about 12 hours milling time. Seven hours milling and extraction in the plant has given a strength of 90 vs. BT-383-D standard. However, this requires reduced capacity.

A new technique for obtaining rapid elimination of Perclene in the extraction has been developed and is called the "70/30" type of extraction. Use of a combination of increased loading in the mill and a "70/30"-surfactant-Na_2CO_3 extraction has given substantial strength improvement without reducing capacity.

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I. INTRODUCTION

The impetus for this work arose from the competitive threats of first, American Cyanamid's Cyan 55-3297, which is about 3% strong by rubout versus our BT-383-D standard. This was the competitive against which most of this work has been done. Another competitive, Holland Suco BT-4614, appeared in 1968 which was even more of a threat than Cyan 55-3297, since it was 5-7% stronger and slightly more transparent than BT-383-D. Samples of this product were not received at Newark, however, until 1969.

In addition to these competitives, it was recognized in 1966 that current production of BT-383-D was normally deficient in dispersibility to the BT-383-D standard. Also, there was the expectation that any beneficial changes in the BT-383-D dispersion milling or extraction could also help improve strength and other properties of the major blue code BT-417-D, which is made from the same mill powder as is BT-383-D.

II. CHARACTERIZATION OF COMPETITIVE CODES

Cyan 55-3297

Measurement of surface area (72 m^2/g) showed this competitive to be considerably larger in surface area than standard BT-383-D, PS-97732 (57 m^2/g) or the current production (range of 57-69 with average of 64 m^2/g) indicating a smaller particle size for competition. X-ray line broadening confirmed this, showing a half-width (9.2°) of 17 for Cyan 55-3297 versus 16 for standard and a range of 15.5-17.0 (average 16.2) for current BT-383-D production.

In addition to being smaller in particle size, this competitive is also about 2% purer than our standard BT-383-D (98.2-98.4% versus 96.2% by mixed solvent extraction). Current production is even lower than standard and is 3-4% lower in purity than the competitive. The X-ray pattern of this competitive shows it to be a pure beta phase product.

Dispersibility of this competitive in oleoresinous ink is about the same as BT-383-D standard.

Holland-Suco BT-4614

This product shows smaller particles in electron micrographs and exhibits a somewhat larger surface area (62 m^2/g) than BT-383-D standard. The X-ray line broadening, however, is anomalous, showing a half-width (9.2°) of 14.5. The purity is low (92.3%), and the X-ray pattern is that of a pure beta phase CPC. Dispersibility in oleoresinous ink is slightly better than BT-383-D standard.

III. DEVELOPMENT OF AN INTERIM PRODUCT

The efforts to reduce costs on BT-383-D and to utilize capacity to the maximum has led, over the years, to a substantially modified extraction process compared to what was used when the present standard, PS-97732, was set up in 1962. A review of these changes is given in Table 1.

Table 1

History of BT-383-D Extraction

Year	Process Letter	Lbs. CPC	Gal. H_2O	Lb. H_2SO_4	Lb. Oxalic Acid	Lb. NH_4OH	Washing End-Point
1961	J	1080	3165	1806	27	770	4 hrs.after NH_3
1963	K	1118	3165	1700	27	770	5000
1965	L	1118x2	991x2	200x2	0	0	5000
1966	M	2236	1982	500	0	0	4000

Since the latest standard for BT-383-D, PS-97732, was set up, the relative volume of water was reduced, the amount of acid cut, the oxalic acid eliminated, the ammonia was eliminated, and the washing end-point was reduced. Each of these changes, by itself, was reported to have no influence on quality. However, our laboratory study of these factors showed that the effect of eliminating the NH_4OH wash was significant, and caused a slight reduction of strength. In addition, there was a drop in purity of about 0.5%.

The concentrating of mill powder, as in Process M, into a smaller volume of water would also be expected to affect strength because this effectively amounts to a reduction in the ratio of surface area/pigment. Since relative surface area is reduced, the rate of removal of Perclene during extraction is lowered and the amount of Perclene retained throughout the whole extraction is greater. Since it has been previously shown that crystal growth takes place rapidly when both acid and Perclene are present, it is expected that this change in relative amount of surface area would give a weaker product. This was checked in the lab by extracting mill powder with a high area/pigment ratio (beaker) and a low area/pigment ratio (graduated cylinder).(1)

Table II

Area/Pigt. Ratio (sq.in./g. CPC)	Extraction A		Extraction B	
	Strength	Half Width (9.2°)	Strength	Half Width(9.2°)
0.75	105	17.5	100	16.5
0.10	105	15.5	98	16.0
(BT-383-D)	100	16.0	100	16.0

Although the strengths are more or less the same for both high and low area type extraction, the X-ray line broadening is consistently greater for the high area type extractions and they may indicate an inherently greater strength. In addition, it was shown in the lab that deliberate addition of Perclene at the beginning of the extraction gives considerably weaker products either by flushout or by rubout.

