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PIGMENT COLOR RESEARCH REPORT

Progress Report

THE FINISHING OF PHTHALOCYANINE PIGMENTS I : WET GRINDING STUDIES

Period Covered: NOVEMBER 11, 1945 - MARCH 30, 1946.

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

THE FINISHING OF PHTHALOCYANINE PIGMENTS I : WET GRINDING STUDIES

NOVEMBER 11, 1945 to MARCH 30, 1946.

F. W. Lane 4/3/46

SUBMITTED BY: F. W. LANE DATE SUBMITTED: 4/22/46

D B Killian 6/3/46

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I N D E X

SOLVENT GRINDING OF PHTHALOCYANINE PIGMENTS

I. OBJECT: To determine whether satisfactory tinting strength in CPC and polychlor CPC can be developed by grinding in either water or organic liquid slurries. If satisfactory quality is possible, to obtain capacity estimates for the preferred methods.

Period Covered by Report:

November 11, 1945 to March 30, 1946
See Newark Research Notebook No. 1187

II. HISTORICAL BACKGROUND

The development of desired tinctorial properties in the phthalocyanine toners requires a considerable reduction in the particle size of the crude products. Heretofore the only effective methods known were acid pasting and salt milling. Other dry grinding methods have been evaluated and found very unsatisfactory. A few earlier attempts at wet grinding were reported unsuccessful. Discussions of salt milling and finishing may be found in the following reports:

JLR-59-1,	No. 59	Serial No. 19316
"	No. 54	18802
"	No. 39	17797
"	No. 41	17880
"	No. 56	19146
"	No. 36	17477
"	No. 52	19099

The following facts stimulated the wet grinding study at Newark. Acid pasting of CPC is expensive due to low solubility and the consequent high acid consumption. Salt milling of CPC blues is cheaper and satisfactory but is not satisfactory for the green CPC. On the basis of wet pigment grinding experience, wet grinding of CPC has apparent economic and operating advantages over previous methods.

III. NATURE OF THE PROBLEM

The initial goal was to develop wet grinding methods for polychlor CPC and chlorine-free CPC made by the urea-phthalic anhydride solvent process. The prime requirement was the development of tinting strength equal respectively to the two current standards GT-486-D and BT-172-D. Electron microscope studies of high strength CPC toners indicate roughly a particle size of about 0.1 μ. This is probably the largest dimention if the assumption of flake-like particle is correct. The crude materials are definitely crystalline, the individual crystals being of the order of 1 x 2 microns to 5 x 30 microns. The blue crudes have more uniformly shaped needles than the green crude prepared by chlorination in $AlCl_3$-NaCl eutectic melt.

This degree of particle size reduction to the 0.1μ range is not, to the writer's knowledge, obtained in present industrial wet grinding installations.

The actual strength development required is indicated by the relative strength of the crudes and standards:

BT-172-D, SD-48342	100
Crude Blue, DW-5829	25
GT-486-D, SD-48335	100
Crude Green, DW-5890	37

IV. PATENT SITUATION

Although solvent grinding patents exist, the following items may have patentability:

1. Solvent grinding applied to CPC particularly since water grinding is shown to be detrimental in the case of Green CPC.
2. Specific alcohols or alcohol-water mixture.
3. Controlled flocculation to obtain soft powder products.
4. Grinding with a mixture of equal numbers of two ball sizes, the smaller just large enough to fit the spaces between the larger.
5. A fluorinated CPC to obtain solvent stability with a minimum of greenness.
6. Increased ball mill capacity by use of downward magnetic force operating to increase impact-force and critical mill speed and to prevent floating of small ferrous balls.

V. SUMMARY AND CONCLUSIONS

Ball mill slurry grinding of polychlor CPC and chlorine-free CPC has been successfully employed on a laboratory scale for the development of tinting strength.

Water alone is not a satisfactory grinding medium probably because of the poor wetting obtained. No wetting or dispersing agent was found effective when used in amounts up to 5% of the pigment.

Several organic solvents are satisfactory and a choice for plant operation will depend on cost, safety, ease of recovery, etc. The solvents giving full strength on prolonged grinding are:

a) <u>for chlorine-free CPC</u>
Alcohol 3A
Alcohol 23A 2 pts. - water 1 pt.

b) <u>for polychlor CPC</u>
Xylol
Mineral Spirits
Methanol 99%
Kerosene
Alcohol 3A
Alcohol 23A
Isopropanol 99%
Isopropanol 3 pts. - water 1 pt.
Toluene
(carbon tetrachloride)

Steel balls may be used except with polychlor CPC when water is present. The combination of metal and water results in dechlorination and marked blueing of the green pigment.

Grinding of chlorine-free CPC in hydrocarbon solvents reaches only about 75% of standard strength. This is believed due to crystal growth in these solvents.

During this study the importance of producing a non-solvent sensitive blue CPC has become evident. Presumably such a blue will grind to standard strength in hydrocarbons. Initial tests indicate this to be true of semi-chlor material from the phthalonitrile process.

Ball mill capacity tests were made with polychlor CPC and kerosene in a one foot diameter mill. This data has been extrapolated to larger mills up to eight feet. For 3/8" steel balls the extrapolation shows an eight foot diameter mill capacity of 113#/24 hrs/linear mill foot and a cycle of about 30 hours. These tests were limited and further tests in the proposed semi-works mills will be necessary. See Exhibit N, Fig. 2.

A new type of ball mill apparatus, the "Attritor" has been partially evaluated. On a laboratory scale it was found to have a capacity 6 to 10 times that of a normal ball mill of equal volume. The manufacturer states that the rate does not increase in larger equipment. Because of this it probably has no advantage over normal mills of 6 to 8 ft. diameters. However, further investigation would be worth while especially if we wish to grind in the absence of metals.

Some work has been done on methods of finishing the ground slurries. Transfer of pigment to water slurries for acid extraction or producing water pastes is readily accomplished by distillation of alcohol slurries. Kerosene does not appear attractive in this respect. A clue to a method of producing a soft bright powder has been found.

VI. EXPERIMENTAL DETAILS

A. General Procedures

Exploratory grinds were made in small mills (1/2 pt. jars to 1/3 gal. porcelain mills). Steel balls, shot, glass beads and Porox balls were used as indicated in the summary. Progressive samples were removed from the mill and air dried at 200°F. Final ground slurries were finished by acid and ammonia extraction. Grinds not miscible with water were dried or steam distilled for the removal of solvent prior to extraction.

Extractions were made by digesting 2 to 3 hrs. in ten volumes of 7% sulfuric acid, filtering, washing, repulping and digesting in 2% ammonia, filtering, washing, drying at 200°F. From experiment 82 on, 2% sulfuric was used instead of 7%.

Tinting strength evaluations were made by comparing adjusted extensions with the standards, the samples being adjusted to match the standards at 100:1 ZnO:toner weight ratios. Rubouts were made on a Hoover Muller using 5 x 50 revolutions. All inks rubbed out contained 1 pt. by weight of toner and 2 pts. of varnish drier. Standard inks were extended with 60% ZnO paste; 0.180 gms. of ink being extended with 10 gms. of paste. The quantity of sample ink was varied to make extensions match the standard extension in tinting strength. The sensitivity and reproducibility of the test appear to be of the order of 2%, when there is no marked difference in shade.

B. Closed Circuit Grinding

Since TiO2 is wet ball milled in a closed circuit system with hydraulic classification, it was proposed that we apply this technique to CPC. The lower limit for separation of TiO2 particles by aqueous elutriation has been experimentally determined to be about 3 microns. On this basis, using Stokes Law, it may be calculated that the lower size limit in the case of CPC would be about 7 microns. Liquids of lower density would give negligible advantage. Our studies of the dispersion of CPC slurries resulted in no dispersion satisfactory for such elutriation. Attempts to prepare high strength fractions by elutriation were therefore abandoned.

