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PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Progress Report

The Finishing of Phthalocyanine Pigments II. Wet Grinding Studies

Period Covered: November 6, 1945 to July 31, 1946

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SUBMITTED BY: A. J. Stratton A. Stratton 8/2/46

APPROVED BY: D B Killian 8/2/46

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INTRODUCTION

For a full statement of the problems involved in this study and of the historical backgrounds thereof, reference is made to KN-46-19 which is the first report in this series. The experimental work coveredin the present report includes much work carried on at the same time as that reported in KN-46-19, as well as substantially all work on the finishing of phthalocyanine pigments by wet grinding methods subsequent to the date of that report and up to the end of July 1946.

SUMMARY AND CONCLUSIONS

1. Polychlor Phthalocyanine Greens

Attempts to finish phthalocyanine green pigments by grinding in water have been completely unsuccessful. In no case was there any significant improvement in strength and in most cases there was a serious loss even from the starting crude. On the other hand, this pigment has been successfully ground to a strength comparable to that of our present standard GT-486-D in a variety of organic solvents. The best results were obtained in hydrocarbons such as mineral spirits or kerosene and in the presence of a substantial amount of an inorganic salt such as sodium sulfate. It is proposed to use such a process in subsequent manufacturing operations.

The use of water soluble polar solvents such as various alcohols has given a satisfactory rate of grinding but their use in other than anhydrous conditions in the presence of iron, such as in iron containers, or with iron balls,has resulted in a serious discoloration of the green pigments.

Altho most of the work has been carried on with a crude green obtained from Orchem and made by chlorination in an aluminum chloride/sodium chloride melt, enough work has been done with green chlorinated in sulfur dichloride at Newark to demonstrate that the only problem peculiar to this type of pigment is a tendency to more serious corrosion of the equipment. It is believed that this problem can be overcome by proper treatment of the crude prior to grinding.

2. Chlorine Free Copper Phthalocyanine Blue

In contrast to the green, copper phthalocyanine blue crude pigment has been significantly improved in strength by grinding in water but, to date, no such grinds have given the degree of improvement necessary for commercial utilization.

Water soluble polar solvents, such as the various alcohols and Cellosolve, have been used in grinding the blue with a fair amount of success even in the presence of substantial amounts of water. One such sample was fully equal to our current standard BT-172-D in strength but, in general, the results with the chlorine free blue have left considerable to be desired.

Although kerosene and mineral spirits have given very excellent grinds up to a certain point (approximately 70% of standard strength), the problem of so-called "crystal growth" of chlorine free copper phthalocyanine in the presence of hydrocarbon solvents has made itself felt and

it has been impossible to obtain the desired strengths with this type of product.

Numerous attempts have been made to stabilize the chlorine free blue by the introduction of various agents or substituted phthalocyanines, but the only method showing any hope of practical application in a solvent grinding process of finishing the pigment has been the synthesis of a blue containing a substantial amount of chlorine. This may be done either thru the use of phthalonitrile and copper salts or thru the phthalic anhydride/urea synthesis in which an appropriate amount of 4-chlor-phthalic acid replaces its equivalent of phthalic anhydride.

I.C.I. uses the latter process to make "Monastral" Blue LB and both the process and terminology have been adopted for use at Newark.

Various methods of carrying out the grinding steps have been studied but the only successful one to date has been the use of a ball mill.

3. "Monastral" Blue LB

With the synthesis of "Monastral" Blue LB at Newark the difficulties in grinding to the desired strength in hydrocarbon solvents have been overcome, and substantially all batches of Blue LB made in this laboratory have been successfully ground to a strength at least equal to that of BT-172-D and most of them have been carried substantially above this point. Since nearly all of the work has been done with kerosene-containing filter cake from the reactor, no successful grinds have been made in water, altho some work in this direction is contemplated for the future. Some successful grinds have been made in alcohol and Cellosolve but this work has been extremely limited.

The evidence favoring a choice of hydrocarbon solvents between kerosene and mineral spirits (or others) is not yet clear-cut. The balance seems to lie between some evidence of a slight quality improvement with the use of kerosene and the much more ready removal of the lower boiling mineral spirits. The latter feature currently favors the use of mineral spirits and it will probably be used unless the quality advantage from the use of kerosene is shown to be substantial. This point is still under study.