A priori, it was evident that the effect of the changes in extraction from 1961 - 1966 were deleterious to quality and that the trend had to be reversed. Laboratory development then led to a process in which two changes were made, viz. (1) the introduction of the anionic surfactant G-3300 into the extraction, (2) the use

of a sodium carbonate wash on the presscake, (3) the G-3300 served to help strength and dispersibility in two ways. First, it effectively neutralizes and, at least partly, precipitates the cationic surfactant Arquad 16 which is used in the milling. This was important in the extraction because of the large amount of foam that normally develops in the extraction when the maximum temperature (205-210°F.) is approached. The foam is a result of the Arquad 16 surfactant and the vaporizing Perclene. As a result of this foam, it had been difficult, on most extractions, to attain the specified temperature range. Consequently, large amounts of Perclene were retained on the pigment in the extraction. This difficulty had, of course, been aggravated when the charge of mill powder in the extraction was increased. The neutralization of the cationic surfactant Arquad 16 in the extraction by the anionic G-3300 surfactant remarkably suppresses the foam which appears as the temperature approaches the maximum, so that the maximum temperature can be approached rapidly and a greater share of the Perclene can be removed. Another effect of the G-3300 surfactant helps dispersibility, and this is because of the precipitation of the Arquad 16 on the pigment by the G-3300. About one-third of the G-3300 that is used (3 to 4%) is retained on the pigment in the form of Arquad 16-G-3300 complex. This results in about 1% less purity for the product.

Other anionic agents than G-3300, e.g., CPC-MS, have the same ability to reduce foam in the extraction, but texture and dispersibility resulting from the use of these other agents were made worse.

Along with the use of G-3300 surfactant in the extraction, it was necessary to use a sodium carbonate wash (N-3-A). Leaving out this wash gave a slightly weaker product (2-5%) which, when tested at minimum work in oleoresinous ink, showed more grit in the masstone and considerably poorer rate of strength development than the corresponding product with the N-3-A wash.(4)

Other variations tried with the G-3300/Na_2CO_3 type of extraction included a dilution of the extraction by using more water. This did not improve strength or rate of strength development. Extractions were also made at room temperature instead of at the boil in the hope of obtaining smaller particle size and strength. However, both dispersibility and ultimate strength were slightly poorer.(5)

The product made by using G-3300 surfactant with the N-3 wash was called an interim product because, although it was improved in strength and dispersibility, its quality was not sufficient to counteract the Cyan 55-3297 competitive.

Full-size plant tests of this process were made with comparison to control lots made from the same set of dispersion mill powders (N-797-A).(6) The first comparison was as follows:

Table III

COMPARISON OF INTERIM PRODUCT WITH CONTROL*

	Control Lab Rubout	Lab. Min-Max. Test** 2X-1	7X-3	Ink Mill Str. -5T	% CPC Mixed Solv.
L48271-Experimental (Interim Prod.)	98,G8,I10,Dk20	99	100	98	92.2
L48280-Control	100,G6,Dk18	105	100	102	94.2
Cyan 55-3297 C#66725	-	97	96	-	98.2
BT-383-D,PS97732	100	100	100	100	96.2

*See Appendix for Ink Mill Data
**See Appendix

The second comparison was as follows:

Table IV

EFFECT OF N-3-A WASH ON QUALITY (7)*

	Control Lab.Rubout	Lab.Min-Max Test 2X-1	7X-1	% CPC
L49288-Control	100, D8	110	102	94.7
L49445-G-3300 (No N-3 wash)	102,G10,D10	101	102	92.7
L49472-G-3300+N-3 wash (interim product)	98,G6	95	99	93.3
Cyan 55-3297	-	97	97	98.2
BT-383-D, PS-97732	100	100	100	96.2

*See Appendix for Ink Mill Data.

The second comparison confirms the laboratory requirement for the N-3-A wash for optimum quality even though this has meant a longer wash time.

