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CHEMICAL DIVISION - COLORS

PIGMENT COLOR RESEARCH REPORT
Progress Report

HF MILLING OF PHTHALOCYANINE PIGMENTS II

STUDIES IN WATER

Period Covered **MARCH, 1950 to APRIL 1, 1953.**

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Progress Report

HF MILLING OF PHTHALOCYANINE PIGMENTS II

STUDIES IN WATER.

MARCH, 1950 to APRIL 1, 1953.

CHARGE: A-II-C-261, 297

SUBMITTED BY: A. F. Stratton 7/16/53 A. F. STRATTON   DATE SUBMITTED: June 15, 1953

APPROVED BY: J H Cooper 7/17/53 J. H. COOPER 7/6/53   DATE ISSUED: July 27, 1953

INTRODUCTION:

It was one of the original objectives of the phthalocyanine research at Newark to condition the product for pigmentary use by milling in water. Research reports KN-46-19 and KN-46-55 summarize the discouraging results of that early work. In general, any phthalocyanine pigments, when ground in a ball mill with water alone, did not increase in strength and frequently showed a loss in strength. On the other hand, a few dispersing agents, notably ammonium naphthenate, did prevent any loss in strength and, in some cases, promoted a significant amount of particle size reduction. However, a rather extensive study failed to give results approaching the desired goal, and the method of milling in water was abandoned in favor of the use of organic solvents, which work ultimately culminated in the acetone milling process now in use at Newport.

More recently, Research Report KN-52-13 has described a new process ("HF" milling) for milling in acetone wherein a mixture of pigment, acetone and a finely divided inorganic salt, such as sodium chloride or borax, was milled in a stirred mill with a high energy input. During the course of this work, attention was turned to the use of water-acetone mixtures and ultimately, again, to the use of water alone. As in the earlier work, water alone in the presence of the finely divided inorganic salt was not an effective grinding medium. However, certain dispersing agents were shown to promote effective particle size reduction in such a system and the studies covered in this report followed.

SUMMARY:

A process for the particle size reduction of phthalocyanine pigments by milling in water with selected dispersing agents has been developed in the laboratory and carried through into equipment suitable for full scale plant operation. In this process, a vessel of 100 gallon working capacity and powered with a 30 H.P. motor is capable of milling about 750-1,000 lbs. of pigment per day. This process has been proved for both CPC-LB and for polychloro CPC Green, and is being used for plant manufacture of specific products at Newark.

The end products of this process are two dispersed pastes coded BT-352-P and GT-735-P, which are capable of being converted in the Newark plant to a number of products for sale. The products include two standardized dispersed pastes (BT-353-P and GT-732-P), two dry colors designed for use in latex dispersed paints (BP-358-D and GP-740-D), and a substantial amount of BT-352-P has been converted to the linoleum lake BL-288-D.

Tentative processes have been worked out for the manufacture of water dispersible dry colors comparable to the W.D. colors now purchased for resale from Orchem. Products under consideration are the regular grades containing dextrin, and also dextrin-free products suitable for coloring cement.

Substantial progress has been made in the preparation of dry toners comparable to the standards now offered for sale, and in the conversion of such products to other standard phthalocyanine colors. The best laboratory products in this work have approached the desired strength, but these results have not been consistent and limited studies in the semi-works have left much to be desired. An incidental result of this last work has been, that, one of the dispersing agents used, though not the most desirable one, has given a substantially flocculation resistant toner.

PATENT STATUS:

Memorandum Report RLM-53-7 summarizes the prior art on particle size reduction of phthalocyanines and related pigments. Although the art is quite close, it is believed that patentable features exist in the new process, and it was recommended that a patent application be prepared.

It should be noted that considerable work has been done by Orchem at Jackson Laboratory, substantially parallel to the work at Newark, but they have emphasized the use of finely divided sand as the grinding agent instead of the finely divided inorganic salts. They also propose a patent application on their modification of the process.

DESCRIPTION OF PROCESS AND EQUIPMENT:

Essentially, the HF process involves the application of an intensive shearing action to a suspension in a liquid of a mixture of the pigment and a finely divided inert solid. In the modifications described in this report, the finely divided inert solid is a water soluble inorganic salt, preferably borax, and the liquid is a saturated aqueous solution of that salt. The liquid also contains in solution a dispersing agent, which is preferably the polymerized condensation product of naphthalene sulfonic acid with formaldehyde, variously sold under such trade names as "Blancol" and "Daxad". When the desired particle size is achieved as the result of the intensive shearing action, the insoluble portion of the inorganic salt is separated from the pigment suspension by decantation and the pigment is isolated by flocculation in acid medium, filtration and washing. For most purposes, it is preferable to retain the pigment in the aqueous paste form.

The equipment used is substantially the same as that described in considerable detail in KN-52-13. However, for the plant development studies and the present plant operation, a 100 gallon prefabricated Cowles Dissolver was obtained and has been quite satisfactory for the purpose. The tank has an actual capacity of 130 gallons and a diameter of about 32 inches. The agitation is provided by a 30 H.P. motor operating at about 900 r.p.m. Various types of discs have been used for the shearing action, but the major part of the work has been done with a 22 inch smooth disc.

One feature, which has made this process economically attractive on a commercial scale, has been a means for separating the undissolved borax and recovering it for subsequent use in a later operation. Substantial dilution (3-4 times the original volume) with cold water permits the borax to settle rapidly, and a Dorr rake classifier has proved an effective means for separating the crystalline borax from the dispersed pigment suspension. The recovered borax, in the form of a sludge of about 65% solids content, is used in a subsequent charge with additional new borax to make up the required total. The settling process also serves to remove from the dispersed pigment any over-size unground pigment. Generally, this is an advantage to the operation; but it has, on occasion, caused difficulty when there has been a substantial amount of hard particles in the crude pigment, because the unground pigment tends to accumulate in the borax sludge and reduce the effectiveness of the over-all operation. This has never been significant in operations with CPC Blue LB, but it is frequently a source of some trouble with CPC Green.

The use of the Dorr classifier for separating the borax has been quite successful on the plant scale. Nevertheless, careful observation leads to the conclusion that more effective separation of the borax could be obtained, if there were an opportunity for a brief period of settling without any agitation in the system. There are available types of classifiers which would meet this requirement or it could, perhaps, be done in a simple settling tank with some special provision for removing the sludge from the bottom. It is believed that investigation of this step is warranted in the future.

Although it is not directly a part of the problem under discussion in this report, mention should be made of the use of the Manton-Gaulin Homogenizer in the standardization of products made from the pastes resulting from the HF milling operation. The homogenizer is essentially a device for passing a fluid suspension through a special valve with a very large (approx. 5,000 p.s.i.) pressure drop through the valve. The actual valve comprises two relatively flat surfaces, with the liquid entering through the center of one of them and passing out between them and then impinging on a ring which surrounds the thin edge of the valve. Although there has been little evidence of actual particle size reduction in such an operation, it has proved exceedingly effective in dispersing products which appear to have been agglomerated, and thus has significantly improved the effective strength of many of the products which have been made available for sale.

In the later stages of this work, consideration has been given to alternative equipment which might be effective in reducing the particle size of phthalocyanine pigments within the general frame-work of the process described here. For instance, the relative merits of single and double discs have been explored in the laboratory, and there has been little evidence that two discs are significantly more effective than one. Recent work in the F&F Department and at Jackson Laboratory suggests that a series of discs, perhaps 6 to 8, spaced fairly close together, may give a marked improvement for continuous operation over one or two discs. This has not been explored at Newark.

It has been suggested that a long cylindrical grinding agitator operating with relatively close clearance within a cylindrical vessel might be more efficient in an over-all operation than a disc type agitator. Such a device was constructed, but not tried out during the period covered by this report. This type of operation was simulated to some extent by repeated passes through a colloid mill with a conical rotor, which operation has given a substantial degree of particle size reduction, but offers no economical advantage over the process described above.

It appears safe to conclude at this time that there is no obvious alternative equipment which offers any economic advantage over the Cowles Dissolver for large scale operation of this process.

DISCUSSION OF EXPERIMENTAL RESULTS:

The experimental results will be considered first in a very general way including the historical aspects of the work and the use of some new testing techniques. Subsequently, more details will be given on a number of individual topics.

During the work on HP milling with acetone, which is reported in detail in KN-52-13, consideration was given to milling the crude pigment in the form of an aqueous paste. This resulted in the presence of some water, and was successful when a crude paste substantially free of kerosene was available. This led to experiments with further dilution with water and it was possible to mill CPC Blue in a 50% acetone - 50% water mixture (by volume) with only a slight loss in efficiency from pure acetone. Below 50% acetone there was a serious drop in efficiency, but even 10% acetone was markedly better than pure water. In March, 1950, a critical experiment (1191-50) suggested that the right dispersing agent would permit the complete elimination of acetone. With 2% high viscosity Carboxy Methyl Cellulose (CMC) in a 2 hour grind with borax, followed by decantation and flocculation with $CaCl_2$ plus HCl, there was obtained a dry color which was about 15% weaker than BT-304-D, but free from dullness. Subsequent work has not supported the use of CMC as a preferred agent, but these indications of success did lend hope to that line of research.

It was quickly shown that "Blancol", a polymerized condensation product of naphthalene sulfonic acid and formaldehyde, was more effective than CMC in promoting particle size reduction in aqueous milling with borax. Beginning with the observation, the following phases in the development can be recognized.