Centrifugal separations in the desired range are of course possible and might be used for academic purposes. The Bird Centrifuges used in TiO2 wet grinding merely serve to remove grit. The lower sizing limit for commercial centrifuge is said to be about one micron.

In view of the above, closed circuit grinding has not received further attention.

C. Specific Surface Measurements

The only particle size measurements available for CPC were from electron micrographs of uncertain value because of difficulty in preparing mounts. Several types of CPC's were therefore submitted to the Experimental Station for surface area determination by nitrogen adsorption (Emmett) with the following results.

Blue Toner	Preparation	$M^2/gm.$	Dia.*	Str.
BT-172-D SD-48342	A semichlor from phthalonitrile, acid pasted, soft powder treated	36.5	0.11	100
B-6091	Salt-milled, urea solvent	70.6		108
N-384	Drip drowned paste lab. washed with alc., water, dried 200°F.	91.4	0.044	103
N-493	Current BK paste 4/5/45 L.T.drowned. Lab. washed with alc. and ether, dried. Hard	6.7		36
DW-5889	Crude urea solvent	8.6	0.46	25
Green Toner				
GT-486-D SD-48335	Polychlor standard	68.3		100
DW-5890	Crude Orchem Polychlor	14.0		37

*Assuming uniform spheres.

The T.E.A.-Cr_2 ester treatment on BT-172-D may blind the surface to N_2. N-493 dried to a hard grain probably accounting for low strength. The low area would indicate that actual particle growth had occurred.

Apparently wide range of sizes or large departure from spherical, or both, account for the small calculated diameter of crude DW-5889 as compared with microscopic appearance.

If the crude particles are assumed to have needle shape of breadth and thickness equal to one-tenth of the length the particle dimensions are calculated to be 0.32 x 0.32 x 3.2 microns from the surface area measurement. Particles smaller than this would be just about invisible at 625 x. However, if unresolved particles were present on the slide, they did not contribute color to the field as do the full strength particles.

Neither electron micrographs nor surface area measurements have been made for solvent ground pigments.

D. Ball Milling

Discussions with Mr. C. E. Berry, attendance at the Brooklyn Polytech Symposium on Particle Size, and information from literature all led to the feeling that ball milling is the most successful method of size reduction in sub-micron ranges. Generally, the high speed, high shear type mills do not grind discrete particles but merely disperse aggregates or droplets. This, plus low investment, and operating economy, dictated that first efforts be expended on ball milling experiments. This report deals entirely with ball milling. However, Mr. A. J. Stratton concurrently investigated numerous types of high shear grinding and found them ineffective except when salts or other extenders were added in relatively large quantities.

In the wet ball milling of TiO2 practically no reduction of primary particle size is obtained, the primary particles having been previously formed at about 0.2 micron. The milling is solely the breaking of cemented aggregates and requires only about 10 hrs. grinding in 1/3 gal. lab. mills with flint pebbles. In grinding CPC a longer cycle was expected, hence grinds were continued in most cases until no further increase in strength was obtained; this reached 500 hrs. and generally required 200 to 300 hrs. in 1/3 gal. mills to equal standard strength.

E. Mixed Ball Charges

Recent literature states that mixtures of ball sizes are additive in their effect. However, it seems reasonable that a special advantage would be obtained by using equal numbers of two ball sizes, the smaller size being just large enough to fill the spaces between the larger. If the large balls are not spread by the smaller, theoretically 33% additional contact points will be obtained if we assume hexagonal packing in the active milling zone. Calculation shows that the smaller balls will occupy only about 7.5% of the void space between the larger.

The high impact force of the large balls should permit handling slurries too thick for intermediate sized balls giving the same number of contacts per unit volume. Thus it seems possible that the over-all mill capacity would be increased.

An experiment was tried comparing a mixture of 3/4" and 1/4" balls with 3/8" balls in 2 gallon mills. One of the mills broke, however, and the experiment has not been repeated. Lifter bars are needed since the 3/4" balls sounded as though excessive slipping occurred.

F. Dispersion of Ball Milling Slurries

It is generally known that dispersed slurries give higher mill capacities than flocculated slurries chiefly because of better flow and the consequent possibility of employing higher solids concentrations. CPC pigments are notably difficult to disperse and tests covered by this report disclosed no satisfactory agents. The use of these agents is noted in the Summary Tables. A more thorough study of wetting and dispersing agents was made by Mr. Stratton.

These CPC pigments are so extremely hydrophobic that water grinding actually decreases the strength of the Polychlor and no significant increase in the blue is obtained unless large amounts of wetting agents are used.

G. Non-Aqueous Solvent Grinding

Hydrocarbons : mineral spirits, kerosene, benzene, xylol, or alcohols; methyl, ethyl, isopropyl, as well as carbon tetrachloride all wet the pigments readily and grinding in them increases strength. Polychlor CPC has been ground to essentially full strength in all of them. CPC chlorine-free blue has been ground to full strength of standard in ethyl (3A) alcohol and a mixture of 23A alcohol and water. Crystal growth in hydrocarbon solvents is presumed responsible for limiting the strength at about 75% of standard. O-chlor benzoic acid, benzyl alcohol, and tin phthalocyanine dichloride fail to remedy this situation in kerosene or mineral spirits.

CPC blue DW-5889 was ground to 105% strength, and slightly greener tint vs BT-172-D in 2 pts. 23A alcohol and 1 pt. water with steel balls. Corrosion of the steel was marked since the ground product before extraction was rated 75% and dirty green. See Exhibit E.

H. Choice of Ball Type

In ball milling, the following factors should be at a maximum to get greatest grind capacity.

1. Number of ball contacts per unit time per unit volume.
2. Ball impact force.

The first maximum, other mill conditions being constant, implies using very small balls. The second is obtained by balls of high density.

Starke and others (Micromeritics p. 327) have deduced the following relation from experiments in the sieve size ranges

$$\frac{\text{dia. initial particle}}{(\text{ball dia.})^2} = 6 \times 10^{-8}$$

Extrapolation to our problem indicates the following:

Initial particle dia.	Ball dia.
5 μ	0.9 cm.
1 μ	0.4 cm.
0.1 μ	0.13 cm.

Our experiments indicate the effectiveness of balls to be in the increasing order:

6 mm glass beads
1/2 inch Perox balls
1/16" steel shot
1/2" steel shot
3/8" steel balls.

The effectiveness is measured in terms of unit weight of material ground per unit time per unit volume of mill space. The range was not completely investigated and in larger mills with more concentrated slurries still larger balls may prove more effective.

Compatibility with the slurry is another important factor. For example, steel corrodes much faster in slurries containing water, even in small amounts, than it does in kerosene. Polychlor CPC and steel balls are definitely incompatible when water is present in appreciable amounts. The water apparently catalyses the dechlorination of the pigment and the product is very blue. In 99% Methanol open to air during grind (Exp. 1183-83) the crude polychloro CPC, DW-5890, did not turn blue but considerable rust formed which was removed by extraction. Even though the product is satisfactory this may represent intolerable erosion of equipment. See Exhibit M.

I. Choice of Solvent

1. CPC Blue

The relative effect of several solvents is shown in Exhibits B, C, G. It is definite that chlorine-free CPC will not grind to full strength in hydrocarbon solvents. If this type is to be ground, ethyl alcohol or ethyl alcohol-water mixtures are most attractive. See Exhibit E, sample K & L, and Exhibit F.

Nothing final can be said at this time regarding the grinding of Blue since the desired solvent stable type has not been developed. There now exist these major possibilities:

(a) Grind Cl free CPC in alcohol or alcohol water systems and add a suitable protective agent either during or after the grind. Tin phthalocyanine dichloride has not proven satisfactory. See Exhibit G. Cont'd. The added agent must survive extraction procedures if present in the grind. If satisfactory post grinding agents are found, grinding in isopropanol, ethanol, methanol and their water solutions should be further further studied. See Exhibit E (samples K & L), Exhibit F, Exhibit G (82 C to H) and Exhibit I (sample B).