Comparison of the control lots with the experimental interim products shows equivalence in bleed tests in 45/45/10 xylene, lacquer solvent, Cellosolve, and 50/50 alcohol/water. Ink mill texture is slightly improved over the control lots and the tests in nitrocellulose fluid ink shows the experimental interim product to be stronger than the control lots, more transparent, and with a better gloss. All tests in vinyl, including migration and heat resistance show equality.

To check the improvement in dispersibility of the interim product, the presscake of L48271 was freeze-dried. This material was then compared to the plant lot itself and there was seen to be no difference in strength between the lab freeze-dried product and the plant product, either at minimum or maximum work by rubout.

A check of the use of the presscake of the interim product in BL-426-D (aluminum benzoate lake) was made and this presscake was found suitable. Tests in 30J, acrylic lacquer and TAE-2 showed equivalence to the control presscake. The changes used in the interim product, i.e., G-3300 surfactant and N-3 wash, were also tried in BT-417-D-type extractions in the lab. In this case, however, these changes harmed the product for use in paint and fluid inks, giving poorer flocculation resistance in paint and poorer strength and gloss in fluid inks.

IV. RELATIONSHIP BETWEEN MILLING CYCLE AND STRENGTH

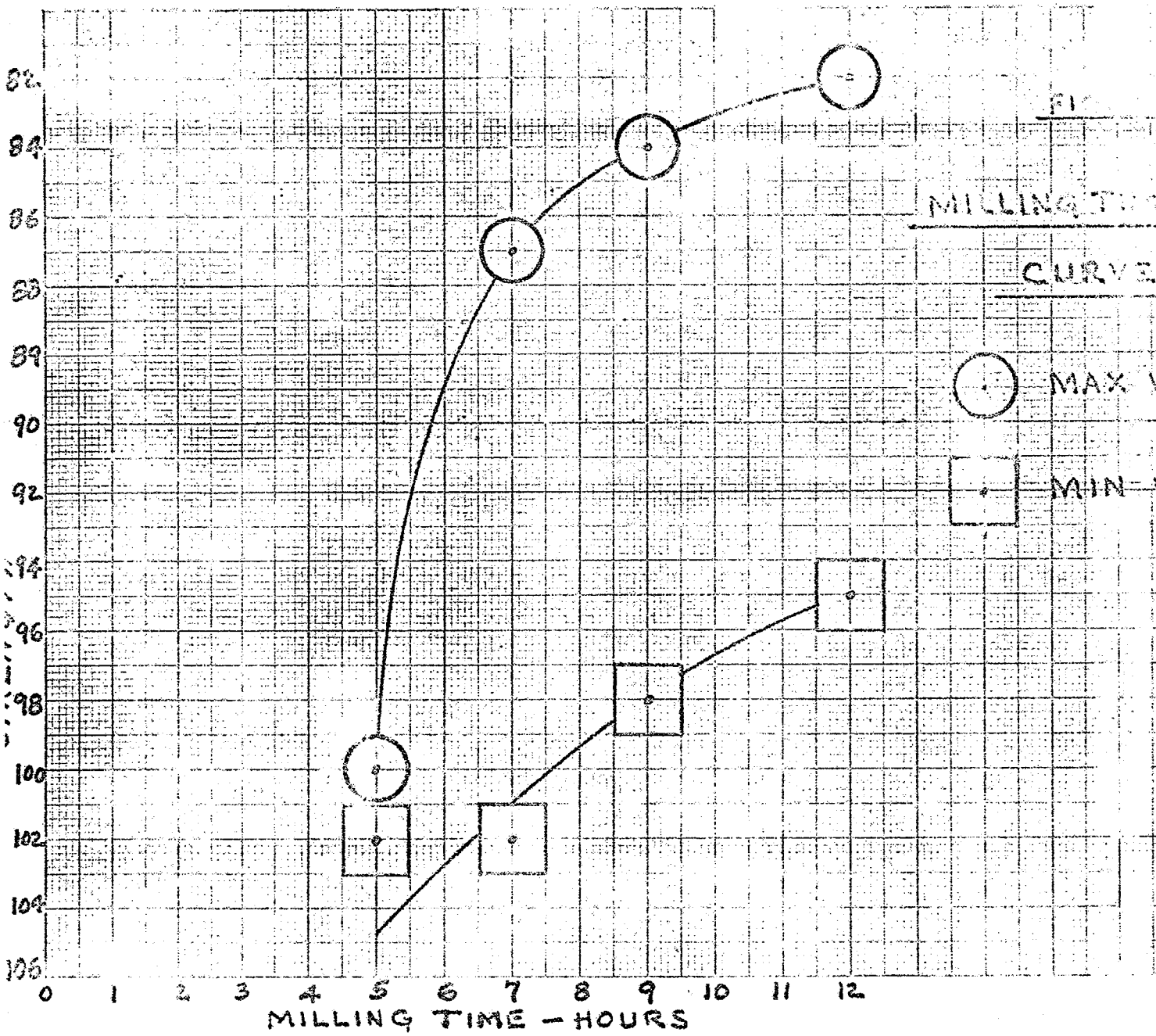
Limited methods have existed for increasing strength of beta-phase dispersion-milled CPC. Principally, this has been through the introduction of the stronger and redder alpha phase into the product. Apart from the less desirable shade, however, this leads to redder, more crystal unstable products. This study, however, sought to improve strength by reducing particle size. Previous studies had attempted to do this by improving the dispersion milling, either by use of different surfactants or by longer milling. Neither of these appeared to give much better strength than the standard milling. The reason for this appeared to be that the extraction process leveled out any potentially stronger products.