It has been demonstrated that the initial increase in strength, up to that of BT-172-D or slightly above, is obtained very rapidly in a ball mill, in less than 24 hours in some cases and in a maximum of 2 to 3 days in laboratory equipment. Prolonged grinding does give some further increase in strength with a maximum of about 120% that of BT-172-D obtained to date. There has been no evidence of harmful results from prolonged grinding.

It has been demonstrated that the quality of the final dry pigment is significantly effected by the methods used in removing the solvent and extracting water soluble impurities. A tendency to slight greenness seems to be characteristic of all "Monastral" Blue LB samples and many of the solvent ground products have shown a significant tendency

to dullness particularly in undertone. However, the best samples obtained have not been dull and have been only slightly green. Therefore, there is every reason to hope that the final product from this development at Newark will be in every way the equal of BT-172-D in quality except for a very slight greenness of shade and will be significantly stronger.

4. Unsolved Problems

It is believed that the major unsolved problem in this development is that of the proper method of separating the finished pigment from the solvent paste after grinding. Altho the process temporarily adopted for use is reasonably duplicable, it is not satisfactory from an operational point of view and there appear to be many points of uncertainty. Furthermore, no satisfactory method has yet been developed for obtaining pigments in a water dispersible form either as water pulp or as water dispersible dry pigment. A part of this same unsolved problem is the preparation of a "Ramapo" Blue and there is some reason to hope that this can be accomplished without the isolation of a pigment pulp as a semi-finished product.

PATENT SITUATION

A recent expensive search of the patent art on phthalocyanine (See KN-46-54) disclosed that all phthalocyanine patents necessary for the operations at Newark are either owned by DuPont or licensed to their use. Furthermore, it is believed that all practical processes for the manufacture of phthalocyanine pigments are dominated by patents controlled by DuPont and with a minimum of nine years in any important case before expiration.

No disclosures of finishing phthalocyanines by grinding in solvents other than water have been found. Furthermore, a casual search of the pigment art, coupled with a fairly extensive knowledge thereof, has failed to disclose any bars to the use of solvent grinding methods and, pending a more extensive search of the art which is contemplated for the near future, it is believed that solvent grinding as a finishing method for phthalocyanines is probably patentable and that it may well be patentable in a broader sense. All other aspects of the process currently contemplated at Newark appear to be disclosed in the art and, therefore, unpatentable.

DETAILED DISCUSSION OF THE RESULTS

As pointed out in KN-46-19, the original objective in this study contemplated the use of a closed circuit wet grinding process, preferably using water as the suspending medium, involving elutriation methods of classification to obtain the desired particle size. As also pointed out in this report, a careful theoretical study of elutriation methods as applied to phthalocyanine pigments soon demonstrated the impracticability of such a process. Nevertheless, wet grinding methods of finishing phthalocyanines were studied further on a batch basis, first with water as the suspending medium and later with a number of other solvents as will be pointed out in more detail below.

1. Polychloro Phthalocyanine Green

Attempts to grind phthalocyanine green in ball mills and other devices with water as the suspending medium have been completely unsuccessful. With water alone there is invariably a loss in strength which progresses with prolonged grinding. This loss in strength is found both with a crude green and with a product of full strength such as our standard GT-486-D. In the case of the standard, the strength resulting from a relatively short grind was actually less than that of a normal crude. The cause of this loss in strength is not known with certainty but, since it was later demonstrated that such products which have lost strength could be subsequently ground to full strength in other media, it would appear that no chemical change occurred and that the loss in strength must have been the result of a physical phenomenon, probably agglomeration. By means of the use of certain dispersing agents, such as ammonium naphthenate, it was possible to inhibit this loss in strength to some extent but, in no case, was a significant improvement obtained.

With the failure to obtain the desired results using water as a suspending medium, attention was turned to the use of other readily available liquids with particular emphasis on the use of low cost hydrocarbon solvents such as kerosene and mineral spirits. It was quickly demonstrated that either of these liquids could be used in a ball mill grinding operation to get a relatively high rate of strength development and an ultimate strength equal to or better than that of GT-486-D. Using small scale laboratory equipment the desired strength was obtained in from 3 to 4 days of total grinding time. Much less time can be anticipated in larger mills.

In view of the low boiling point of mineral spirits and the greater ease of removal from the ground paste, it is presently preferred over kerosene for this operation. Some study of the use of treating agents with the mineral spirits has indicated that a small amount (about 5%) of an organic acid such as naphthenic acid promotes the efficiency of grinding.