(b) Use semi or monochlor type. In this case a wider choice of solvents including kerosene is applicable (See Exhibit I (sample E).

2. Polychlor Green

Satisfactory quality has been obtained by grinding with steel balls in mineral spirits, kerosene, xylol, toluol, synthetic methanol (99%) and isopropanol (99%). See Exhibit I,L & N.

If ceramic mills are used, an isopropanol-water mixture will give full strength. The grinding capacity of ceramic ball mills is doubtful for reasons previously discussed. See Exhibit M (A, D, & E).

The following are 1946 tank car prices per gallon.

Kerosene	$0.06 to .08	
Mineral Spirits (VM&P)	0.12	
Xylol	0.26	
Toluol	0.27	
Methanol (syn.)	0.24	
Ethanol 190 proof	0.54	No. 1 spec.
Isopropanol 99%	0.35	
" 91%	0.31	

The initial low cost of kerosene may be offset by the greater ease of recovering any of the other solvents.

The alcohols may be preferred because of ease in getting water pastes and slurries and the possibility of a softer, brighter dry product. See Soft Powder Finishing.

An unfavorable aspect of the use of anhydrous alcohols for Green CPC in conjunction with steel mills and steam distillation is found in the formation of azeotropic mixtures.

Azeotropic Compositions

Ethanol-water	4.5% water
Isopropanol-water	12.1% "
Methanol	none listed.

Toluol also forms an azeotropic at 13.5% water.

Further capacity studies of mineral spirits or kerosene and xylol should be made. Kerosene is now favored only because of its lower fire hazard and lower initial cost.

The amount of mill wear seems small with kerosene and mineral spirits. It may be worth while to investigate extraction of the crudes only. Certainly the filtration and washing of the crudes is much easier than that of the fine ground products. It could be employed provided iron contamination is negligible. No effect has been noted on tinctorial properties in the case of these solvents.

J. Ball Mill Capacity - See Exhibit N and Figs. 1 & 2

The only valid capacity studies were made with Green DW-5890 in kerosene. See Exhibit N. These data have been extrapolated to mills of larger diameter by use of information found in "A Manual of Ball Milling" compiled by the Engineering Department, Technical Division.

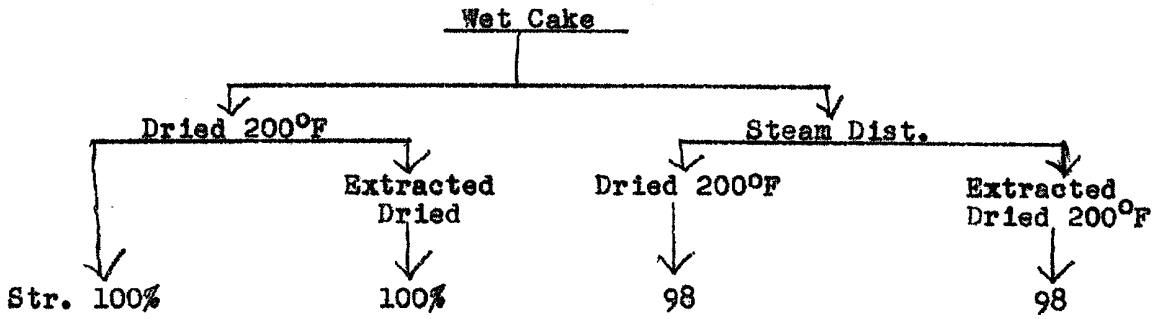
The material used, DW-5890, was essentially pure toner having been extracted after chlorination in $AlCl_3$-NaCl eutectic melt. The effect of by-products solids from solvent chlorination is not known. It is felt that any non-CPC solids present will merely dilute the charge, be ground along with the CPC and decrease millcapacity proportionately. On this account it may be economical to extract the crudes, particularly the blue, prior to grinding.

Similar capacity studies should be made on the blue when the type is established. So far the indications are that capacity will be of the same order.

K. Finishing Hydrocarbon Solvent Grind of DW-5890(Crude Green)

Exp. No. 1487-59, Mineral Spirits

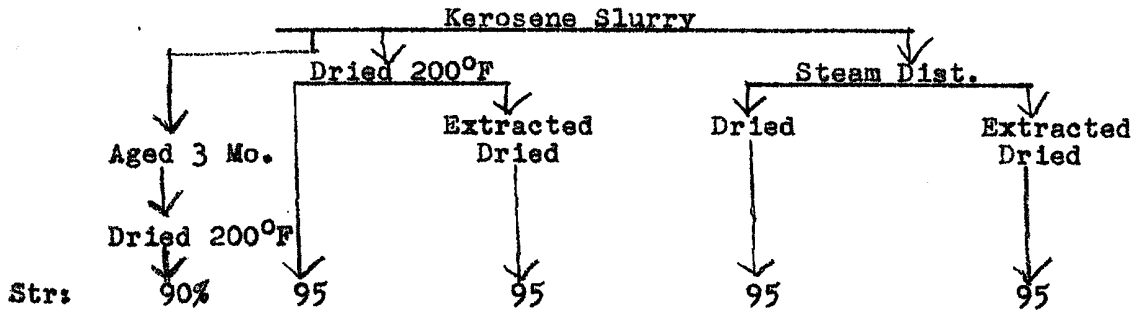
The above pigment was ground to full strength in mineral spirits. The mineral spirits slurry aged 35 days prior to filtering and treating according to the following scheme.



The pigment is not appreciably damaged tinctorially by the above treatment. Since the crude was essentially pure, no improvement is noted on extraction.

Exp. No. 1187-60, Kerosene

DW-5890 was ground to an average of 97% in Expts. 51, 52, 53. These were composited four days later and treated as follows without filtration.



The steps of steam distillation, extracting and drying appear safe. This was frequently verified in later experiments.

L. Soft Powder Finishing - Green CPC

The products ground in kerosene or mineral spirits, when finished by drying, or by steam distillation, extraction and drying, are unattractive in appearance. Although they are readily mulled to full strength, they are dark and granular and inferior saleswise to the standard. In Expt. No. 1187-79, it was found that by washing out the kerosene from the finished mill product with 99% isopropanol and then pouring the isopropanol slurry into water, small stable flocs were formed. These flocs persisted through the extraction step, making filtration much easier. The washed product dried to a soft bright green powder freed of lumps by very gentle crushing. No strength was lost.

The recovery of 99% isopropanol from water is not desirable. Investigation of kerosene removal by washing with the isopropanol-water azeotrope is suggested.

The formation of stable flocs is believed to be the effective factor in this process. A cheaper method of obtaining them may be possible.

This procedure has not been applied to Blue CPC.

M. The Szegvari Attritor

To obtain the maximum grinding effect obtainable by the combination of a large number of contacts per unit volume with a high impact force, a combination difficult to obtain in normal ball milling with high slurry concentrations, an apparatus was designed in which steel shot were stirred by wooden paddles. See Exhibit N, Fig. 1. (Expts No. 1187-70).

The agitation was surprisingly easy and the mill was run a week with only slight wear on the edges of the wooden paddles. The experiment was run in a 1/3 gal. mill and the grinding time was about 1/6 of that for normal operation of the mill.

Subsequently it was learned that such a device called the Szegvari Attritor was marketed by the Union Process Company, Akron, Ohio. They claim ten times the grinding rate as compared with normal small ball mills. Correspondence with them has disclosed that the #60 mill, approx. 60 gallons, the largest available, has a capacity equal to a 500 gal. mill. They also stated that the grinding rate does not vary with the Attritor size. From this it appears that ball mills having diameters greater than 4.5 ft. will have greater capacity per unit volume than the Attritor.