Since the extraction had been improved by using the interim process, however, it seemed likely that the combining of a longer milling with the interim type of extraction might yield additional strength. This was tried by running extended plant millings[8] along with laboratory interim-type extractions.[9] The strengths obtained at both minimum work and maximum work by the Hoover Muller MIN_MAX Rubout Test are plotted in Figure 1. All strengths are plotted in comparison where BT-383-D, PS-97732 is 100.

The Figure shows that strength is still improving at 12 hr. milling time although it appears to be leveling off to a strength level about 20% strong, at maximum work, compared to BT-383-D standard. The strength curve is paralleled by a reduction in particle size as shown by electron micrographs and X-ray line broadening. The latter depends somewhat on the manner of extraction, e.g., a 12 hour mill powder yields a half-wide (9.2°) of 18.7 when finished by the improved extraction, but when given a short extraction in the cold, along with a lower drying temperature, the value is 21.0. Dispersibility, however, is poorer with the short, cold extraction, so that the strength is not significantly affected, even though the particle size is smaller. It is significant that the ability to obtain greater strength from longer millings depends upon the extraction with the improved (G-3300+Na_2CO_3 wash) extraction yielding the higher strengths.

Enough mill powder was then made under the following milling conditions to make a plant extraction:

200 lb.	LC crude)	
1200 lb.	Alum)	
10 lb.	Arquad)	N-22-A
30 lb.	Perclene)	
7 hr.	milling)	



The extraction (L-51280)[10] was made with the improved type of extraction (G-3300+Na_2CO_3 wash). At this time, there was an insufficient number of frames for the press so that a reduced batch size (1608 lb.) was employed.

This product was close to the laboratory comparison, showing a strength of 90 by TF rubout and a recheck. Ink mill strength at 5T passes was 88 and the X-ray half-width value was 17.8 compared to 16.0 for BT-383-D, PS-97732. Purity was 93.2% CPC by mixed solvent extraction which was about what was expected because of partial retention of G-3300 surfactant.

With this background, an extended series of similar millings were made under XOP-369A and extracted with the improved extraction process.

Table V

QUALITY FROM IMPROVED EXTRACTION OF N-22-A

BT-383-D Lot	% CPC	Strength by TF Rubout Control Lab.	Lab-RLS	Half-Width
L55794	92.8	96	93,94	16.0
L55956	92.2	98,86	95	16.5
L56174	92.6	98	98	15.5
L56210	93.0	95	95	16.5

These strengths obtained were markedly different from the first extracted product (151280). It turned out, upon inspection, that the major difference between these batches and L51280 was the batch size approximately 2300# (full size extraction) vs 1608 lb. respectively. The consequences of the larger batch size were that, first, the maximum temperature reached in the initial heating was, on the average, a little lower (201°F.) than in L51280 (205°F.). This lower temperature means that a greater amount of Perclene is retained on the pigment. In addition, because of the larger batch size, which has less freeboard, the final flooding after the extraction yielded a temperature of 180°F. compared to 160°F. for L51280. The presence of more Perclene, along with the higher temperature, during the period after flooding, results in greater crystal growth and is evidenced by the smaller half-width values. In addition, these later batches were required to stand, for scheduling reasons, after flooding, an average of over 5 hours before starting to press, whereas the L51280 stood a comparatively short time of 2 hours. It seems clear that these are the reasons for the poorer strengths of these last four batches. However, to test this theory, a number of "split" batches were made. The "split" batch extracts the CPC necessary for a full press load in two separate extractions of one-half size each, with the second half being pressed into the same press. The freeboard of each half-batch is greater, allowing a higher initial temperature and greater removal of Perclene, and it also allows flooding to a lower temperature (160°F.). Comparisons were made in the plant extractions by using 7 hour mill powder from the same lots in both the "split" lot and the control lot (both using G-3300 surfactant and Na_2CO_3 wash).