1. The study of other agents and combination of agents in a dry color process.

2. The recognition that many products made with a large amount of dispersing agent, although weak as dry colors, were quite strong in the paste form.

3. The development of a particle size index and the demonstration that, with large amounts of dispersing agent, the particle size index continued to decrease with time of milling, and went considerably below that of the W.D. pigments obtained from Orchem for resale.

4. The development of tentative processes for W.D. colors, but the ultimate decision to set these colors aside because of their high sodium content.

5. Laboratory development of processes for dispersed pastes and their translation to plant operations. This also included the tentative standardization of products for sale and considerable assistance to the plant in the standardization of these processes.

6. The re-examination of some dispersing agents and the recognition that some of them were especially promising in the preparation of dry colors.

<u>Study of Dispersing Agents.</u>

The following table summarizes the various dispersing agents used in these studies, together with the supplier and information on composition where known.

I - <u>Best Agents</u>

Best Agents	Supplier	
Blancol	General Aniline	) Polymerized condensation
Daxad 11	Dewey & Almy	) product of naphthalene
Tamol N	Rohm & Haas	) sulfonic acid and
Compound 8	DuPont	) formaldehyde

II -<u>Agents of Value</u>

"Pontamine" Fast Turquoise 8GL,	DuPont - CPC	polysulfonic acid.
Indulin XS-3	Industrial Chem.Sales Div. (West Va.Pulp & Paper Co.)	(Sulfonated Lignin - (3-sulfonic acid groups. Lignins with more or less sulfonation also of value.
Orzan	Crown-Zellerbach	Ammonium Lignin Sulfonate.
Marasperse CD) Marasperse N)	Marathon Corp.	Lignin Sulfonates.

III- <u>Agents of some Promise</u>

CMC	DuPont & others.	Carboxy Methyl Cellulose
Petronate	Sonneborn	Petroleum Sulfonate
Indulin	Industrial Chem.Sales	Lignin
Brij 35	Atlas	Polyoxyethylene-Lauryl alcohol
Pluronic F-68	Wyandott	Polypropylene oxide derivatives
Sodium Rosinate	-	-

IV- <u>Agents of no value when used alone</u>

Triton X-100	Rohm & Haas	Polyethylene oxide derivative
Aerosol OT	Amer. Cyanamide	Dioctyl ester of sodium sulfo succinate
Aerosol C-61	Amer. Cyanamide	A quaternary salt.
Span 20	Atlas	Sorbitan monolaurate
Victawet 12	Victor Chemical	non-ionic phosphoric acid ester
Victawet 35B	" "	Phosphated higher alcohol
Santomerse DT	Monsanto	A poly amine
Igepon T	General Dyestuffs	Sulfonated amide of oleic acid
Arctic Syntex T	Colgate Palmolive Peet	Same as Igepon T
Ammonyx CO	Onyx Oil & Chem.	A quaternary iodide
Ammonyx AO	" " "	Dodecyl dimethylamine oxide
Areskleno 400	Montanto	Dibutyl phenyl phenol sodium disulfonate
Hypodynes	Ferro Chem. Corp.	Acid esters of polybasic acids & their amine salts.
Ucon 50 HP	Carbide & Carbon)	Polyalkylene alcohols
Ucon 75 H	" ")	

Atlas G 3300	Atlas	Probably an amine derivative
Lustrex 820	Monsanto	Styrene Maleic acid "
$TEAC_{12}$ ester	DuPont	Triethanolamine ester of lauric acid
$Na_4P_2O_7$	-	See formula
Sodium Polyphos	Victor Chem.	Sodium polyphosphate
Methyl Cellulose	Dow	See name
Ammonium Styrene Maleamate	Du Pont	See "
Aromatic Sulfonates	Wyandott	See "
Triethanolamine Titanate	Du Pont	See "

Considering some of these agents in more detail, the agents in the first group are all similar in chemical composition, but they differ somewhat in the ratio of the alpha and beta isomers of naphthalene sulfonic acid present. There are only minor differences in effectiveness.

The agents in the second group are less effective than Blancol for aqueous dispersed pastes, but have been more effective (especially Indulin XS-3) in the preparation of dry colors. The sulfonated lignins have seemed to offer peculiar advantages in such products. The value of the sulfonated CPC ("Pontamine" Fast Turquoise GL) as a dispersing agent in such a system was surprising, and offered the additional advantage of a flocculation resistant toner. The high cost, however, makes its use economically unattractive.

The agents in the third group have shown just enough promise to list as of potential value. CMC has given some good products, but the results have been undependable. It is speculated that it may hydrolyze to varying degrees during the flocculation stage, but this has not been confirmed. Petronate and sodium rosinate have given evidence of particle size reduction, but this has been accomplished with severe foaming, which reduces the effectiveness of the milling operation. If the foam could be controlled, it is believed these agents might have definite value in the preparation of lakes. The non-ionic agents, Briz 35 and Pluronic F-68 have seemed more effective than other agents of this general type. There was also some evidence that they were beneficial in combination with Blancol. They may, therefore, deserve more study.

Some of the agents in the last list, noteably Victawet 12, Arctic Syntex T and tetra sodium pyrophosphate, gave some slight evidence of value when used in combination with Blancol, but the improvements were slight and not always consistent. Many of the agents were not tried in such combinations; hence it is lack of information, rather than negative results, which is reported in these cases.

In studies on the effect of the amount of agent, particularly Blancol, it was noted that an optimum strength of dry color existed at about 5% agent. Above this point there was a serious drop off in dry color strength, yet flushed color strength continued to rise. This led to testing these colors as dispersed pastes by casein brushout, and colors with 10% or more agent were found to exhibit high quality in this use. When the amount of agent exceeded about 10%, however, there was considerable difficulty in flocculation and filtration, hence the great bulk of the work was done with 10% of agent.

On the other hand, it was known that the W.D. colors (BP-192-D and GP-501-D), which are made by Orchem, contain the agent in an amount of about 60% the weight of the color component. Some charges were milled with large amounts of Blancol, and examined both as aqueous suspensions and as dry colors obtained by simple evaporation of the water in the suspensions. At about this time the Physics Group at Newark proposed a method for a particle size index based on a spectrophotometric transmission curve of a dilute suspension of the dispersed color. This method is described in detail in KN-51-43 and the theory back of it will not be repeated here. It will suffice to point out that the particle size index (PSI) is defined as the ratio of the optical density (D_1) at the point of maximum transmission to the optical density (D_2) at the point of minimum transmission. Since this ratio is always less than 1, it has usually been multiplied by 100 to give a whole number. The formula then becomes:

$$PSI = \frac{D_1 \times 100}{D_2}$$

This number becomes smaller as the particle size becomes smaller, but no correlation has been established between actual particle size and the P.S.I.

When the particle size index was obtained on the experimental products ground with a large amount of Blancol, it was found to be less, in many cases, than those of dispersions of the W.D.colors. It was also shown that the P.S.I. in such cases was a function of the time of grinding, and it was utilized as a routine testing method to follow the degree of particle size reduction. It then became apparent that, when small amounts of agent are used, the particle size reduction did not proceed smoothly. For instance, with 5% agent, the curve comparing particle size index vs time would reverse after about 15 minutes and the P.S.I. would increase sharply. Using 10% agent, the decrease in P.S.I. would continue for about 40-45 minutes and then a slow increase would start. With about 15% or more of agent, there was no evidence of the reversal in P.S.I. with time of grinding, though there was a tendency to level out sooner with lower amounts. During the time of actual grinding the slope of the curve was more or less independent of the amount of agent present, so that one may conclude that increasing the amount of agent functions largely by increasing the time of effective grinding.

Another important observation regarding the effect of the amount of agent may be made when additional agent is added after the particle size index has started to increase markedly as in a charge ground with 5% agent. The charge will be seen to become much thinner, and within one or two minutes the P.S.I. will drop to a point approximating that which it would have reached in that time if all the agent had been present throughout.

The following explanation appears to fit the observed facts. As new surfaces are formed by fracture of particle, the agent is adsorbed thereon as long as there is any free agent in the solution. During this interval, the system is well dispersed and thin, and the particle size index decreases with time. When, however, all the agent has been adsorbed on new surfaces, any further new surfaces which are formed attract each other and the absence of free dispersing agent results in a flocculated system, wherein the particles tend to grow in effective size, even though some of them continue to be fractured. If, now, one adds more agent, a minimum of work is required to redisperse the system and to take advantage of all the fractures which have occurred in the meantime. No serious conflict with this explanation has been found.

Figure 1 shows curves relating the P.S.I. to the time of grinding and to the amount of Blancol used.

When colors, which have been ground beyond the point of minimum particle size index, are tested by casein brushout in the normal manner, they become weaker with increasing time of grind. It is believed, though not fully established, that such colors are inherently strong and this strength can be realized by applying a certain amount of work, as in the homogenizer, with additional agent present. It has also been argued that strength as a dry color should increase with continued grinding after reversal of the P.S.I. There have been observed trends in this direction, but not to the extent hoped. However, there has never been any significant decrease in strength as a dry color in these samples which do show decreases in casein brushout strength.