The Attritor consists of a ceramic container, small pebbles and a steel shaft agitator fitted with specially hardened arms which are readily replaceable. The device might have value:

(a) in experimental work where short cycles are desired to hasten results.

(b) by replacing the steel agitator with "micarta" or wood, the green CPC could be ground in alcohol-water slurries. Laboratory experiments disclosed that glass beads were nearly as effective as steel shot in this type of grinding. Our laboratory device of this type is referred to in the data tables as the "Ballitator".

Further evaluation of the Attritor is suggested because of the possibility of capacity advantage to be gained by using small pebbles or shot. See Exhibit N, Fig. 1 and accompanying discussion.

TABLES I AND II

EXPERIMENTAL SUMMARY AND SOLVENT GRINDING

The following pages contain a tabulated summary of all grinding experiments. Many of them are exploratory and have very little capacity significance. Those having more conclusive capacity data are given more fully elsewhere.

Explanation of Symbols in Table I

Column

Agents:	ocba	=	ortho chlor benzoic acid
	$SnCl_2PC$	=	Tin Phthalocyanine Dichloride The MD-958 signifies Orchem product. Others are Newark preparations.
Pigments:	DW-6076		Urea solvent CPC. Supposedly equivalent of DW-5889. Str. = 25% vs BT-172-D.
	1201-5A		Newark chlorine-free CPC ex. Urea-phthalic anhydride kerosene. About 65% CPC dry basis.
	DW-6091		Chlorine-free CPC salt milled.
	Crude PN		Orchem semi-chlor crude. No. 33246
	1191-7-B		Newark CPC ammon. extracted.
	DW-5890		Standard Orchem crude green. Str. = 37% vs GT-486-D
Balls:	g =		6 mm glass beads.
	s =		2-3 mm steel shot
	S 3/8" etc.		Steel balls of indicated dia. in inches.
	P = 1/2"		Porox balls.
Miscl.:	"Ballitator"	=	grinding by stirring ball charge in vertical vessel.

TABLE I

EXPERIMENTAL SUMMARY - SOLVENT GRINDING BLUE CPC

(Strength & tinctorial properties rated vs. BT-172-D)

SOLVENT	AGENTS	PIGMENT	GRINDING			TESTING				EXPT. NO. 1187-	
			Mill Dia.	Balls	Hours	Dried Str.	Dried Shade	Extracted Str.	Extracted Shade		
Water		DW-5889	4"	g	245	65	dull			33	pre-extracted
	NH_3,NH_4Cl	"	2"	g	70	60		60		36	
	" "	"	2"	s	70			50		37	
	NH_3,Am.Napht.	"	6"	s	230	55	v.dull			40	
	7% H_2SO_4	"	6"	s	161	50		55		47	
	NH_3	D-6091	2-1/2"	s	88	50	dull				
	-	DW-5889	4"	s	231	55	s.dull			66	K
Min.Spirits		DW-5889	3"	g	205	74				23	See Exhibit A
					298	68	grn.			23	
			4.75"	s	89	71				26A	
	NaCl(4 pts)	"	4.75"	S 1/2"	431	70	grn.	70	grn.	34	
		"	6"	s	42	70				39A	
					230	75	sl.grn.	75	sl.grn.	39B	
		D-6091	2-1/2"	s	88	75	sl.grn.			$64A_1$	Orig.str. 108%
		BT-172-D	2-1/2"	none	400	90				42	some cryst. growth
Kerosene	H_3BO_3	DW-5889	4.75"	S 1/2"	137	40	grn.	40		56	
	-	"	4.75"	S 3/8"	256	55				65D	See Exhibit B
	5% ocba	"	4.75"	S 3/8"	256	60	sl.grn.			65E	
	15% $SnCl_2PC$	DW-6076	4.75"	s	109	78	sl.grn.			72	SnPC= 1195-1
	10% $SnCl_2PC$	"	3"	S 1/4"	232	69				75A	SnPC= 1195-13,14
	10% $SnCl_2PC$	"	3"	S 1/4"	228	60	sl.grn.	60	s.grn.	77A	SnPC=Orchem MD-958
	-	1201-5A	4.75"	S 3/8"	325	55		80	s.grn.	82A	
	10% SnCl PC	"	4.75"	S 3/8"	325	55		75	s.grn.	82B	SnPC=MD-958
	-	Crude PN	4.75"	S 3/8"	316	80		80		89E	
		D-6091	3"	s	177	90		75		64B	Orig.Str. 108

TABLE I Cont'd.

SOLVENT	AGENTS	PIGMENT	GRINDING Mill Dia.	Balls	Hours	TESTING Dried Str.	Dried Shade	Extracted Str.	Extracted Shade	EXPT. NO. 1187-	
Methanol	$SnCl_2$PC MD-958	DW-6076	3"	S 1/4"	228	75		90	vs.grn.	77D	
	-	DW-5889	4.75"	S 3/8"	316	70		80	grn.	89B	
	$SnCl_2$PC MD-958	"	4.75"	S 3/8"	316	65		75	grn.	89C	
	-	PN Crude 33246	4.75"	S 3/8"		80		80		89E	
Alcohol 3A		D-6091	3"	s	177	125		130		64F	Dried alcohol
	5% HOH	"	3"	s	177	125		130		64I	
	-	1191-7-B1	3"	s	166	103		115	vvs grn	68	Newark made CPC
	-	1201-5A	4.75"	S 3/8"	305	55	grn.	82		82G	
	10% $SnCl_2$PC MD-958	1201-5A	4.75"	S 3/8"	305	55	grn.	82		82H	
	-	(ext)1201-5A	7.5"	S 3/8"	287	85	grn.	90	vvs.grn	88	Dehydrated Alc
Alcohol 23A	-	DW-5889	6"	s	74	78	sl.grn	90	sl.grn.	49B	
	33% water	"	4"	s	231+	82	sl.grn.	105	sl.grn.	66L	See Exhibit E
	-	"	4.75"	S 3/8"	256	60		86	sl.grn.	65G	
	ocba 5%	"	4.75"	S 3/8"	"	65				65H	
Isopropanol (99%)	-	DW-6076	4.75"	S 1/2"	260	50				76B	
	25% H_2O	"	4.75"	S 1/2"	260	53				76C	
	- Pulp-	1201-5A	4.75"	S 3/8"	325	60				82C	
	$SnCl_2$PC MD-958 "	1201-5A	4.75"	S 3/8"	325	60	grn.	90	grn.	82D	
	- Dry	1201-5A	4.75"	S 3/8"	325	60		90	grn.	82E	
	$SnCl_2$PC MD-958 "	1201-5A	4.75"	S 3/8"	325	60	grn.	85	grn.	82F	
	"	DW-6076	3 1/4"	S 1/4"	228			75		77C	
C Cl_4	-	DW-5889	6"	s	111	90	sl.grn	90	sl.grn	38	
	-	DW-6076	4.75"	5 3/8"	256	60				65F	
	-	DW-5889	4.75"	5 3/8"	256	70	sl.grn.			65A	thick slurry
	1% ocba	"	4.75"	5 3/8"	256	67	"			65B	" "
	5% ocba	"	4.75"	5 3/8"	256	67	"			65C	" "
Trichlor Bz.	-	DW-5889	6"	s	230	70	s.grn.			41	