The resulting data show the "split" batches to have a consistently higher X-ray half-width value and consequently a smaller overall particle size compared to their control batches.

Table VI

COMPARISON OF "SPLIT" EXTRACTIONS WITH CONTROL EXTRACTIONS

	Control Lab. R.O.Strength	H.W.(9.1°)	% CPC (Mixed Solvent)
BT-383-D, Lot 57853 "split"	94	17.5	92.7
" 57966 control	95	16.7	92.6
" 58002 "split"	92	18.0*	92.6
" 58054 control	94	16.5*	92.2
" 58261 "split"	92	17.6	93.0
" 58297 control	97**	16.4	93.3

*Rechecked values.
**Remixed to 1.6% moisture.

These data for the "split" batches compare well with the earlier strong batch, L51280 (reduced size) which showed a value of 17.5-17.8 with a control lab R.O. strength of 90, and 93.2% CPC purity. Comparison of all full-size batches with "split" or reduced batches (all 7 hr. mill powder) was as follows:

Table VII

COMPILATION OF EXTRACTION RESULTS (IMPROVED TYPE USING N-22-A)

Full Size Batch			"Split"or Reduced Batch		
	Str.	Half-width (9.1°)		Str.	Half-Width (9.1°)
L55794	96	16.0	L51280	90	17.6
55956	98,97	16.5	57853	94	17.8
56174	98	15.5	58002	92	18.0
56210	95	16.5	58261	92	17.6
57966	95	16.7			
58054	94	16.5			
58297	97	16.4			
Avg.	96	16.3	Avg.	92	17.8

V. CAPACITY CONSIDERATIONS - THE "70/30" EXTRACTION AND INCREASED MILL LOADING

Each of the steps taken to this point have had the effect of reducing capacity. First, the extended milling at Newport and then the use of "split" batches at Newark.

In order to obtain the benefits of the "split" batch, i.e., to remove Perclene efficiently and rapidly, a method of extraction was devised which is called the "70/30" extraction[11]. The steps in

this type of extraction are as follows:

1. 70% of the amount of water is added to the vat along with all of the surfactant G-3300.
2. The vat is heated to 205-210°F.
3. 70% of the amount of CPC mill powder is added.
4. The vat is heated to 205-210°F. and held at 205-210°F. for 30 minutes.
5. The remaining 30% of the water is added.
6. The vat is heated to 205-210°F. and held at 205-210°F. for 20 minutes.
7. The H_2SO_4 is added.
8. The vat is heated to 205-210°F. and then the steam is turned off and the vat stirred for 1 hour.
9. The vat is then flooded to the top.
10. Press, wash with Na_2CO_3, dry, pulverize.

In this type of extraction, the delayed addition of 30% of the acid and CPC allows a greater freeboard for the first portion of 70% of the CPC mill powder. This permits a higher temperature to be reached during Step 3 and consequently efficient removal of Perclene from the major part of the CPC. Since, by Step 6, most of the Perclene has already been removed, a higher temperature can also be obtained here along with better removal of Perclene. The growth of the CPC crystal takes place most rapidly when both strong acid and Perclene are present. For this reason, the delayed addition of the acid until after the Perclene is removed helps to avoid crystal growth.

The "split" type of extraction reduces Newark capacity by requiring just about twice the length of time as a single full size bathc; the"70/30" type of extraction, however, needs no additional time and there is no capacity loss.

Newport capacity would be considerably reduced by a 7 hour-200 lb. CPC milling of the order of a 25% reduction from the 5 hr. 200 lb. milling. Turnaround time must be added to milling time and this is about 1 hour per cycle, the same for either a 5 hour or a 7 hour milling.