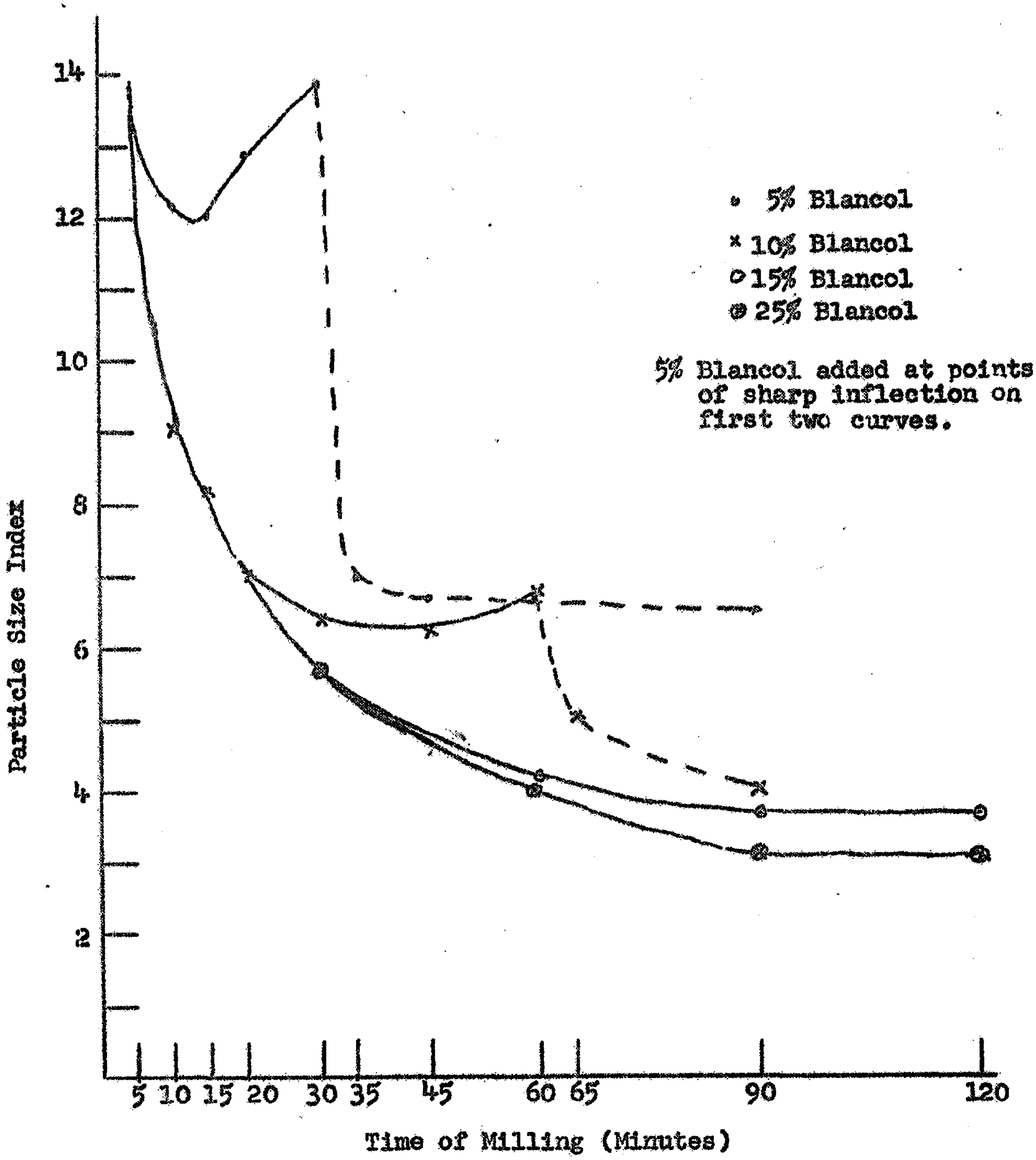

Figure I

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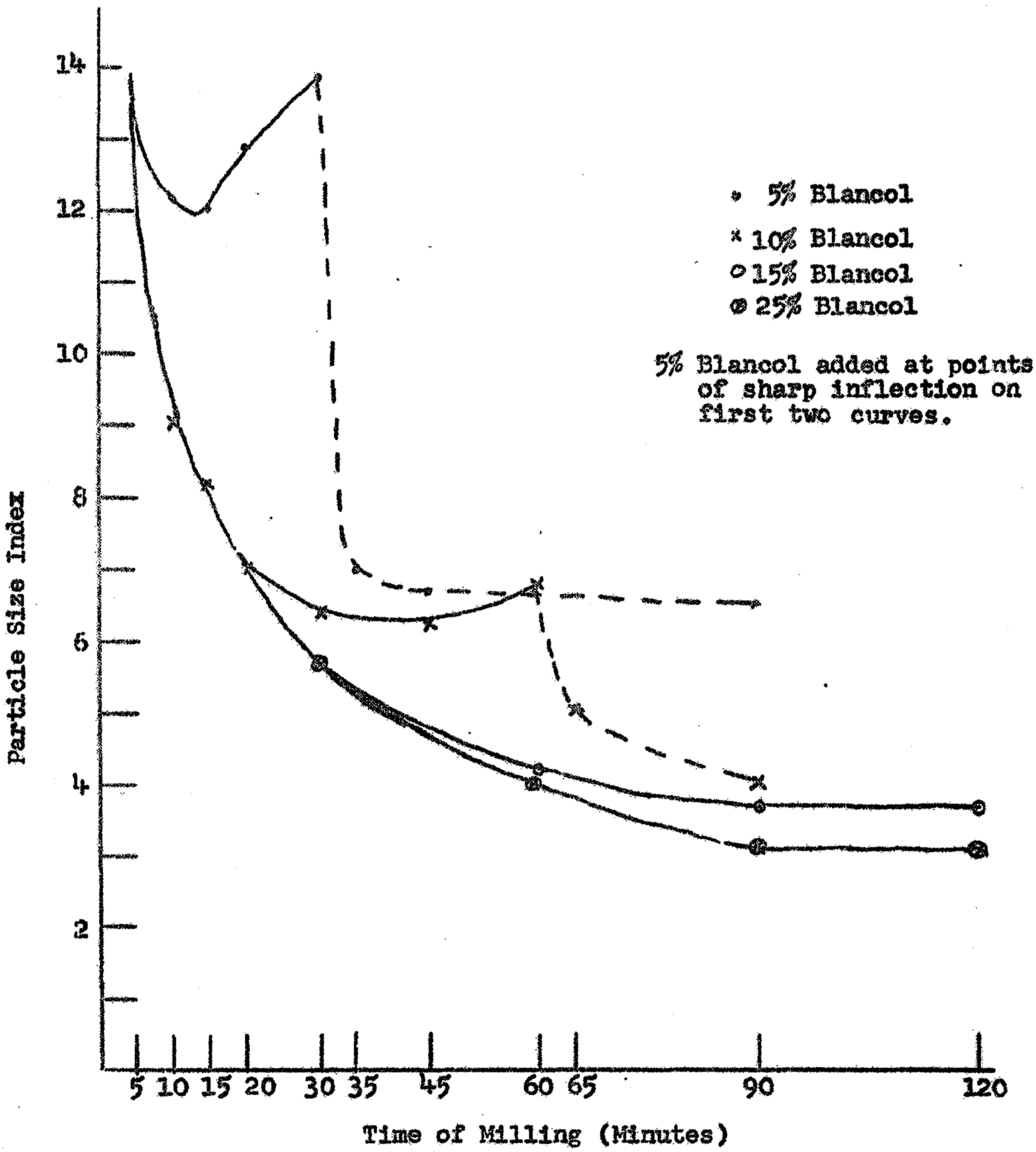
14
12
10
8
6
4
2
Particle Size Index
5% Blancol
10% Blancol
15% Blancol
25% Blancol
5% Blancol added at points of sharp inflection on first two curves.
5 10 15 20 30 35 45 60 65 90 120
Time of Milling (Minutes)

Figure I

OPERATING VARIABLES

Before continuing with a detailed discussion of the process as it applies to different types of colors and to specific codes, it is well to consider, in a general way, some of the operating variables which have been studied. The following statements are quite general and applicable to the process as a whole.

In the first place, it is necessary that the crude pigment which is used in this process shall be in a powder form before attempting to mill it. Any lumps of pigment are ground very slowly, if at all, in this process, and it is therefore necessary that the product be pulverized at the beginning. In most of the work, a simple low speed pulverization was used, and proved quite satisfactory. However, some samples of crude pigment, particularly CPC Green crude, have shown a considerable content of very small, but very hard particles, which do not readily lend themselves to further sub-division in this process. A partial solution to this problem has been high speed pulverization. It would appear, however, that the basic solution to the problem goes further back in the process in avoiding the formation of such very hard particles. This problem has not been significant with CPC Blue, and low speed pulverization has been satisfactory there.

Substantially all of the evidence accumulated in this work points to the rather clear conclusion that the rate of particle size reduction bears a direct relationship to the amount of power applied to the system. Hence, most of the ordinary operating variables are effective only in so much as they influence the amount of power which can be applied to the system. For instance, the rate of application of power to such a system is in direct relationship to the speed of the agitator and, high speed agitation, other factors being held constant, always gives a faster rate of particle size reduction. In the laboratory equipment, speeds of 1250 r.p.m. and 2450 r.p.m. have been readily available, and the higher speed has given a substantially higher rate of milling at all times. As the size of the equipment has been increased, it appears that the peripheral speed of the agitator disc should be kept more or less constant at a value somewhere above 2,000 ft./min.