In view of the known use of salt milling operations in the finishing of phthalocyanines in which a mixture of pigment and an inorganic salt, such as sodium chloride or sodium sulfate, is dry-ball milled to obtained high strength, some study was made of the use of such salts in the presence of mineral spirits. The results indicated that, in the case of the green, a pronounced beneficial effect resulted from this combination use, that ammonium chloride or sodium sulfate gave better results than sodium chloride and that these two were substantially equal in their effect. The presently preferred process involves the grinding of approximately equal parts of pigment and sodium sulfate in mineral spirits.

A limited amount of work was done on the use of such water soluble polar solvents as methanol, ethanol, isopropanol, and cellosolve. When used in non-metallic equipment, these agents appear to be satisfactory grinding media. But in the presence of any appreciable amount of iron, there is a serious tendency for the pigment to become very much bluer and this tendency is promoted by the presence

of water. It has been assumed, without any rigid proof thereof, that this change in shade is caused by a certain amount of dechlorination of the pigment under the conditions used. However, regardless of the explanation, the change in shade is so serious as to preclude the use of these solvents for grinding greens in equipment now contemplated for use.

Most of the studies on grinding phthalocyanine greens were made with a crude green pigment obtained from Orchem and made by chlorinating phthalocyanine blue in an aluminum chloride/sodium chloride melt. However, several grinds were made of green made at Newark by chlorinating in sulfur dichloride, and the resulting pigments were at least equal to, and in some ways superior to, products obtained by acid pasting the same crudes. All of these products were distinctly bluer than our standards but the degree of blueness was not noticeably influenced by the method of finishing. One problem did arise which may be serious on a large scale and that is, a noticeable degree of corrosion of the grinding equipment when any of the mineral spirits slurry is allowed to dry in contact with it. This was presumably caused by residual by-products of the chlorination and we believe it can be overcome by proper treatment of the crude pigment prior to grinding.

Early in the study of grinding in the presence of water, attempts were made to grind mixtures of the crude pigment with certain water soluble extenders, such as whiting, blanc fixe, or alumina hydrate. The first indications were that a substantial improvement in strength had been obtained but a careful evaluation of the testing method demonstrated the hitherto unrecognized fact that, apparently, all phthalocyanine pigments will exhibit a greater tinctorial strength when ground with a vehicle in the presence of these extenders than can be obtained from the equivalent amount of toner pigment in the absence of the extenders. The phenomenon appears to hold true with either full strength or crude pigment and with both the blue and the green. Thus, if our standard GT-486-D is tested by rubbing out a mixture of one part standard and three parts of alumina hydrate in a lithographic varnish, and a tint of this mixture is compared with a tint of the same standard rubbed in the absence of alumina hydrate, so that the two samples of tint contain the same amounts of standard green pigment, that sample rubbed in the presence of alumina hydrate will show in the order of 15% additional strength. Most of the so-called extender type pigments exhibit this phenomenon as well as many inorganic salts such as sodium chloride, ammonium chloride, and sodium sulfate. It seems to be a very strange fact that the prime white pigments, such as zinc oxide, lithopone or titanium dioxide fail to exhibit the effect. No practical application of the observation has yet been made but it suggests that extended phthalocyanine pigments may have an economic advantage not heretofore recognized. It was, however, an extension of this observation in which the lithographic varnish was replaced by a volatile solvent and the extender was removed by chemical means that the first indication of merit in the use of hydrocarbon solvents as grinding media was obtained.

2. Chlorine Free Copper Phthalocyanine Blue

The only phthalocyanine blue pigment available in crude form for use during the early part of this study was a sample of chlorine

free blue obtained from Orchem and made thru a phthalic anhydride/urea synthesis carried out in trichlorbenzene as the diluent. Subsequently, a similar product made at Newark in kerosene was given some study with essentially the same results as originally obtained on the Orchem material.

As with the green, the first attempts to grind the blue were made using water as the suspending medium. In contrast to the green, a significant improvement in strength was obtained in nearly every instance but, in general, it fell far short of the desired degree of improvement. The most promising results were obtained with large amounts of dispersing agent (upwards of 25%) such as ammonium rosinate and petronate. In these cases, the pigments were so completely dispersed that it was necessary to flocculate them by precipitating the dispersing agent before they could be filtered. Consequently, the resulting pigments were no longer toners but were extended with significant amounts of the precipitated dispersing agent. When tested on the basis of their theoretical toner content, some of these pigments did approach very near to standard BT-172-D in strength.