To avoid reduction in Newport capacity, 7 hour millings were made at higher loadings:

260 lb. LC crude)
1200 lb. Alum)
10 lb. Arquad) N-40-A
30 lb. Perclene)
7 hr. milling))

This ratio of 260 lb. LC crude/8 hr. (counting 1 hour for turnaround) for N-40-A is the same as that for N-797-A (200 lbs./6 hr.). Plant extractions were then made by the "70/30", G-3300/Na_2CO_3 improved type of extraction process on N-40-A with the following results.

Table VIII

"70/30" EXTRACTIONS OF 7 HOUR-260 LB. MILL POWDER (N-40-A)

BT-383-D Lot	T. F. Rubout Strength (Control Lab)
61217	98
62076	95
62175	95
62471	94
62591	97
63358	98
63225	95
63493	96
Avg.	96

This average strength from N-40-A is not as good as that from the "split" or reduced batch size extraction of 7 hr./200 lb. mill powder, N-22-A (92 strength), but it is equal to that from the non-"70/30" type of extraction (full size) of N-22-A, even though the loading in N-40-A is 30% higher than in N-22-A.

This series of millings and extractions in Table VIII shows the improvement which can be obtained at the equivalent of our present Newport and Newark capacities. The combining of the "70/30" extraction with the N-40-A type of mill was made for this reason. However, this did not allow us to assess the individual effect of the "70/30" type of extraction compared to a regular extraction in which all of the CPC mill powder is added right in the beginning. Laboratory comparisons have shown no differences, presumably because the Perclene is removed fairly rapidly in any laboratory extraction. The requirements of production did not allow us at this time to make "70/30" G-3300/Na_2CO_3 extractions of N-22-A so as to compare with the G-3300/Na_2CO_3 extractions of N-22-A (Table VII). A comparison was made using N-797-A, however, all extractions with G-3300/Na_2CO_3:

Table IX

COMPARISON OF "70/30" TYPE OF EXTRACTION WITH REGULAR METHOD IN EXTRACTION OF N-797-A

Regular Method		"70/30" Extraction	
Lot	Control Lab. TF RO Str.	Lot	Control Lab. TF RO Str.
L48271	98	L59717	98
		L60197	96
L49472	98	L60264	98
		L60368	97
		L60438	99
		L60628	100
Avg.	98	Avg.	98

On the 5 hr./200 lb. N-797-A mill powder, the "70/30" type of extraction appears to be of little effect. It would be expected, however, that in the case of the 7 hr./200 lb. N-22-A, where the particle size is smaller, that there might be a distinguishable difference. The "70/30" extraction of the 7 hr./200 lb. N-22-A should, therefore, be made in some future study when production demands are not so tight, so as to compare with the strength of those batches in Table VII.

VI. SUMMARY

The improved extraction process which uses G-3300 surfactant and the Na_2CO_3 wash has been shown to yield considerably improved dispersibility and slightly improved (2%) strength. Presently, the surfactant G-3300 (or the same structure Emcol P1059) and the Na_2CO_3 wash are being used on all production of BT-383-D.

Second, it was shown that particle size can be reduced and strength considerably increased by longer millings if the extraction is such as to be able to remove Perclene quickly and effectively, this being done by the "70/30" - G-3300 - Na_2CO_3 type of extraction. The highest strengths, however, can be attained only at the expense of some decrease in Newport and/or Newark capacities. For example, if a strength of about 90 becomes eventually a necessity, this can be done by producing 7 hr./200 lb. mill powder at Newport and making a reduced size "split", or possibly a "70/30" type batch extraction using G-3300-Na_2CO_3.

Further, even without reducing capacity either at Newport or Newark, strength can be noticeably improved (96) over standard strength by using higher mill loadings along with the longer millings and the "70/30"-G-3300-Na_2CO_3 type of extraction. At the time of writing this report, Production is taking advantage of higher loading (220 lb. LC crude/1100 lb. alum/5 hr.) along with the G-3300-Na_2CO_3 improved extraction to increase milling capacity 10%, thus trading strength for capacity. This current production is averaging about 2% strong vs BT-383-D, PS-97732. This mill powder is also being currently used in BT-417-D production since the strength and transparency are satisfactory.

VII. MISCELLANEOUS STUDIES

A. Stronger BT-417-D from Longer-Milled Powders

Laboratory extractions of longer-milled powders 200 lb. crude, 1200 lb. Alum, 10 lb. Perclene, 30 lb. Arquad, were made analogous to the (F)BT-417-D process. These products tested as follows:

Table VIII

TESTS IN HIGH GLOSS "LUCITE" OF BT-417-D FROM LONGER-MILLED POWDERS

Label	Milling Time Hours	Tints Str.	Sh.	Int.	Floc. Resis.	Metallic
1861-55A-2	5	97	G	I	=	=
55B-2	7	95	G	I	=	Dk 15
55C-2	12	92	G	I	=	Dk 12
BT-417-D,84871		100				

The strength previously seen in the BT-383-D products from longer-milled powders holds in this evaluation.