In the small laboratory vessels, the diameter of the disc does not seem to be a critical factor, although nearly all of the work has been done with a 4" disc in a 5" vessel. Also, most of the work has been done with two discs whereas recent evidence indicates that a single 4-1/2" disc is fully equal to the two 4" discs. In a 14" diameter vessel in the semi-works, discs of 8" and 10" diameters, operating at speeds of about 1750 r.p.m. and 1500 r.p.m. respectively, have given results substantially equal to the laboratory results. When the diameter of the vessel was increased to 18" with these same discs, the rate of milling was materially reduced but, since the charge was larger, the rate per pound of color was not markedly different. Using still larger vessels, a 32" vessel with discs from 18" to 22" operating at about 900 r.p.m. gave results comparable to these smaller vessels in terms of rate of milling.

The ratio of borax to the pigment being ground has been varied over a considerable range with rather interesting results. Much of the early work was done with ten parts of borax per part of pigment, but substantial reductions have been possible in the use of borax without any major changes in the effectiveness of the operation. Simple reduction in borax without other changes results in a thin mixture which does not grind well, but if the pigment is increased somewhat, and the water reduced somewhat, so that the over-all charge in the vessel is substantially the same in volume and viscosity as with the original ten parts of borax, the rate of milling per pound of pigment is very close to the same. Nearly all of the large scale manufacturing operations have been carried out with a maximum of five parts of borax per part of pigment, and a few charges using somewhat lower amounts of borax have been successful. It is believed possible that the amount of borax might be reduced to as little as three parts per part of pigment if some additional work were done.

The particle size of the borax appears to be rather critical in this operation. Crystalline borax which has a particle size of roughly 20-30 mesh, has been quite poor in this process as compared to the finely powdered borax, much of which is finer than 100 mesh. Very little is known about the particle size of the recovered borax which has been used again and again in the commercial operations. Generally, it is believed to be quite small and comparable to the powdered borax which is used in the beginning. However, it is suspected that some charges which have been allowed to become unduly hot have grown larger crystals of borax, and there have been some indications that such charges of borax do not grind as well as the more conventional fine particles.

The influence of the temperature of the grinding charge has been rather mysterious. In the laboratory, there has been no difficulty in keeping the charges cool, and substantially all of the work has been done at temperatures approximating that of the cooling water, which has been below room temperature. On the other hand, in the larger vessel used for commercial operation, it has not been possible to prevent some temperature rise. It is not believed that such a temperature rise has any effect on the pigment as such, but it has two effects on the over-all system, both of which are undesirable. In the first place, more of the borax goes into solution at the higher temperatures and is thus removed as an effective grinding aid. In the second place, the higher temperature reduces the viscosity of the mix and this, in turn, reduces the ability of the mixture to absorb the energy applied to the agitator. Consequently, it has been observed that all charges which exceed about 40°C in temperature show a markedly lower rate of grinding. Also, in the large vessel at these higher temperatures, a complex system develops in which borax goes into solution in the main body of the liquid, but tends to crystallize out near the cold walls and build up a layer of crystalline borax, which becomes an effective insulator and reduces the rate of heat transfer from the main body of the liquid. This, of course, becomes a viscious circle and the main body of liquid, under these conditions, may heat up quite rapidly. It is essential to avoid these drastic conditions by cleaning any crystalline material from the walls between batches, and by keeping the general conditions in the vessel such that an excessive temperature build-up cannot occur.

It has been generally accepted that the viscosity of this system should be kept fairly high. However, the system is quite thixotropic, and very little is known as to the exact viscosity which exists or which should exist. Obviously, the viscosity can be influenced by the temperature, and by the concentration of either the pigment or the borax, or both, in the liquid of the system. It also shows an apparent increase during the grind as the particle size of the pigment becomes smaller. In laboratory grinds with small amounts of treating agent, the apparent viscosity shows a very marked increase coinciding substantially with the point where the particle size index begins to increase, and presumably corresponding to the point where all of the dispersing agent has been adsorbed on the particles of the pigment.

Substantially all of these variables influence the ease with which energy is absorbed by the system, and the direction of the variable which increases the absorption of the energy has been the desired direction. Thus, with a thin slurry, or a small disc, or with low speed agitation, it is impossible to apply a large amount of power to the system and the rate of grinding is always slow. On the contrary, a thick slurry, or high speed agitation resulted in consumption of more power and, invariably, in a more rapid rate of particle size reduction. In general, it appears to require very close to 0.5 H.P. hours per pound of pigment to result in the desirable particle size reduction. Although a plant charge of 125 lbs. using about 25 H.P. for 2 hours applies only 0.4 H.P. hours per pound of pigment, such charges have been on the border edge of satisfactory grinding. In the laboratory, the power consumption has been nearer 1 H.P. per pound of pigment, but even this maximum figure is a small fraction of the average consumption of power in the ball mill at Newport.

WATER DISPERSIBLE DRY COLORS:

When it was shown that the particle size index of a product ground with relatively large amounts of dispersing agent was actually less than that of either the water dispersible dry colors (BP-192-D and GP-511-D) purchased from Orchem for resale, it was immediately suggested that the new product should be capable of being converted into satisfactory water dispersible colors. As the first attempt in this direction, all of the ingredients of the W.D. colors (CPC about 30%, Blancol about 20%, and Dextrin about 50%) were charged to the mixer with water to give a fluid mass and sand as the grinding aid. In the absence of cooling, this mixture became quite hot in the HF mixer and there was sufficient evaporation to cause the mixture to become quite viscous. However, when starting with CPC in the form of a crude pigment, although there was a considerable development of strength, the resulting product was always markedly weaker than the standard W.D. colors. Products were then prepared by grinding in the normal HF milling operation with Blancol and borax, followed by a physical separation of most of the borax, and drying of the resulting aqueous suspension. Such products always contain some borax, usually around 40-50% of the total dry pigment, although, under some conditions, the borax content could be held to around 20%. Such products showed a remarkably good ability to redisperse in water to a relatively sediment-free suspension, and with particle size indices appreciably lower than those obtained from suspensions of the standard color. As expected, these products exhibited strength by casein brushout substantially better than the standard colors now being sold. In nearly every case, however, this strength could be appreciably increased by adding some dextrin prior to drying the products.

This process was studied rather extensively on both the laboratory and the semi-works scale and, in general, the process variables outlined above apply throughout. In the laboratory, grinding times of from one to two hours were quite satisfactory with a charge which included 60% Blancol on a pigment basis and about ten parts of borax per part of pigment. However, the particle size index and the strength would show additional advantages up to four hours or more of grinding. The semi-works appeared to require somewhat longer grinding time, with two hours a bare minimum, and a somewhat longer time definitely advantageous.

It would appear that the Blancol could be reduced considerably below the 60% level, which was used in most of this work, and it is believed probable that there is little advantage in the use of more than 40%, and that it might well be reduced to around 25-30%

Most of the semi-works studies were carried out on CPC Green and a tabulation of all of the batches made in the semi-works is included as a part of the appendix to this report. (See Table I)

Although tentative laboratory standards were set up on both the blue and the green, and although a rather sizeable amount of material was prepared in the semi-works, and made available for evaluations, several difficulties resulted in this work being abandoned for the present. In the first place, all of the crude pigment available for our use is unextracted, and contains a rather substantial amount of impurities, the most serious of which is a significant amount of ionic copper. The process, as described above, does not provide for any further purification by extraction, and these impurities will necessarily find their way into the final product. It was judged that, before this process could be successful, it would be necessary to obtain a purified crude pigment, and this was not then available.

The second difficulty lay in the finding of a practical means for separating the borax from the ground pigment without excessive dilution and consequent solution of some of the borax. On a small laboratory scale with a well ground pigment, separation from the borax can be readily effected by simple filtration, either through a porous stainless steel funnel or through #8 duck filter cloth. This filtration can be accomplished with only that amlunt of dilution necessary to wash out the grinding vessel, which is considerably less than one volume of water; and a small wash with cold water leaves a relatively light colored borax cake on the filter. Attempts to carry out this filtration operation on a larger scale, however, invariably resulted in blinding of the filter and a very rapid dimunution in the rate at which the dispersed pigment came through the filter bed. On the other hand, to dilute with water to a sufficient degree to obtain separation by settling results in dissolving a large amount of borax, all of which appears in the final dry color. Most of the semi-works charges were finished by the latter process and contained approximately 50% borax in the final dry color. For some purposes, this borax is not objectionable, except for the fact that in the drying operation at normal drier temperatures some of the water of crystallization is lost, and if care is not exercised in dispersing the pigment in water, there is a marked tendency for caking as the borax is rehydrated. Much more serious, however, is the presence of the large amount of sodium which has been found to be very objectionable in certain applications of such colors, particularly in paint based on rubber latex as the vehicle, wherein such a large sodium content invariably tends to result in efflorescence in the final paint film.

On the other hand, colors containing dextrin as in the current standards of the water dispersed colors, have been quite objectionable because of the tendency for the dextrin to cause putrefaction of paints containing such pigment, and to attract insects to surfaces painted therewith. Also, colors containing dextrin are unsuitable for use in coloring products made from Portland Cement, because they result in a serious loss of structural strength of the cement. The products containing borax and no dextrin are free from these defects, but the high sodium content does not permit their general acceptance. It is apparent that the desired type of color would contain no dextrin and be substantially sodium-free.