An extensive study was made of the use of surface active agents in water grinds using 5% ammonium naphthenate as the control. No agent was found which was superior to ammonium naphthenate in this amount but the following agents seemed substantially equal thereto.

tetra sodium pyro phosphate	polydioxolane
soda ash	amino-capronitrile
tri-sodium phosphate	ammonium benzoate
sodium meta-silicate	

The following agents gave results poorer than those obtained with ammonium naphthenate.

Alkanol B	Atlas Spans & Tweens
Duponol WA	Aerosol OT
Lauryl amine hydrochloride	Fixanol
Igepal CA	Diglycol stearate
Polyethylene oxide	Turkey Red Oil
MT-189	Petronate (5%)
$TEAC_{12}$ ester	

Altho these results suggest that a way might very probably be found to obtain the desired degree of grinding in water, at the time the use of other solvents appeared to offer greater promise of a prompt solution to the problem and the study of grinding in water was eventually dropped.

The very promising results of grinding the green pigment in hydrocarbons, such as mineral spirits and kerosene, led to a comparable study with the chlorine free blue. With the solvent in a ball mill the strength development was very rapid up to approximately 70% that of standard BT-172-D but all efforts to exceed this strength level with

hydrocarbon solvents were fruitless. The conclusion was eventually reached that the so-called "crystal growth" problem characteristic of chlorine free blue was influencing the grinding rate and the 70% strength level probably represents the balance between rate of crystal growth and rate of particle size reduction in the grinding step.

A study of the use of treating agents to improve the rate of grinding in mineral spirits demonstrated that a number of organic acids, such as naphthenic acid, oleic acid, stearic acid, benzoic acid and K Wood Rosin could be used to obtain a slight improvement in grinding rate. The use of 5% naphthenic acid based on the pigment content of the grind has been adopted for most of the subsequent work.

It is an interesting and important comment on the behavior of chlorine free blue in hydrocarbon solvents that, when full strength blue pigments obtained either by acid pasting or salt milling are ground in mineral spirits, the pigments actually lose strength ,ending up at substantially the same level as is reached by grinding the crude. This point has been repeatedly confirmed with chlorine free blues.

A study was also made of the use as a suspending medium in ball mill grinding of a number of water soluble polar solvents, such as methanol, ethanol, isopropanol and cellosolve, both in relatively anhydrous condition and in the presence of substantial amounts of water. One grind made in ethanol containing some water gave a product fully equal to BT-172-D in strength, but this has not been repeated and all other attempts have fallen short of the goal. Nevertheless, grinds in this type of solvent with chlorine free blue have,in general, given higher strengths than have been obtainable with mineral spirits. There has been no evidence that anhydrous solvents were significantly better than the same solvents containing some water and, in the case of cellosolve, mixtures of water and cellosolve were better than either one alone. Very little attention was given to the use of dispersing agents in these solvents.

In addition to the superior results obtained with this type of solvent (still short of the goal) they offer the possibility of much more easy isolation of the finished dry pigment and the probability of obtaining a much better water pulp because of their ready solubility in water. On the other hand, they are inherently more expensive than hydrocarbons, the recovery problem is somewhat greater because of the necessity of distilling larger volumes of liquid to remove them from the water in which they are soluble, and a serious corrosion problem is presented when they are used in iron ball mills.

It is noteworthy that the addition of inorganic salts such as sodium chloride or sodium sulfate to ball mill grinds of the blue pigment in any solvent have in no case given the same beneficial results as were obtained with the green. This is difficult to understand but the results of a number of tests have been so consistent as to leave little doubt of the validity of this conclusion.

A number of different devices have been examined for obtaining the desired grinding action. As noted above, the first indications of benefits in grinding with hydrocarbon solvents were obtained in rubouts, mostly made on a Hoover Muller. Consequently, a number of large scale devices using similar grinding principles have been tried.

A major improvement in strength was obtained by grinding a mixture of pigment and either sodium chloride or sodium sulfate with mineral spirits on a roller mill. However, the operation was extremely unsatisfactory from a mechanical point of view and the strength obtained was no better, if as good, as obtained in a ball mill without the salt. The use of glycerine as the vehicle in place of the mineral spirits gave a much more satisfactory mechanical operation and a relatively easy separation of the pigment because of the water solubility of the vehicle but the results were still far short of the goal. It does not seem that any practical operation can be developed on a roller mill.

Similar attempts were made to use a Banbury mixer with absolutely no evidence of improvement in strength in the absence of a crystalline salt and only minor improvement in the presence of the crystalline salt. These results did not encourage further study of the Banbury mixer.