TABLE II

SOLVENT	AGENTS	PIGMENT	GRINDING			TESTING				EXPT. NO. 1187-	
			Mill Dia.	Balls	Hours	Dried Str.	Dried Shade	Extracted Str.	Extracted Shade		
Water	S.S.G.	DW-5890	4"	P	16	37	dull			3,4,84	
	SSG NH_3,$CaSO_4$	"	4"	S 3/8"	40			37	dull	5	
	" NH_3 "	"	3"	g	271	40	dull			24	
	" Tartaric	"	3"	g	271	40	"			25	
	SSG, NH_3	"	2 1/2"	s	16	v.blue				6	
	SSG	"	4"	Cu	46	40	blue			55	
	Daxad #11	"	4"	P	66	37				8	
	Aerosol OT	"	4"	P	66	37				8	
	Fixanol	"	4"	P	66	37				8	
	Sod. m-silic	"	4"	P	66	40				8	
	Fixanol, H_2SO_4	"	2"	g	50	35				30	
	H_2SO_4 40%		-	g	98	40	dull			81	Ballitator
	None		4"	P	66	37	"			8	
Mineral Spirits	-	DW-5890	2"	g	130	85				12	
		"	4.75"	P	213	75				13	
		"	4.75"	SM	213	95	bright			14	
		"	4.75"	s	206	100				18	
		"	4.75"	S 1/2"	206	96				20	
	1.3% oleic acid	"	4.75"	s	206	103				19	
	"	"	4.75"	S 1/2"	206	100				21	
	-	"	4.75	g	206	91				22	
	-	GT-486-D	2"	s	140	125				27	
					277	125				27	
					469	115				27	
	-	DW-5890	4.75"	P	499	100				31	
	-	"	6"	s	376	108	s.yel.	110	s.yel.	32	
		"	3"	s	162	95				44	
		"	4"	s	162	100				45	oval mill
		"	4.75"	Cu	85	86	br.s.yel.			62	See Exp. 55

TABLE II Cont'd.

SOLVENT	AGENTS	PIGMENT	GRINDING			TESTING Dried		TESTING Extracted		EXPT. NO. 1187-	
			Mill Dia.	Balls	Hours	Str.	Shade	Str.	Shade		
Kerosene	-	DW-5890	3"	s	160	95	br.s.yel.			51	
		"	4"	s	160	98	"			52	
		"	6"	s	160	98	"			53	
		"	4.75"	s	279	95	"			58G	
		"		S 3/8"	279	100	"			58G	
		"		S 1/2"	279	90+	"			58H	
		"	-	g	46	86	"			69	Ballitator
		"	-	s	118	100	"	100	br.yel	69	
		"	-	s	42	97	"			70	Ballitator
		"	4.75"	S 3/8"	Study of slurry concentration					73	
		"	12"	S 3/8"	78	100	br.s.yel			78	
		"	12"	S 5/32	101	98	"			79	
		"	4.75"	S 1/2"	140	90	"			80	Single layer balls
		"	-	s	126	100				86	Ballitator
		"	4.75"	S 3/8"	268	100		100	bri.	89	
Methanol (Syn.99%)		DW-5890	5 5/8"	s	34	50	dirty	90	bri.	83	Ballitator
		"	4.75"	S 3/8"	268	105	"	105	bri.	89A	
Alcohol 3A		"		s	49	90		102	bri. s.yel.	71	Ballitator
Alcohol 23A		DW-5890	4"	P	51	45				10	
	Whiting	"	4"	P	51	50				10	
	Na_2SO_4	"	4"	P	40	30				15	
Isopropanol (99%)	25% H_2O	"	4.75"	S 1/2"	446	95		105	br.s.y.	76A	
	25% H_2O	"	4.75"	S 1/2"	200	?	blue	?	blue	76D	
		"	4.75"	g	446	95	br.s.y.	102	br.s.y.	76E	
		"		g	55	83				87	Ballitator
$C Cl_4$	-	DW-5890	2 1/2"	g	85	80				11	
		"	4.75"	S 3/8"	279	95				58I	
		"	4.75"	S 3/8"	210	86	hard			74C	
Xylol	-	DW-5890	4.75"	S 3/8"	210	105	soft			74A	
Toluol	-	DW-5890	4.75"	3 3/8"	210	100	soft			74B	

APPENDIX I

A. EXHIBITS A to I

Pertaining to Grinding of

CPC BLUE

EXHIBIT A

BEHAVIOR OF VARIOUS TYPES OF BLUE IN MINERAL SPIRITS

EXPT. NO. 1187-46

OBJECT: To note the relation between type of CPC and strength development in mineral spirits in the light of known crystal growth phenomenon.

GRINDING: Pint jars, steel shot, 20 gm. CPC, 110 cc H-287

	A	B	C	D	E	F
PIGMENT:	BT-172-D semi-chlor ex phthalo-nitrile	DW-5889 crude Urea-solvent	D-5315 crude Semi-chlor via PN	D-5316 crude Mono-chlor via PN	D-6094 BX Paste Mono-chlor dried 200°F	D-6091 Salt milled Urea solvent
HRS.	Strength vs Standard BT-172-D					
0	100	25	39	41	50	108
119	100	75	90	68	50	75
213	90	75	90	58	50	75
380	95	62	95	78	60	80

EXHIBIT B

COMPARISON OF SOLVENTS FOR GRINDING DW-5889

EXPT. NO. 1187-54

OBJECT: To make a direct comparison of solvent.

GRINDING: 1/2 pint jars, 500 g. steel shot, 10 g. CPC, 55 cc solvent.

	Strength vs BT-172-D		
HRS:	50	141	207
A. Mineral Spirits	70	75	72
B. Alcohol 3A	80	82	85
C. Iso Amyl Acetate	75	85	85
D. Dioxane	75	85	90
E. Mono ethanolamine	50	56	50
F. Morpholine	58	72	72
G. Acetone	82	86	85
H. Kerosene (Deo Base)	58	75	75
I. Benzol	70	82	82
J. Xylene	60	75	75

CONCLUSIONS: Alcohol appears the most desirable solvent for grinding solvent sensitive CPC. 3A is ethanol plus 5% methanol. Samples were too small to get tests on extracted products.
See Exhibits C, E and F.

EXHIBIT C

EFFECT OF SOLVENT GRINDING ON HIGH STRENGTH SALT MILLED CPC.

EXPT. NO. 1187-64

OBJECT: To subject D-6091, a salt milled urea solvent process type CPC, of the same type as DW-5889 crude, to solvent grinding action. It is postulated that if solvent does not produce crystal growth no strength loss will occur.

MILLS: 500 cc jars, 3 1/8" O.D. turned at 135 R.P.M.

BALLS: Steel shot. 1165 gms.

VOL. SOLVENT: 120 cc. 60 cc added later when thickening occurred.

D-6091 - 20 gms. - Orig. Str. = 108% vs BT-172-D

GRINDING TIME:	88	134	177 hrs.'	Ext.
Ageing after Grinding			5 days	11 days
Solvent	Strength versus BT-172-D			
A. Mineral Spirits	78	75	85	-
B. Kerosene	78	82	90	75
C. C Cl_4	90	90	90	-
D. Perchlorethylene	72	78	78	-
E. Acetone, dried	90	85	95	80
F. Alc. 3A, dried	120	130	125	130
G. Turpentine	70	86	105	67
H. Water + NH OH	50	50	50	-
I. Alc. 3A + 5% HOH	120	120	125	130
J. Mono ehtanolamine	85	82	75	-

CONCLUSIONS:

1. 3A alcohol. (methanol denatured ethanol) appears the best candidate for grinding CPC.
2. The amount of water which can be tolerated is an important feature. See Exhibit E.

EXHIBIT D

ORTHO CHLOR BENZOIC ACID AS A GRINDING AID.

EXPT. NO. 1187-65

OBJECT: Since o-chlor benzoic acid has been found to decrease flocculation of CPC in paint systems, it may have dispersing action in solvent grinding. The slurries used here were deliberately made rather thick to show any dispersing of the o.c.b.a. treated samples.

MILLS: 1/3 gal. Porc. containing 2500 g. 3/8" steel balls.

CHARGE: 100 g. DW-5889 and 300 cc solvent.