An approach to such products has been made by adding additional dispersing agent to the dispersed paste colors (which will be described in the next section), and subsequently drying them out either with or without mechanical treatment before the drying. The Orchem process involves the evaporation of water from a mixture of the pigment and dispersing agent, and subsequent plastic milling in a kneading type mixer. As a replacement for this expensive equipment, an alternative procedure tried involved evaporating the water from such a mixture in the HF mill and accomplishing the plastic milling in this machine. Such products approached the desired strength with pigmentation approaching 50%, but the operation was not particularly attractive from the operating point of view. Some further work on this type of operation might be justified. A more practical approach involved the vigorous homogenization of a mixture of the dispersed paste and added dispersing agent, followed by drying of the pigment paste. This has resulted in products which closely approach the strength, on a pigment basis, of the present W.D. colors. Products of this type have been made and proposed for use in cement.

DISPERSED PASTES:

The general effect of variables in the milling operation has been adequately covered above. However, two closely related problems, not specifically a part of the milling operation, required study before this phase of the problem could be established on a commercial scale. As already pointed out, the efficiency of grinding increased markedly with increases in the amount of Blancol used. However, this increase also resulted in a marked increase in the difficulty of isolating the pigment from the dispersed slurry. In the laboratory, products ground with 5% of Blancol were relatively easily filtered from an acid slurry. Products made with 10% of Blancol could be filtered, but the operation was apt to cause considerable difficulty. In the first semi-works study with 10% Blancol, filtration proved impossible, and it was necessary to search for better means of flocculating the dispersion.

It has been reported elsewhere that products similar to Blancol can be precipitated by means of many cation active compounds. Multivalent metal salts such as barium chloride or aluminum sulfate have been said to precipitate the Blancol type product, but in this work such agents have not precipitated Blancol in acid solution. On the other hand, many cationic organic agents have been successfully used. Such products as quaternary ammonium salts and diphenyl guanidine have been especially successful, and the choice turned to diphenyl guanidine as a readily available product of moderate cost. Thus, upon the addition of a small amount of a solution of diphenyl guanidine sulfate or diphenyl guanidine hydrochloride to the acid slurry of the dispersed product obtained by milling with 10% or more of Blancol, the slurry is completely dispersed and can be readily filtered and washed. Although this product is flocculated and readily filtered, the washed cake is readily redispersed to a fluid slurry which remains completely in suspension. There is frequently some loss in strength compared to products which have been filtered without the flocculation, but, even with this loss of strength, the final products, which have been ground with 10% Blancol, have been considerably stronger and more intense than the standards which had been heretofore available for sale as dispersed pastes, namely BT-287-P and GT-675-P. The blue dispersed paste obtained by this process is always greener than the prior product, and the green dispersed paste has generally been bluer than the previous standard. Although these hue deviations from previous standards are considered to be in the undesired direction, nevertheless, the marked intensity of the products has made them more desirable than the previous standards.

Table II summarizes the experience in ten semi-works batches during the development study of a dispersed paste of CPC-LB. Most of these batches were made in a 13 gallon unit on the Cowles Dissolver using a single 10" disc at 1500 r.p.m. Some of them were made with 5% Blancol and some of them with 10% Blancol. Most of the batches were made with 10 parts of borax per part of pigment; one batch used five parts of borax and another used only three parts of borax per part of pigment. All of these batches, both those with 5% and those with 10% Blancol, except the first two in which no diphenyl guanidine was used, were stronger than the previous standard BT-287-P (BT-321-P). The particle size index was always smaller with 10% Blancol than it was with 5% Blancol. The maximum range of power consumption on the Cowles unit was between 2.5 amperes and about 3.5 amperes. Within this range there was no obvious effect on the particle size index by variation in power. There was a general impression of more efficient grinding with high power consumption, but positive proof of this was not readily obtained.

Table III summarizes the experience in ten semi-works charges of CPC Green designed as a development study on the preparation of dispersed pastes. The equipment was the same as that used in the Blue, but all but two of the charges were ground with 5% Blancol and only a few of them were tested for particle size index. Again, the use of 10% Blancol gives a markedly smaller particle size index and distinctly better strength. However, all of the products were stronger than GT-689-P) except one, in which case the test is believed to be inconclusive, because it did not seem to detract from the strength of a mix in which it was included.

In this study, for the first time, borax sludge from a previous batch was re-used with a make-up of fresh borax and the results were completely satisfactory.

DISPERSED PASTES - PLANT DEVELOPMENT

Largely based on the excellent results obtained with the Cowles Dissolver in the semi-works, a much larger unit with an operating capacity of 100 gallons (actual capacity about 130 gals.) and powered with a 30 H.P. motor was purchased and installed near the end of 1951. The vessel has a diameter of about 32" and the manufacturer recommended 16" or 18" toothed discs as proper agitators. Based on our previous experience, they also supplied smooth discs of 18", 20", 22" and 24" in diameter. The motor speed is approximately 900 r.p.m.

After consultation with the DuPont Engineering Department and with the Dorr Company, a 14" Dorr rake classifier was purchased and installed for separating the borax from the dispersed pigment after grinding. Auxiliary vats already available in the #10 building semi-works were used for the dilution prior to the separation from the borax and for the pigment extraction and filtration of the pigment slurry.

Table IV summarizes the experience in the use of this equipment with nine batches of CPC Green as dispersed paste, followed by two batches at a somewhat later date. The first three of these batches were made with an 18" toothed Cowles disc with a maximum power usage of about 25 amperes. The products obtained were, however, universally of excellent quality. An attempt to use an 18" smooth disc in the next batch demonstrated that it would not impart the desired amount of energy to the batch, and it was replaced by a 22" smooth disc which has been used since that time. It has been possible with this disc to use from 30-35 amperes in most of the charges. The first nine charges were all made with a borax ratio of ten parts per part of pigment. All but the first and eighth charges re-used the borax sludge on an analyzed basis, with fresh borax added to give the desired figure. The maximum usage of borax for make-up purposes was about three parts per part of pigment, but the average use was in the vicinity of two parts per part of pigment. The charge used in these batches was 75 lbs. of pigment and 750 lbs. of borax with 10% Blancol. In the last two charges made at a later date, the pigment charge was 120 lbs. and the borax 600 lbs. with 10% of Blancol. Particle size index measurements were made on all of these batches, and showed a rather uniform reduction of particle size to substantially the same point which was obtained in the semi-works charges. The maximum grinding time was four hours, but there was little evidence of benefit beyond about 2 or 2-1/2 hrs. It was recommended that subsequent operations be conducted at a 2-1/2 hr. cycle using the 125 lb. charge with 600 lbs. of borax.

The unstandardized CPC Green dispersed paste obtained by this process was coded GT-735-P. A mix of most of these charges was made in the plant Abbe' Lenart mixer, thickened with barium chloride and standardized at about 19% solids. This mix was coded GT-732-P, and at 19% solids was approximately equal in strength to the GT-689-P standard which contained about 22% solids. Subsequently, this batch of material was stirred up and put through the homogenizer to give a slight additional strength advantage, and it was decided that future batches should be treated with a preservative such as Dowicide to inhibit mold growth.

This product has shown two deficiencies in use which have not yet been completely corrected. The first is a tendency to develop a slight acidity on prolonged standing. It is believed that this can be corrected by the addition of the proper buffer salt to the system. A potassium phosphate compound has been suggested for this purpose. The second deficiency comes about by reason of the fact that the barium chloride used for thickening the paste also causes some flocculation and, on prolonged shaking or vibration of the type encountered during shipment, these pastes tend to show a marked settling, with the separation of more or less clear water on the surface. It should be emphasized that this settling is a soft settling and the product is readily redispersed as contrasted to the very hard settling which is sometimes observed with thoroughly dispersed products, which type of settling is very difficult to reincorporate in the paste. More recent attempts to solve these problems will be covered in other reports.

With the successful development of a process for making a green dispersed paste in the Cowles 100 gallon unit, attention was turned to a process for CPC/LB as a dispersed paste, and Table V summarizes the experience in seven batches of CPC/LB made immediately following the work on the Green, followed by two batches at a somewhat later date. All of these batches were made with 10% Blancol, three of them using 75 lbs. of pigment, and 750 lbs. of borax, and the remainder using 120 lbs. of pigment and either 750 or 600 lbs. of borax. The average power consumption in these batches was about 30 amperes and all of them showed excellent particle size reduction as judged by the particle size indices. Evaluation of the final dispersed pastes, coded BT-352-P, showed all of them to be stronger than BT-321-P on an equal pigment basis. A mix of several of these batches was standardized in the plant Abbe' Lenart mixer at about 19% solids content, and thickened with barium chloride substantially as described above for the green paste. This product was a little stronger than BT-321-P, at a solids content of about 22%, when tested on the equal commodity basis. After careful study of competitive products, this strength was judged a little deficient to meet average competition, and it was increased rather markedly by putting the whole batch through the homogenizer. The tendency to develop a slight acidity on standing has also been noted with this standard (BT-353-P), but the tendency to show a separation of water on the surface is very much less than has been observed with the green. Another difficulty, however, which has developed in recent experience with plant manufacture, is a serious foaming tendency. The efforts to solve this problem and other problems in connection with this color will be reported elsewhere. CPC-LB appears to grind a little more rapidly in the Cowles unit than does the Green, and a time of about 2 hours has appeared to be adequate for this operation.