A study was made of the use of a Marco Kombinator. This machine is essentially an efficient gear pump which forces the material under very high pressure thru the plates of a colloid mill. Studies were made in kerosene, anhydrous alcohol and water both with the pigment alone and with extenders such as sodium sulfate and alumina hydrate. Only minor improvements in strength were obtained and, in any case, the machine appears impractical for the proposed operation.

A study was made of grinding the crude blue with extenders in a Gemco blender with no significant evidence of improvement in strength.

These studies of various grinding devices confirm the original choice of ball mills for the operation as a wise one. Substantially, all subsequent work has been carried on in this type of equipment and some investigation of the merits of various types of ball mills will be reported below.

In view of the known behavior of chlorine free copper phthalocyanine in the presence of hydrocarbon solvents, referred to above, and in view of the demonstrated inability to grind it to full strength in such solvents, a considerable study was made of methods of stabilizing the blue against the action of these solvents. It is already known that a product containing from 1/2 to 1 atom of chlorine per molecule of copper phthalocyanine is relatively stable to the action of hydrocarbon solvents. Altho such products are easily made by way of the phthalonitrile synthesis they are not so readily made in the phthalic anhydride/urea process. However, a sample of the crude "semi-chlor" copper phthalocyanine made by Orchem from phthalonitrile and cuprous chloride was ground in solvents, and, for the first time, satisfactory strength relative to BT-172-D was obtained. Equally good results were obtained in kerosene, mineral spirits, alcohol and cellosolve. This was the first convincing evidence

that the solvent grinding method for finishing the blue was on a sound basis but, since Newark had only academic interest in this type of crude, it has not been investigated extensively.

Orchem has demonstrated that co-salt milling of a mixture of tin dichloride phthalocyanine and chlorine free copper phthalocyanine results in a finished pigment which is apparently stable to the action of hydrocarbon solvents. Attempts were, therefore, made at Newark to co-solvent mill these products but without any success. Co-synthesized products of the same chemical composition were equally unsatisfactory in the solvent milling process. For that matter, Newark has been utterly unable to confirm the benefits of co-salt milling in samples prepared at Newark. However, we have confirmed the properties of samples submitted by Orchem, but there are certain apparently inherent properties in these samples, such as reactivity and some chemical instability, which reduce their interest for our uses and this method of attack has been dropped.

Certain methods of introducing chlorine into the molecule, such as synthesis in the presence of a small amount of polychlor copper phthalocyanine and synthesis in the presence of a small amount of tetra chlor phthalic anhydride, gave products which were not satisfactory in solvent grinding procedures. Other methods of synthesis were also tried unsuccessfully and these will all be reported in more detail in another report. It was only when the I.C.I. process for "Monastral" Blue LB (involving the introduction of about 4% of chlorine thru the use of 4-chlor-phthalic acid in place of its equivalent of phthalic anhydride) was used at Newark that a product synthesized via the phthalic anhydride/urea route was obtained that could be satisfactorily ground in hydrocarbon solvents. With only one or two exceptions, and these readily explainable, all products synthesized at Newark by this process have been successfully ground to the strength of BT-172-D or better.

3. "Monastral" Blue LB

The first LB type copper phthalocyanine blue crude was made available for grinding at Newark near the end of March 1946. It was immediately demonstrated that such products could be ground in either kerosene or mineral spirits to the desired strength in a reasonable period of time. All such products have been made at Newark using 4-chlor-phthalic acid of our own manufacture and, for the most part, have been made using kerosene as the diluent. They have been made available for grinding either as a kerosene slurry from the reactor or, more generally as a filter cake containing on the average about 40 to 45% of CPC, a total solids content of about 65 to 70% and about 30 to 35% kerosene. The physical appearance is that of a slightly wet granular solid.

In view of the kerosene content of the material available for grinding, no successful grinds have been made to date using water alone as the suspending medium. Some study is contemplated for the future along this line involving the removal of the kerosene from the presscake prior to grinding.

A limited amount of work has been done on the use of isopropanol and cellosolve as the solvents for grinding. Satisfactory grinding was obtained with these solvents even when the cellosolve was mixed with an appreciable amount of water but the residual

kerosene in the filter cake used for grinding posed a problem in the removal of the solvent by drowning in water. The other disadvantages pointed out above as inherent in the use of such solvents were also present. Their use has not been followed up, altho it seems probable that some of the serious problems, which will be pointed out as apparently inherent in the proper separation of impurities from the pigment ground in kerosene or mineral spirits, may not be present with these solvents.