	Strength versus BT-172-D			
GRINDING TIME:	48	90	186	256 Hrs.
Solvent				
A. C Cl_4	45	55	60	70
B. C Cl_4 + 1 gm. ocba	45	57	60	67
C. C Cl_4 + 5 gm. ocba	45	50	55	67
D. Kerosene	45	50	55	55
E. Kerosene + 5 g. ocba	45	50	60	60
F. C Cl_4 (DW-6076 used)	45	47	55	60
G. 23A Alcohol	45	55	60	60*
H. 23A + 5 g. ocba	45	55	60	65

*Residue of G on steam distillation and extraction = 86% str.

CONCLUSIONS:
1. ocba does not aid grinding.
2. Since additional solvent was required after 90 hrs. it appears that a higher solvent:pigment ratio will be required for the blue than for the green.

EXHIBIT E

FURTHER TRIALS WITH 23A ALCOHOL AND ORTHO CHLOR BENZOIC ACID.

EXPT. NO. 1187-66

MILLS: 1 qt. porcelain, containing 700 g. 1/2" Porox Balls, except K & L which had 2325 g. steel shot (eq. vol.)

PIGMENT: DW-5889, 50 gms. per mill.

				Strength versus BT-172-D			
	23A	Water	ocba	Hrs: 66	113	231	359*
A.	300	-	0.5 gm.	45	45	55	
B.	200	100	0.5	45	47	60	
C.	150	150	0.5	45	50	60	
D.	100	200	0.5	45	50	60	
E.	300	-	2.5	40	45	50	
F.	200	100	2.5	40	45	50	
G.	150	150	2.5	40	45	55	
H.	100	200	2.5	45	47	60	
I.	300	-	0.0	45	47	58	
J.	100	200	0.0	40	45	53	
K.	000	300	0.0	45	53	55	
L.	200	100	0.0	70	78	82	75*

*After 231 hrs. L was diluted with more solvent solution and ground in Ballitator. The product at 359 hrs. was dirty green but on extraction cleaned up to 105%, sl. green.

EXHIBIT F

ALCOHOL GRIND OF NEWARK MADE CPC

EXPT. NO. 1187-68

OBJECT: To high spot grinding characteristics of freshly prepared CPC made by urea solvent process. Sample used was a dry ammonia extracted crude coded 1191-7-B_1

MILL: 500 cc jar, 3 1/8" O.D. containing 250 cc steel shot.

CHARGE: 20 gm. 1191-7-B_1
120 cc 3A Alcohol, dried with soluble anhydrite.*

Strength versus BT-172-D

43 hrs.	90%	
113 "	103	sl. dull
166 "	103	sl. dull
Extracted	115	equal or vvs green.

*It is suspected that the $CaSO_4$ used did not remove the water. Since strength development in Exhibit H was not obtained the presence of 5 to 10% of water may be desired.

EXHIBIT G

EVALUATION OF TIN PHTHALOCYANINE DICHLORIDE

EXPT. 1187-77

OBJECT: Addition of $SnCl_2PC$ to grind as a crystal growth preventive to permit grinding to full strength in hydrocarbon solvents.

PROCEDURE: Mills - 500 cc jars, containing 1 kg. 1/4" steel balls.
Charge- 300 cc solvent, 27 g. DW-6076 and 3 g. MD-958.

Strength versus ET-172-D

Hrs.	Solvent:	A Kerosene	B Xylol	C Isopropanol	D Methanol
47		50	53	50	53
127		62	60	64	75
180		60	53	64	60
228		62		70 s.grn.	75 grn.
Extracted Residue		60 grn.	60 grn.	75	90

A and B were steam distilled before extraction

C and D were poured into water, filtered, before extraction.

There is some indication that DW-6076 is slightly harder to grind than DW-5889. On acid pasting and flushing it is 105% while DW-5889 is somewhat higher.

EXHIBIT G. Cont'd.

EXPT. NO. 1187-82

OBJECT: To observe grinding of Newark made CPC in several solvents with and without 10% of Orchem Tin Phthalocyanine Dichloride.

PROCEDURE: Mills - 1/3 gal. containing 2500 gm. 3/8" steel balls.
Charge: 40 g. CPC - crude (65% CPC) 1201-5A on a dry basis.
4 g. MD-958
Solvent added to give total of 175 cc.

The kerosene pulp used was 69% total solids.

	A	B	C	D	E	F	G	H
1201-5A Pulp, gms.	58	52	58	52	-	-	58	52
1201-5A Dry crude	-	-	-	-	40	36	-	-
MD-958, gms.	-	4	-	4	-	4	-	4
Kerosene, cc	153	150	-	-	-	-	-	-
Isopropanol 99%, cc	-	-	153	150	175	175	-	-
Alcohol 3A, cc	-	-	-	-	-	-	153	150

Strength vs BT-172-D

Hrs.							Hrs.		
97	45	42	51	43	45	45			
94	53	53	60	55	55	55	67	50	50
161	65	55	64	60	60	60	143	53	53
229	56	53	60	60	62	60	239	60	60
325							305	55	55
Extracted	80 g	75 g	95 g	90 g	90 g	85 g		82 g	82 g

EXHIBIT H

PREPARATION OF FULL STRENGTH ALCOHOL GROUND NEWARK CPC.

EXPT. NO. 1187-88

OBJECT: To prepare a fair sized sample of Newark CPC for studies in solvent stabilization.

PROCEDURE: Anhydrous 3A alcohol was prepared by refluxing with and distilling from quick lime. In this case the last traces of water were not removed.

The CPC used was received as a kerosene pulp, 1201-5A, 69% solids and 45% CPC. It was dried at 200°F and extracted with 7% H_2SO_4 then with aqueous ammonia and dried. Yields verified the above analyses.

A one gallon mill containing 11.8 kg of 3/8" steel balls (50% load) was charged with 276 gms. of the dry CPC and 750 cc of the prepared alcohol.

Grinding Time, Hrs.	Strength vs ET-172-D	
67.5	75	
119	82	200 cc dry 3A added
287	85	
287 extracted	90	greenish
325 "	85	"

Masstone rather light but not dull. The presence of water in the grind may effect masstone.

See Exhibit F.

EXHIBIT I

SOLVENT GRINDING WITH METHANOL.

EXPT. NO.1187-89

OBJECT: To evaluate synthetic methanol,99%, as a solvent for grinding both green and blue. Two kerosene grinds are included as controls.

PROCEDURE: Mill: 1/3 gal. porcelain with 2500 g of 3/8" steel balls. 300 cc solvent, 75 g. pigment. E was included 24 hrs. after start of grind.

	A	B	C	D	E
PIGMENT:	DW-5890	DW-5889	DW-5889	DW-5890	Crude E, PN (33246)
SOLVENT:	Methanol	Methanol	Methanol	Kerosene	Kerosene
$SnCl_2PC$, MD-958	-	-	10 g	-	-

GRINDING TIME:

HRS.	Strength vs BT-172-D or GT-486-D				Hrs.	
96	86	60	55 gr.	75	72	65
146	95	60	62 "	90	122	75
189	100	63	63 "	100	165	75
268	105 d	70	65 "	100	144	86
316		70	65 "		282	82
Extracted:	105	80 grn.	75 "	100		80

d = dirty.

Methanol shows promise of somewhat faster grinding of polychlor CPC than kerosene. Although contamination with iron occurs it is removed on extraction.

B EXHIBITS

J to N

PERTAINING TO GRINDING OF

POLYCHLOR CPC GREEN

EXHIBIT J

EFFECT OF VISCOSITY OF LIQUID, SLURRY CONC. AND BALL SIZE

EXPT. 1187-58

This experiment is a test of the idea that a low viscosity liquid gives faster grinding. At the same time it is a quick survey of mill loading conditions to indicate the probable ranges for ball mill capacity studies.

Mills 1/3 gal. porcelain. 4.75" I.D.

Balls: 2500 g. steel

Solvent: 200 cc as indicated.