The separation of the borax following the grinding, using the Dorr rake classifier, has substantially come up to expectations. The equipment used during most of this process and continuing up to the present is not ideally adapted to the use, but has served the purpose. The charge from the Cowles dissolver has been pumped to a vat on the third floor of #10 building, where it has been diluted to approximately 350 gallons and kept in vigorous agitation until the classification can be carried out. Failure of the agitator in this vat on a few occasions has been serious in that very rapid settling occurs and the agitator cannot then be started again. The charge has been run from this vat to the rake classifier by gravity at a rate between 3 and 3.5 gallons per minute. Control of this flow is difficult, because there is a tendency for the borax to clog the small valve opening. Various conditions were used in the classifier, with changes in the slope of the classifier having relatively little effect on the condition of the sludge discharged. On the other hand, the speed of the rakes did have a marked effect, and it was necessary to reduce the speed to about seven or eight strokes per minute to obtain borax in the desired high concentration in the sludge. There is always some borax in the pigment overflow, and it is believed that this will always be true as long as there is a significant amount of agitation in the settling bed. Perhaps some other equipment might be more efficient for this purpose. Possible improvement might include the use of a combination of bowl and rake classifier which is a standard piece of equipment, or it is possible that a simple settling tank from which the dispersed pigment could be syphoned, and which contained some device for removing the sludge from the bottom might be successful in the operation. Such modifications should be studied in the future.

The sludge obtained during these operations was analyzed on several occasions and found to contain between about 70% and 75% of borax. On the basis of these analyses, it was specified for later operation that the borax sludge be weighed and estimated as 72% for the purposes of calculating the additional borax to add. However, recent plant experience has demonstrated that the sludge in practice is not as high in borax content as had originally been estimated, and that it is more apt to be about 65% then the originally estimated 72%.

Some effort during this work was expended toward obtaining a borax with less water by means of some filtration operation to remove the water from the sludge near the upper end of the rake classifier. A device was built and installed to use a short vacuum bed, about 6" in length, beyond the end of the classifier as originally designed. Although the liquid in a small amount of sludge is readily filtered in the laboratory through #8 duck filter cloth, no such filtration could be achieved in the actual operation, for the cloth seemed to blind immediately. When the cloth was replaced by a small wire screen, approximately 40 mesh, it was possible to remove a substantial amount of liquid from the sludge. However, this then caused the dry borax to build up on the rakes from which it did not readily drop off and the over-all advantage was very slight. This was not deemed sufficiently successful to continue in use.

In estimating the consumption of borax in these operations, it is noted that eleven batches of CPC Green, all but two of them using the 10:1 borax/pigment ratio, totalling approximately 900 lbs. of pigment, used about 2100 lbs. of borax. On the other hand, nine batches of blue, only four of them at the 10:1 ratio, totalled approximately 900 lbs. of pigment, and consumed about 1400 lbs. of borax. It is believed that an over-all realistic consumption of borax will be slightly less than 2 lbs. per pound of pigment ground.

It has been difficult to estimate the recovery of pigment in this work for two reasons. In the first place, the crude pigment with which we start is not pure and has been of unknown purity for the most part. In the second place, all of the pigment is never recovered, for some of it recycles with the borax sludge. Another difficulty is that of obtaining accurate solids content on large batches of paste. However, the best estimate on this work, which is borne out by later plant experience, is that the over-all recovery of pigment is substantially quantitative.

DISPERSED PASTE - PLANT EXPERIENCE

Several phases of the plant experience in the operation of the processes for BT-352-P and for GT-735-P deserves mention at this time. There are two problems in the practical operation of the unit which appear to be closely related. In the procedure as originally specified, it was somewhat difficult to obtain the desired viscosity of grind at all times, because the original specifications called for controlling it by the addition of water during the grinding cycle. On the other hand, the viscosity will change with grinding and also with the development of heat so that the ordinary plant operator found it quite difficult to control this situation. Ultimately, the situation was brought under control by specifying the addition of a definite amount of water to be followed after about one-half hour grinding with additional borax, if necessary, to develop the proper viscosity and the consequent proper utilization of power.

As noted earlier in this report, the cooling facilities on the plant unit have never been adequate to prevent some temperature rise during the grinding cycle. Sometimes this has gotten seriously out of hand and has resulted in a marked tendency for crystallization of borax against the cold walls of the vessel. This crystalline layer in turn becomes a good insulator and the heat accumulation proceeds more rapidly so that a vicious cycle results, and the temperature rise becomes quite large. This situation has been seriously aggravated on occasion by adding more borax to a charge which had become hot until some charges have actually set up to almost solid crystalline masses when allowed to cool slightly after the agitation is stopped. Careful removal of the crystalline layer from the walls of the vessel between charges has been quite successful in avoiding any serious temperature rises if the water and borax content are correct.

Another problem which has seriously handicapped the grinding of CPC Green in this process has been the tendency of many batches of CPC Green crude to contain substantial amounts of undispersible pigment in the form of quite small, but very hard, granules or pellets. These pellets do grind slightly but very slowly and result in some rather coarsely ground particles in the pigment overflow from the classifier; but, probably more serious, also result in an accumulation of unground pigment in the borax sludge. This has been controlled somewhat by high-speed pulverization of the crude, and it is believed that it can be kept under reasonable control by avoiding excessive re-use of the borax sludge. Rather, this sludge should be dissolved and the pigment recovered and pulverized for further use after a predetermined number of cycles, perhaps five or ten.

As to capacity, it is believed that the Cowles unit now installed is capable of milling at least six charges per day of 125 lbs. each or a total of 750 lbs. of pigment per day. With careful scheduling, it seems reasonable to believe that seven batches could be done, and it is not impossible to conceive of eight batches if the grinding cycle is no more than two hours. At present, the plant is able to accumulate five Cowles charges for filtration; but the filtration and the washing have proved to be the bottleneck in the process and the contemplated over-all capacity has not been, in general, achieved. Thus, with everything considered, it seems reasonable to conclude that the capacity of one Cowles unit operating under optimum conditions approximates that of two ball mills in the Newport plant.

CONVERSION OF AQUEOUS MILLED PASTES TO LAKES

L.D. Colors

The two dispersed pastes described above have been converted to colors especially designed for use in rubber base latex paints by the addition of other ingredients, particularly a special resin compatible with the latex paint vehicles and subsequent drying. These products have been coded BP-358-D and GP-740-D, and more details on their preparation will be reported elsewhere. They contain approximately 65% pigment and show excellent dispersion and strength development in latex paints, but are less desirable for other aqueous thinned systems.

"Ramapo" Lakes

A substantial amount of our phthalocyanine production is sold in the form of the "Ramapo" Lakes, BP-173-D and GP-501-D. It was, therefore, considered highly desirable to convert the aqueous ground dispersed pastes to such "Ramapo" lakes. Although the first attempts in this direction were somewhat promising, it has not been possible to make consistently satisfactory lakes in this way, whether one starts with products ground with 5% of Blancol or products ground with 10% of Blancol. Substantially all such lakes have been markedly weak and also quite poor in texture. The strength deficiency can be overcome by using higher toner content in the lakes, but such products are even worse in texture than the products with the normal toner content. This experience is in line with earlier experience on attempts to make "Ramapo" lakes from phthalocyanine pastes containing Blancol, and it seems quite probable that such lakes will not be made until some other dispersing agent is found suitable for milling CPC in water.

Linoleum Lakes

In contrast to the experience with the rosinated "Ramapo" lakes, it has been possible to make lakes similar to BL-288-D from the CPC/LB dispersed paste with relatively simple modification in the process. Some dispersed pastes ground with 5% Blancol have been used in the BL-288-D process without any changes to give products of excellent strength. However, this has been somewhat undependable and attempts to use products ground with 10% Blancol in the standard process were quite unsuccessful, because such products would not absorb the Resinous Oil X-1, and the latter invariably floated to the surface during the drying step. However, by adding a small amount of barium chloride during the lake formation, this difficulty has been largely avoided and products of rather good strength have been obtained. By increasing the toner content slightly, products fully equal to BL-288-D were obtained, and, for some months past, a substantial portion of the BL-288-D production in the Newark plant has been made by this method. The only deficiency appears to be a slight deficiency in texture and it has been the established policy of the plant that all such products which may be slightly poor in texture, and which may contain slightly more than the standard amount of toner, shall be consumed by blending with products made in the normal manner. This use has consumed a major shart of the BT-352-P manufacture and continues in active operation.

DRY COLORS

It is noted above that all of the early experiments on aqueous milling of phthalocyanine pigments were evaluated by rubout comparisons of the dried colors with our standard phthalocyanine toners. Although the quality of these products was promising, the general strength level was, at best, from 15-20% below that of the current standards. Nevertheless, occasional products showed strength approximately equal to BT-304-D.

A study of these few strong samples showed that all of them had been obtained from relatively long grinds with 5% Blancol, which had been carried beyond the point of minimum particle size index. Further experiments of this sort were then carried out both in the laboratory and the semi-works, but it has not been possible to confirm the hypothesis that effective particle size reduction with respect to ultimate dry colors continues beyond this point of minimum particle size index. However, one set of experiments with 5% Blancol, in which the borax/pigment ratio was increased substantially above the usual 10:1 ratio (actually 800 grams borax to 60 grams pigment), did give products which approximated the strength of BT-284-D. By carrying the borax ratio somewhat higher, dispersed pastes containing only 5% Blancol were obtained which approximated the strength of the standard paste from 10% Blancol. These conditions appeared impractical and have not been followed up. Nevertheless, they demonstrate that it is possible to obtain dry colors of satisfactory strength in aqueous milled processes.