Tests in nitrocellulose of these analogs of BT-417-D did not appear to show any noticeable trend in strength or transparency. However, another laboratory comparison of 5 hour with 7 hour mill powder showed improved strength and transparency for the 7 hr. mill powder product [13]. Viscosity was not changed. A plant lot was then made with the following results:

	Rubout	Nitrocellulose
BT-417-D, Lot 52171	93, I18, Dk99, G29, I20	95, I18, Trans.18
BT-417-D, Lot PS-84871	100	100

This plant lot indicates that strength and transparency can be attained in BT-417-D by using longer-milled powders.

B. Effect of the G-3300/Na_2CO_3 type of Extraction on Quality of BL-426-D

BL-426-D is an aluminum benzoate lake made from the presscake of BT-383-D (BT-395-P). Laboratory comparisons have shown [19] that this code, made via the G-3300/Na_2CO_3 extracted presscake, has equivalent quality to the product made without these treatments in 30J alkyl, acrylic, TAE-2, and by rubout.

C. Effect of Reduced Perclene in the Milling on Strength of BT-383-D

Under XOP-369, millings under the following conditions were made:

200 lb. LC Crude
1200 lb. Alum
10 lb. Arquad 16-50
15 lb. Perclene

These mill powders were laboratory extracted with the G-3300-Na_2CO_3 improved extraction. Comparison is made with products from the normal milling (30 lb. Perclene);

Table IX

MILLING TIME - STRENGTH RELATIONSHIPS*

Milling Time-Hrs.	Normal Perclene	Reduced Perclene
5	99	97
7	87	92.5
9	85.5	90
12	83.5	85.5

*Fractional strengths are the average of 2 or more determinations.

These results show that at 5 hrs. milling time, there may be a slight advantage in strength for the milling with reduced Perclene; however, each of the comparisons at longer milling times showed a strength disadvantage for the reduced Perclene products. Unexpectedly, the products from the reduced Perclene millings were green in shade vs BT-383-D. Because of the strength relationships, no further work was done on millings with reduced Perclene.

D. Alkaline Extraction of Mill Powder

Since phthalimide and other alkali soluble materials are present in dispersion mill powder, an alkaline extraction was added onto the normal acid extraction, after reslurrying. The products were about 0.5% purer and the dispersibility and strength were slightly improved. The difference in strength (1-2%) was not sufficient to warrant further work[14].

Direct alkaline extraction of mill powder (with no prior acid extraction) was also made, using a large amount of alkali to dissolve the amphoteric $Al(OH)_3$. This product was considerably poorer in dispersibility than a control but of about equal strength[15].

E. Effect of Improved Purity of Crudes

Under XOP-350, high purity crudes were made by using 10% less CuCl in the synthesis and then milled in the normal way. Comparison of the normal (95.4% crude purity) vs high purity (96.9% crude purity) products after the regular extraction (not G-3300/Na_2CO_3) showed a 5% strength difference in favor of the high purity crude. However, if the improved type of extraction was used (G-3300/Na_2CO_3), then this difference dropped to only a 2% strength advantage which is equivalent to the difference in crude purity itself[16].

F. Identification of Impurities in BT-383-D Production Lots

LC crude purities have sometimes ranged as low as 88% with the usual range somewhere at 92-95%. The extraction of mill powder improves the purity a little, but there is still considerable opportunity for binders to be present. To find out what type of

impurity is present, extraction of BT-383-D lots was made with alcohol[17]. This yielded about 3% of dark brown extractables which showed I.R. bands at about 3 microns (OH and/or NH), aliphatic CH, carbonyl, aromatic CH and carboxylic OH. This could represent a trace residue of Arquad 16 (used in the milling) which would show aliphatic CH, but primarily material such as phthalic acid and/or phthalic acid amide. A DTA curve using glass beads as an absorber showed endotherms at 160-180°C. and at 300-350°C. These endotherms could correspond to mixed melting points of some of the following materials:

	m.p.
Phthalic acid	207° (d)
Phthalimide	238°C.
Phthalic acid (diamide)	220°C.
Phthalic Anhydride	131°C. (sublimes at 285°C.)
Deo base	250°C.
Arquad 16	255°C. and 330-340°C.