					Strength vs GT-486-D		
	Ball Size	Solvent	DW-5890	Hrs:	65	135	279
A	3/8"	Kerosene	50 gms.		85	90	100
B	3/8"	"	60		82	90	100
C	3/8"	"	75		80	90	100
D	3/8"	"	100		67	87	98
E	3/8"	Nujol	50		47	50	50
F	3/8"	"	75		55	56	55
G	1/8"	Kerosene	75		78	85	95
H	1/2"	"	75		63	82	90
I	3/8"	$C Cl_4$	75		69	85	95

CONCLUSIONS:

1. Conditions of D give highest rate of grinding in terms of gms. pigment ground per hour. See calculation of relative rates in Monthly Report 1/30/46.

2. More viscous liquid of same chemical type gives slower grinding probably due to protection of small particles by the viscous liquid film.

3. 3/8" ball size seems most efficient.

EXHIBIT K

BALL MILLING DW-5890 IN KEROSENE

EXPT.NO. 1187-73

OBJECT: A preliminary study of mill loading vs capacity.

PROCEDURE: Mills 1/3 gal. mill containing 2000 g. 3/8" steel balls, rotation 47% of critical speed. Charge made up with kerosene and DW-5890.

	A	B	C	D
DW-5890, gms.	100	100	125	150
Kerosene, cc	300	500	500	500
Slurry conc. g/l	280	180	220	254

Tinting Strength vs GT-486-D

HRS:				
46	70	75	65	60
88	82	82	75	75
159	90	88	82	80
207	95	95	95	86

Grinding rates are calculated by the formula:

gms. pigment/hrs. x increase in str.

and tabulated below for the different periods.

HRS.	A	B	C	D
46	72	82.6	76	75
88	51	51	54	65
159	33	32	35	46
207	28	28	35	35.5

CONCLUSION:

Unfortunately the grinds were not carried to 100% Str. However, since D rate is dropping off rapidly at the end, the C slurry is judged best and serves as a guide for further capacity studies. These results relate only to slurry concentration and may not be translated to larger mills with lifter bars.

EXHIBIT L

COMPARISON OF SOLVENTS FOR GRINDING DW-5890

EXPT. NO. 1187-74

OBJECT: To compare solvents more readily removed by steam distillation with kerosene.

PROCEDURE: Mill: 1/3 gal. porcelain containing 2000 g. 3/8" steel balls, 100 g. DW-5890, and 500 cc solvent.

	A	B	C	D
Solvent:	Xylol	Toluol	C Cl_4	Kerosene
HRS.	Tinting Str. vs. GT-486-D			
47	69	67	56	69
115	90	88	75	86
163	97	97	82	90
210	105	100	86	92

The final slurries were dried at 200°F.
E was hard. A & B were at least as soft as D.

CONCLUSIONS:

Xylol or Toluol appear to give considerable capacity advantage over kerosene.

Further comparison with mineral spirits and methanol (See Exhibit I) should be made.

EXHIBIT M

EVALUATION OF ISOPROPANOL

EXPT.NO. 1187-76

1/3 gal. mills, 2000 g. 1/2" steel balls or 760 g. glass beads, 100 g. pigment.

	A	B	C	D	E
Ball charge	Steel	Steel	Steel	Steel	Glass
Isopropanol, 99%, cc	500	500	400	400	400
Water			100	100	100
Pigment, DWP	5890	6076	6076	5890	5890
HRS.	% Strength vs. GT-486-D				
45	60	36	39	36	50
93	69	45	43	blue	60
212	82	50	53	v.blue	75
260	90	50	53	"	80
372	90				87
446	95				95
Extracted:	105	53 dull	60 dull		102

EXHIBIT N

BALL MILL CAPACITY FOR GRINDING DW-5890 IN KEROSENE

EXPT. NO. 1187-78

OBJECT: To make a high spot mill capacity test in a 12" dia. mill equipped with lifter bars.

PROCEDURE: Mill: 12" dia. by 6" steel mill at Experimental Station, Engineering Department Laboratory fitted with 10 1/4" bars.

Ball charge used: 47.25 lbs. 3/8" steel
Materials: 1.125 lbs. (510 gms.) DW-5890
1.14 liters kerosene
.3 liter added at 20 hrs.
.3 liter more at 40 hrs.

The mill was operated almost continuously and small progress samples withdrawn for immediate test. The addition of more solvent was governed by the sound of the mill. It was thus judged that the run was made with a slurry of close to optimum concentration. Maximum mill temperature was 40-45°C.

HRS.	STR.
5	55
20	88
40	93
60	98
78	100

This operation is compared graphically with small mill grinds in Exh. N, Fig. 1 and the mill conditions tabulated.

EXHIBIT N Cont'd.

Extrapolation of Data of Expt. 1187-78 to Large Mills.

By assuming the mill conditions of the Expt. calculations for larger diameter mills are shown below. The basic assumptions taken from known ball milling practice are:

1. Material capacity proportional to D^2
2. Grinding capacity proportional to the power input.
3. Power input proportional to $D^{2.5}$
4. Grinding cycle proportional to $D^{0.5}$

The following quantities are given for one foot of mill length for easy conversion to mill of any length.

Mill Dia. ft.	1	2	3.5	4	6	8
Ball charge, lbs.	94.5	378	1150	1512	3400	6050
Pigment, lbs.	2.25	9	27.4	36.1	81	144
Cycle, hrs.	80	57	42.6	40	32.7	28.4
Loading, etc.	2	2	2	2	2	2
Total Cycle	82	59	44.6	42	34.7	30.4
# Pig/24 hrs.	1.3	3.67	14.85	20.8	56	113

This bold extrapolation is shown graphically in Exhibit N, Fig.2

EXPLANATION OF EXHIBIT N, FIG. 1

Legend

⋮	Expt. 1187-27	small mineral spirits grind of GT-486-D using steel shot. This is included to show that ball milling has inherent characteristics suitable for the degelopment of high strength. In this case ball milling is super-imposed upon acid pasting.
⊖	Expt. 1187-70	Kerosene grind of DW-5890 in Ballitator with steel shot.
x	Expt. 1187-78	Kerosene grind of DW-5890 in 1 ft. dia. mill at the Experimental Station.
⊡	Expt. 1187-79	Same as 78 but using steel shot and more solvent.
◈	Expt. 1187-58C	A fairly comparable grind in 1/3 gal. mill. See Exhibit J.
*		This point represents theoretical conversion of the 279 hr. ◈ cycle to the conditions of Expt. 78. Corrections are made for mill dia., mill speed, and ball:pigment ratio. The remaining discrepancy is thought due to slipping of the ball charge in the porcelain mill.

MILL CONDITIONS FOR FIG. 1

	⊙	x	⊡	◇
Expt. No. 1187-	70	78	79	58C
Mill dia., inches	4.75	12	12	4.75
% Crit. speed	-	66	66	47
Ball dia., inches (steel)	1/8	3/8	5/32	3/8
Ball Load %	70	40	40	50
M:V vol.	1:1	1:1	2:1	1:1
Ball:Pig. wgt.	33	42	42	33
Kerosene:Pig. cc/gm.	4.15	3.9	6.5	4.77
Lbs.Pig./cu.ft. mill space	4.75	2.89	2.89	3.36
Grinding rate in #/cu.ft./hr. at 100% Str.	.091	.037	.025	.012

REMARKS:

The sharp breaks in the 78 and 79 curves come at the point where thickening occurred and in each case about 20% additional solvent was added at this time.

Further evaluation with semi-works mills may show a shorter cycle and a major increase in capacity by using thicker slurries and larger balls.

If the grinding rate in terms of #pig. ground/hr./cu.ft. of total mill space (last line) increases in a ball mill with the square root of the diameter, it may be calculated that a 73 inch mill is required to equal the Ballitator rate.