Since some of the early experiments had been made with carboxy methyl cellulose, the use of this dispersing agent was reviewed again, both as the sole agent in the mixer and when used together with other agents. Carboxy methyl cellulose has continued to give erratic results, and does not appear to deserve further attention.

In some of the earliest work on particle size reduction at Newark, copper phthalocyanine polysulfonate ("Pontamine" Fast Turquoise 8GL) was tried as a dispersing agent in aqueous milling, and it was found to be quite effective in bringing about particle size reduction in the HF process. It is a water soluble dye which can be precipitated with a metal salt, such as aluminum sulfate; and this method of precipitation has been used to flocculate the dispersion and to enable the products to be filtered without significant bleeding. Products ground in the presence of about 10% of "Pontamine" Fast Turquoise 8GL (about 50% purity so thatactual dye content is only about 5%) can be flocculated with alum, so that they are substantially free of any bleed during the filtration step. However, as the soluble salts are washed out of the precipitate, some tendency to bleed frequently develops. The dry colors obtained in this manner are close in strength to BT-284-D by rubout, and fully equal to BT-284-D in alkyd enamels. Furthermore, they are substantially free from flocculation in alkyd enamels. The dispersed pastes from these products are on the defensive against the Blancol ground products, but are of relatively good quality. They are quite poor in texture in either varnish drier or alkyd roller mill grinds, and appear to be poorly wet by oil in substantially the same manner as products ground with Blancol are poorly wet in oil. Two semi-works charges made with this dye as a dispersing agent were markedly inferior to their laboratory counterparts.

Another agent showing some promise in the early work was Petronate, (a petroleum sulfonate), and its use was reviewed at this time without much evidence of promising results.

It had also been suggested that sodium rosinate might function as the dispersing agent and permit the preparation of a rosinated "Ramapo" type lake directly from the crude. This agent does appear to promote particle size reduction in a rather efficient manner during the first few minutes of a grinding operation. However, it develops rather copious amounts of foam in the process, and any further particle size reduction is greatly inhibited thereby. The best products were at least 20% weak against BP-173-D on an equal toner basis. Several anti-foam agents were tried without success; but it is still believed that this process might be successful if the presence of foam could be eliminated.

Another group of agents, which has consistently shown results of interest in this work, comprises the lignin sulfonates which are widely available as by-products from the paper pulp industries. These are typified by the "Marasperse" products of the Marathon Corporation and by "Orzan" from the Crown Zellerbach Corporation. These products have been a little inferior to Blancol as a dispersing agent, when judged by the particle size index; but they have not shown the harmful effect of amounts above 5% when judged as dry colors. Nevertheless, they have continued to be on the defensive with respect to the properties of the dry colors obtained from their use. More recently, the West Virginia Pulp & Paper Company submitted to us four samples of sulfonated lignin under the designations "Indulin" XS-1, XS-2, XS-3, and XS-4, which were said to have been obtained by directly sulfonating a relatively pure lignin and to contain respectively 1, 2, 3, and 4 sulfonic acid groups per lignin molecule. When 10% of these products was used in aqueous grinds, the resulting pigments exhibited the best strength of any products heretofore obtained in aqueous milling. Differences between the four products were small, but the Indulin XS-3 was selected as giving the most consistently strong product. The best strength in such products has been substantially equal to that of BT-284-D; they have dark masstones, intense undertones and green but intense tints. The first agents were obtained in the form of solutions, but the supplier has since given us dry powders which have been in every way equivalent to the original solution supplied. Charges milled with 10% of Indulin XS-3 and 10 parts of borax per part of pigment for about one hour in the laboratory, have given very interesting results at about the strength level mentioned above. Increasing the time of grind to two hours has shown only a very slight advantage. Increasing the amount of agent beyond the 10% level has not given consistent improvement. Three semi-works charges have been made. The first was rather poor in results for reasons unknown. The second run was ground for six hours and gave rather good quality material, but appeared to require at least four hours to equal the quality obtained in the laboratory in one hour. The third charge was ground with 20% Indulin XS-3 and gave weak products. Further work in the semi-works is obviously required if this process is to be made practical.

Mixtures of Indulin XS-3 and Blancol have shown definite promise of superiority over either one alone, but this field has not been thoroughly explored. For instance, one sample prepared with 5% Indulin XS-3 and 3% Blancol was actually on the strong side of BT-284-D. Another interesting combination proved to be the addition of a substantial amount of sodium tartrate to a charge ground with Indulin XS-3. This product was also on the strong side of BT-284-D, but it was not reproduced in a subsequent experiment. Other salts such as sodium citrate, sodium pyrophosphate, or urea gave no advantage in this type of experiment. Another agent, which proved harmful whether used along or in combination with Indulin, was dimethyl formamide.

It is obvious from these rather sketchy results that the work on the use of Indulin XS-3 in the preparation of dry colors is incomplete, and many additional experiments are suggested by the results reported.

MISCELLANEOUS TOPICS

Chlorine-Free Blue

Several experiments, including one charge in the Cowles 100 gallon unit (S.W.3031), were carried out in an attempt to develop a green shade dispersed blue paste. The results were disappointing in two respects. In the first place, although the product was considerably greener than BT-353-P, it was also markedly duller. In the second place, the strength developed was considerably less than had been anticipated from the work on CPC/LB. The crude used in these experiments was the "EF" type of chlorine-free crude and was believed to be 100% in the beta form. Nevertheless, the degree of greenness was considerably less than was anticipated. The over-all properties led to a loss of interest and the work was not carried further.

More recently, efforts have been directed to the preparation of a counterpart for BT-297-D by milling the same chlorine-free/EF crude with Indulin XS-3. These products did develop fairly good strength with respect to BT-297-D, but were very much redder, being only slightly greener than CPC/LB ground in the same manner. Very limited work was done on this problem during the period covered by this report and further work will be reported elsewhere.

CPC Green as a Dry Color

The use of Indulin XS-3 as the dispersing agent for milling CPC Green has been explored very briefly. The products obtained were appreciably weaker than GT-674-D (about 10% weak), but there was only a trace of dullness and this definitely represents the best CPC Green toner obtained in any aqueous milling operations.

Ball Mill Studies in Water

Since the very early attempts to ball mill phthalocyanine colors in water had been unsuccessful, it was considered desirable to review some of this work after it was demonstrated that particle size reduction could be brought about in the HF mill in water. The poor results obtained by ball milling with water alone or with water plus Blancol were amply confirmed. However, when both Blancol and borax were introduced in the ball mill, the results of the grind were markedly superior to anything hitherto obtained with either pure water or with either agent alone. It was also found that borax would similarly improve the results obtained with a number of other dispersing agents, among which Brij. 35 (Atlas Powder Company) gave results substantially comparable to those with Blancol. Carboxy methyl cellulose was also similar to Blancol in this process. Several materials were tried in place of the borax, and only trisodium phosphate showed comparable properties.

In spite of a considerable number of experiments with this type of ball mill operation, there seemed to be a limit beyond which significant particle size reduction was not obtained, and this limit was still very much weaker than the product which could be obtained by HF milling in the normal manner. A limited amount of work on the green was even less successful than the experience with CPC/LB. Accordingly, this work was discontinued, and there is no apparent reason for giving it further attention.

EXPERIMENTAL DETAILS

The experiments reported herein are recorded in the following notebooks.

N.B. 1191
1345
1383
1393
1404
1424
1439

This information is classified in more detail as follows:

CPC-LB - BASIC STUDIES AND DISPERSED PASTES

1191 - 26, 50, 53, 55, 66, 71, 78

1345 - 42, 51, 54, 69, 100, 103, 107, 108, 110

1383 - 1, 8, 11, 15, 16, 22, 26, 28, 33, 35, 44, 46, 55, 57, 58, 63, 65, 67, 68, 69, 72, 73, 74, 77.

1393 - 10, 12, 61, 74.

1404 - 2, 6, 7, 11-20, 22, 25, 29, 32, 34, 56, 57, 60, 63.

1424 - 1-4, 6, 10, 11, 14-22, 24, 33, 37, 40, 42, 45, 50, 51, 53, 55, 56,58, 60, 62, 63, 67-70, 72, 74, 76.

CPC-GREEN - DISPERSED PASTES

1393 - 14, 35, 38, 45, 49, 59, 66, 71, 75, 76.

1404 - 4, 23, 24, 27, 31, 35-41, 44-55, 57, 58, 64.

1424 - 5, 7, 9, 23, 34, 35,36, 38,39, 41, 48, 59, 64, 75.

1439 - 16, 17, 24, 27, 36, 38-42, 45.

W.D. LAKES - CPC BLUE

1383 - 56, 61, 75, 81, 83, 84, 85, 88, 89, 90

1393 - 4, 6, 7, 9, 57, 62.

1404 - 21, 33, 34.

1424 - 29, 30, 54, 60.

W.D. LAKES - CPC GREEN

1383 - 86

1393 - 4, 9, 14, 17, 26, 40, 45, 46, 47, 50, 54, 58, 59, 60, 64, 65, 67, 75.

1404 - 5, 43, 65.

1424 - 44, 47, 52, 57, 59, 61.

OTHER LAKES

1383 - 80

1393 - 29, 42, 44.

1404 - 1, 26, 28, 30.

1424 - 12, 13, 28, 46.

1439 - 19, 32.