The endotherm at 300-350°C. could represent the melting of that part of Arquad 16 that melts at 330-340°C.

That these materials do act as binders was confirmed by Min-Max rubout tests of the original and extracted BT-383-D lots. Three different lots, one of which included the standard PS-97732, showed, after alcohol extraction, improved dispersibility and increased ultimate strength of 3-6%. The improved dispersibility and strength obtained in the improved G-3300/Na_2CO_3 extraction is obtained, at least partly, by extraction of phthalic acid residues during the Na_2CO_3 wash.

G. Quality from 7 Hour-Reduced Alum Millings

Efforts were made under XOP-355 (J.R.Glasscock) to lower alum usage in dispersion milling. The results showed that reduction to 1100 lbs. instead of 1200 lbs. gave strength in both BT-383-D and BT-417-D. In connection with our longer milling studies, 7 hour millings were made under XOP-367 in which reduced alum was used and then the mill powder extracted in the lab by the G-3300/Na_2CO_3-type of extraction[9]. The products were then tested by the MIN-MAX rubout test:

Table X

QUALITY OBTAINED FROM 7 HOUR-REDUCED ALUM MILLINGS

"Alum"	Milling Time Hours	Strength Min.Work	Strength Max.Work	H.W.(9.1°)	Size of Particle by Electron Micrograph
1200	7	97	87	18.3	
1100	7	100	87	18.5	About the same
1000	7	100	93	17.8	Sl. larger

This shows a slight advantage in dispersibility for the standard 1200 lbs. alum in the mill when the longer millings are made and the G-3300/Na_2CO_3 type of extraction is used.

H. Removal of Perclene in Extraction of Mill Powder via Flash Distillation

Attempts were made to flash distill the Perclene off from the regular type of mill powder in the Semi-Works unit at Newport [18]. Foaming, however, prevented rapid removal of Perclene and longer running times gave increasingly weaker products. None of the products were as strong as that made by the ordinary extraction in a beaker. Since G-3300 was found to reduce foam, this was tried in the feed mixture. The foaming, however, was still considerable, making the distillation slow and difficult, and the products were weak vs. the corresponding control made using G-3300.

VIII. REFERENCES

1. 1841-24
2. 1841-36,40,42,46
3. 1861-18
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5. 1861-37
6. 1861-18
7. 1861-28
8. XOP-367
9. 1861-54
10. 1861-50
11. 1905-11
12. XOP-369
13. 1862-60
14. 1861-1
15. 1861-6
16. 1861-22
17. 1861-3
18. 1841-38
19. 1861-40

MIN-MAX RUBOUT TEST

1.000 g Pigment
2.000 g Varnish Drier
Mull 2 x 50 passes with one weight
Remove 0.50 g. masstone
Add 2 weights
Continue mulling with 5 x 50 more passes
Tint out both masstones
Compare tints.

INK MILL COMPARISON OF INTERIM PRODUCT WITH CONTROL AND STANDARD

	Wet	Ball	Break	1T	2T	3T	4T	5T	1T	2T	3T	4T	5T	1T	2T	3T	4T	5T	1T	3T	5T
L48271 Interim Product	35"	=	=	8	10	→			1	4	5	7	8	10	5	2.5	1.5	1	101	98	98
L48280 Control	1'25"	=	=	8	10	→			0	1	4	7	9	10	6	3	2	2	102	99	102
BG-383-D,PS97732	1"25"	↓	↓	9	10	→			2	6	10	10	10	6	4	3.5	3	3	100	100	100
																			TF Rubout Control Lab.		
L49288 Control	50"	vvs soft	vvs long	8	10	→			2	6	10	→		7	4	3.5	2.5	2		100	
L49445 (No Na_2CO_3 wash)	1"30"	"	"	9	10	→			3	8	10	→		8	3	2.5	2	2		102	
L49472 Interim Product	50"	"	"	9	10	→			2	7	10	→		7	3	2.5	2	2		98	
BT-383-D,PS97732	1'20"	"	"	9	10	→			5	9	10	→		8	3	3	2.5	2.5		100	
Cyan 55-3297 C#66725	2'40"	↓	↓	9	→				6	9	10	→		7	5	3	2.5	2.5		-	

IX. APPENDIX

New Jersey Office Supply Co.

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