EXHIBIT N FIG. 1

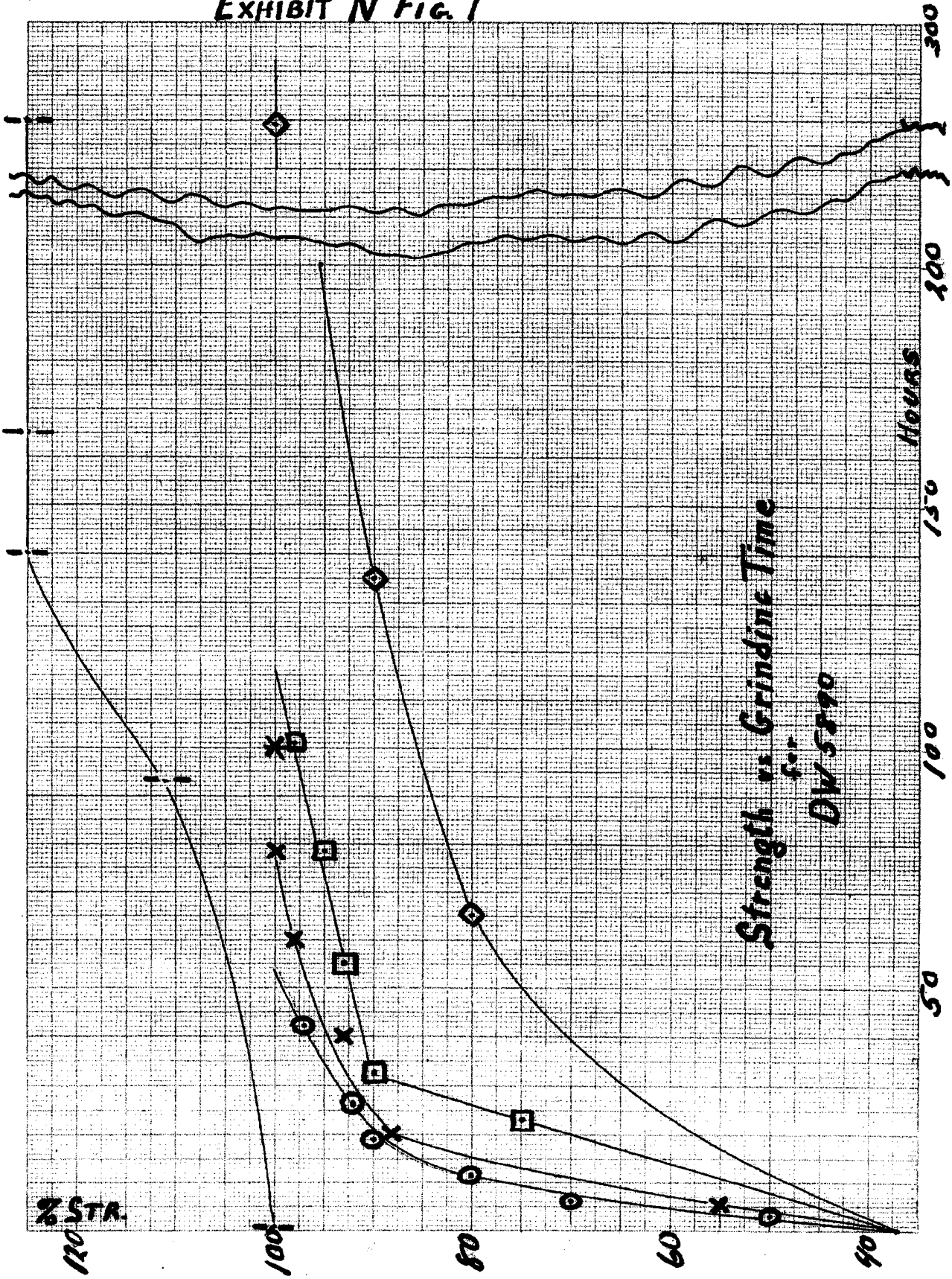


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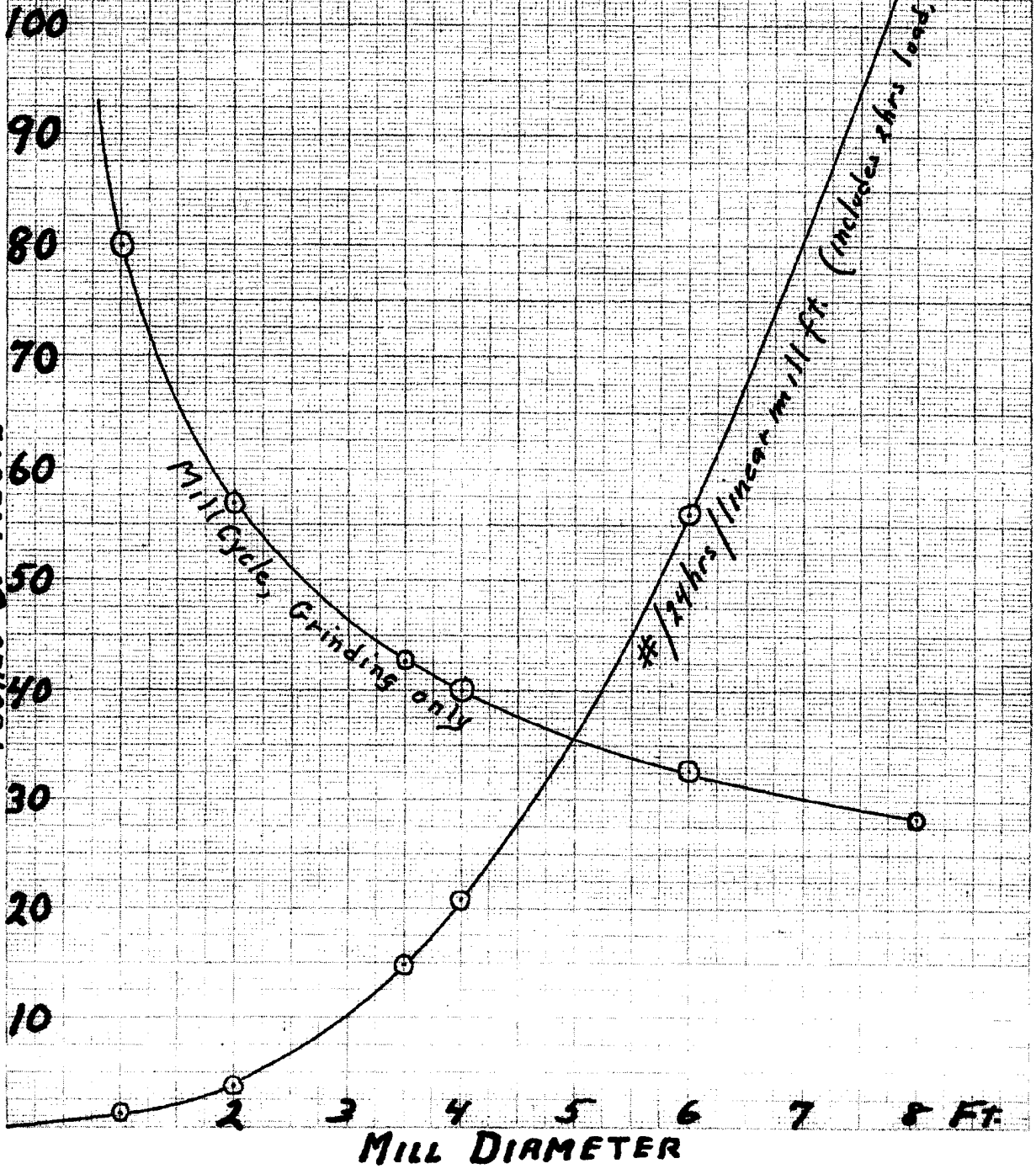
EXHIBIT N, FIG 2
CALCULATED BALL MILL CAPACITIES
BASED ON EXP NO. 1187-78
DW 5890 IN KEROSENE



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