CPC-BG - DISPERSED PASTES

1393 - 57

1424 - 65, 66, 73

1439 - 4.

DRY COLORS

1424 - 45, 50, 51, 53, 55, 76.

1439 - 2, 5-11, 13, 14, 15, 18, 21-26, 28, 29, 30, 34, 35, 37, 43, 44, 46, 59, 64, 68, 69, 70.

BALL MILL STUDIES IN WATER

1383 - 12, 18, 19, 25, 29, 32, 36, 37, 41, 42, 43, 45, 47, 53.

1393 - 28, 36, 39.

TABLE I

CPC GREEN W.D. LAKES - S.W. DEVELOPMENT

S.W. Lot	2593	2595	2596	2597	2598	2600	2604	2628	2642	2647	2651	2665	2673	2678
Equipment	Drill Press 13 gal	Cowles 22 gal							Drill Press 13 gal	Cowles 25 gal			Cowles 13 gal	Cowles 13 gal
Speed-RPM	700	1750						1500	715	1500	1500		1500	1500
Discs	2+9"	8"					10"	10"	2+9"	8"	10"		10"	10" toothed
Crude Lot	C1-331							C1-417						
# Crude	4	8	7	10	10	10	10	8	4	8	8	8	5	5
# Blancol	2.5	5	4.5	6	6	6	6	5	2.5	5	5	5	3.1	3.1
# Borax	40	80	Re-use + 10	Re-use + 30	100	100	100	80	40	80	80	80	50	50
P.S.I.														
1/2 hr.	19.1	22.8	17.1	20.6	24.7	22.5	20.1	20.0	16.6	27.4	18.4	15.5	14.2	14.5
1 hr.	15.9	18.5	13.6	18.0	20.7	17.7	18.2	16.1	12.4	18.5	13.8	12.3	10.8	10.3
1-1/2hr.	13.2	15.1	-	-	-	-	-	-	9.7	17.2	11.3	10.1	8.7	8.5
2 hrs.	11.4	13.6	8.9	13.1	14.6	13.6	13.2	11.7	8.5	16.0	9.7	8.6	6.6	7.0
3 hrs.	8.4	9.5	6.6	11.1	11.6	10.5	10.4	9.6	6.6	13.3	7.5	6.4	4.9	5.1
4 hrs.	6.7	10.6	5.4	9.6	10.5	8.6	9.2	8.1	5.0	11.8	6.0	5.0	3.8	4.5
5 hrs.				8.9	9.2	8.2		6.9	4.2	10.1	5.0	4.5	3.1	3.6
6 hrs.								5.9	3.6	8.8	4.3	4.0	3.0	3.2
7 hrs.								5.6						
8 hrs.								5.0						
Strength vs GP-511-D	vs str.	OK	s.str.	str.	s.str.	vs str.	vs weak	str.	str.	weak OK when dextrin added	O.K. str. with dextrin	str.	str.	str.

TABLE II

CPC-LB DISPERSED PASTE - S.W. DEVELOPMENT

S.W. LOT	2546	2547	2861	2862	2871	2872	2873	2880	2881	2977
Equipment	Drill Press		Cowles							
	13 gal.	13 gal.	13 gal.							
Speed-RPM	700	700	1500							
Discs	2+9"	2+9"	10"							
Crude Lot	439	439	S.W. 2789							
Lb. Crude	4	4	5	5	5	5	5	10	15	12
Lb. Blancol	0.2	0.4	0.5	0.25	0.5	0.25	0.5	1	1.5	0.6
Lb. Borax	40	40	50	50	50	50	50	50	50	60
Power(amps)	-	-	2.5	3-3.3	2.5	3.3	3-3.5	2.7-3.0	3.4	-
P.S.I.										
1/2 hr.			8.5	9.6	6.9	10.2	7.8	10.5	11.5	16.
1 hr.			6.6	9.1	6.0	9.6	6.1	8.0	9.5	13.2
1-1/2 hr.			5.9	10.4	5.7			7.7	8.3	-
2 hrs.			5.8	9.8	6.2			6.5	7.7	12.5
2-1/2 hrs.								5.2	7.2	-
3 hrs.								5.5	6.8	11.9
3-1/2 hrs.									6.8	-
4 hrs.									6.3	10.1
Use DPG	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Strength vs BT-321-P	O.K.	Could not be filtered	str.	str.	str.	str.	str.	str.	str.	± equal

DUP050069414

TABLE III

CPC GREEN - DISPERSED PASTE - S.W. DEVELOPMENT

S.W.LOT NO.	2696	2758-1	2758-2	2758-3	2769-1	2769-2	2769-3	2769-4	2802-1	2802-2
Equipment	Cowles 13 gal.									
Speed-RPM	1500									
Disc	10"									
Crude Lot	CL-417									
Lbs.Crude	5	5	5	5	5	5	5	5	5	5
Lbs.Blancol	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.5	0.5
Lbs.Borax	50	50	Re-use + 7.5	Re-use + 7.5	50	Re-use + 20	Re-use + 9	Re-use + 6.5	50	Re-use + 15
P.S.I.										
1/2 hr.		15.4	17.9						15.7	14.5
1 hr.		12.5	15.4						10.9	10.4
1-1/2 hr.		11.0	14.2						8.5	8.3
2 hrs.		12.8	14.0						7.3	7.2
2-1/2 hrs.									7.0	7.0
3 hhrs.									7.3	7.3
Strength vs GT-689-P	strong	str.	str.	str.	vs.str.	vs.str.	weak (?)	vs.str.	str.	str.

DUP050069415

TABLE IV

CPC GREEN DISPERSED PASTE - COWLES 100 GAL. UNIT

	2806	2816	2831	2838	2839	2856	2857	2867	2885	3058	3059
Crude Lot	Cl-417	Cl-417	Cl-417	Cl-417	Cl-773	S.W. 2850	S.W. 2851	Cl-773	Cl-773	S.W. 3060	S.W. 3060
Lbs.Crude	70	75	75	75	75	75	75	75	75	120	120
Lbs.Blancol	7	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	12.	12.
Lbs.Borax	700	220	175	250	107	113	178	750	160	29	268
Borax in sludge	-	530	575	502	643	637	572	-	590	571	332
Disc.	18" Cowles	18" Cowles	18" Cowles	18" smooth 22" "	22" smooth	22"	22"	22"	22"	22"	22"
Ave.Power	25-35 amps.	23 amps.	25 amps.	30	34-36	30-35	40	25-26	35	35	30-34
P.S.I.											
1/2 hr.	20.5	15.75	12.7	12.0	14.2	12.8	14.3	21.1	11.2	16.4	17.2
1 hr.	17.8	12.7	10.0	10.6	10.4	10.0	10.3	15.5	8.9	12.5	13.7
1-1/2 hr.	15.9	10.75	8.8	8.6	8.6	8.5	9.1	12.0	8.8	10.9	11.5
2 hrs.	13.6	9.6	8.3	8.2	8.0	8.1	8.9	10.3	8.2	9.9	10.2
2-1/2 hrs.	11.0	-	-	8.5	7.8	7.9	9.3	9.4	8.0	10.2	9.5
3 hrs.	9.3	8.3						9.1		10.2	9.3
4 hrs.	7.3										
Strength vs GT-675-P	strong	str	str	±equal	±equal	str.	±equal	s.str.	s.str.	str.	str.

DUP050069416

TABLE V

CPC-LB DISPERSED PASTE - COWLES 100 GALLON UNIT

	2893	2895 S.W.	2900 S.W.	2909	2910	2918	2931 S.W.	3055 S.W.	3056 S.W.
Crude	10026	2892	2789	20003	20002	20001	2906	3057	3057
Lbs.Crude	75	75	120	75	75	120	120	120	120
Lbs.Blancol	7.5	7.5	12	7.5	7.5	12	12	12	12
Lbs.Borax	750	350	86	131	141	-	59	227	102
Borax in sludge	-	400	664	619	609	627	541	523	498
Disc	22"	22"	22"	22"	22"	22"	22"	22"	22"
Ave Power	30	33	28	30	32	26	30	38	30
P.S.I.									
1/2 hr.	9.4	7.6	11.3	-	-				
1 hr.	7.0	6.2	10.2	-	-	8.1	8.4	9.2	10.4
1-1/2 hr.	5.9	5.7	8.6	5.8	-	7.0	7.7	-	-
2 hrs.	5.4	5.4	7.4	5.3	-	6.1	7.0	6.8	7.8
2-1/2 hrs.	5.7	-	6.8	-	-	5.5	6.5	-	-
3 hrs.	-	-	6.3	-	-				
3-1/2 hrs.	-	-	6.0	-	-				
Strength vs BT-321-P	strong	str.	str.	str.	str.	str.	str.	str.	str.

TABLE VI

CPC-LB - S.W. DEVELOPMENT OF DRY COLORS

	2977	3118	3130	3167	3177	3178
Equipment	Cowles 13 gal.					
Speed-RPM	1500					
Disc.	10"					
Lbs. Crude Lbs. Borax	12 60	12 60	12 60	6 60	6 60	6 60
Dispersing Agent	Blancol	Pontamine Fast Turquoise 8GL		Indulin XS-3		
Amount	0.6	1.2	1.2	0.6	0.6	1.2
Strength 1/2 hr. 1 hr. 2 hrs. 3 hrs. 4 hrs. 6 hrs.						
Final Str. vs BT-284-D	weak	weak	weak	weak	105	weak