Except for this limited work on the use of water and of alcohols, all of the grinding studies with "Monastral" Blue LB have been made in either kerosene or mineral spirits and in ball mills. The choice of these solvents is dictated by a relatively low cost and by sufficiently high boiling points to minimize fire hazards in the operation. Since kerosene is the diluent in the reaction, it is the logical solvent for the grinding operation, particularly if it is possible to grind the reactor slurry without filtration. On the other hand, it is notably difficult to remove the last traces of kerosene by steam distillation or, for that matter, by any evaporative process. On the score of the ease of solvent removal alone, mineral spirits is greatly to be preferred and it has even been proposed to remove the residual kerosene from any reactor cake by washing with mineral spirits after filtration. It has likewise been suggested that an even lower boiling solvent, such as VM & P naphtha should be used but no trials in this direction have yet been made. A final choice between these two solvents is not yet possible and will unquestionably be influenced by both the quality of the finished product and the ease of solvent removal. Unless a substantial quality advantage can be demonstrated in the use of kerosene, it is highly probable that the more easily removed mineral spirits will be the ultimate choice. Temporarily, it has been selected as the solvent for routine experiments. It is interesting that the best products made to date have all been ground in kerosene; yet in a number of direct comparisons of the two solvents, only one of them has shown any outstanding superiority in the use of kerosene.

No comprehensive study has yet been made of the use of dispersing agents in the mineral spirits grinds but several agents have been tried on occasion. Confirmation has been obtained of the beneficial effect previously observed with the use of about 5% naphthenic acid (based on the pigment) in the mineral spirits. This has been tentatively adopted as a standard procedure. Other agents tried include Aerosol OT, $TEAC_{12}$, and Glyceryl Monoricinoleate. The only beneficial effects observed by the inclusion of these other agents in the grinds, not obtainable in other ways, have been that certain combinations, particularly that of Aerosol OT with either of the other agents, result in a materially lower viscosity of the grinding paste than can be obtained with any agent alone. It is doubtful if this improvement alone justifies the use of the additional agent at this point. In one comparison of various types of ball mills for this operation, it was found that products ground in 1/2 pint glass jars using steel balls of 5/32" diameter reached their maximum

strength in from 4 to 5 days. In stirred ball mills of the "attritor" type (see KN-46-19 for a description of this apparatus) equivalent results were obtained in about 2 days. Attempts were made to grind in a larger ball mill, 6" in length x 12" in diameter, using 1/2" steel balls and equipped with lifter bars. It was not possible at Newark to drive this mill at a higher speed than about 30 RPM (approximately 1/2 the optimum speed). The maximum strength in this device was reached in about 2 to 3 days but it was considerably below that obtained in other devices. The reason for the poor results with this mill is not clearly understood but it is assumed to have been the result of the slow speed of the mill. A somewhat similar result was obtained with 1/3 gal. porcelain mills using steel balls in which it required from 200 - 300 hours to equal the results obtained in 1/2 pint jars in a much shorter time. One possible explanation is the peculiar thixotropic nature of the paste and its complete freedom from tackiness so that there may have been excessive slippage of the balls instead of the desired type of cascading action.

A similar study has been completed quite recently comparing the rate of strength development in 1/2 pint jars and in the stirred ball mill or "attritor", with essentially the same results. In this case the crude pigment used had a strength of approximately 65% that of BT-172-D before grinding. The following table summarizes the results of this study.

Time of Grind	Strength vs BT-172-D 1/2 pint jars	"Attritor"
0 (Crude 1213-29)	65%	65%
6 hrs.	-	92%
1 day	-	106%
2 days	-	112%
3 days	108%	116%
4 days	112%	-
5 days	115%	120%
6 days	115%	120%
7 days	116%	120%
10 days	116%	-

This study demonstrates that the initial improvement in strength to something approximating that of BT-172-D is obtained quite quickly, that an additional improvement of about 10% is still possible within a practical grinding time, that the last 5% or so of strength is obtained rather slowly and that the maximum strength obtainable with this sample is in the order of 120% that of BT-172-D. There was no evidence in this study of any harmful effects from prolonged grinding.

As the work has progressed on the finishing of "Monastral" Blue LB by solvent grinding, it has become quite evident that the real problem is not that of obtaining satisfactory strength but it is the problem of obtaining satisfactory tinctorial properties comparable to those obtainable by acid pasting or salt milling operations

on the same crude pigment. Three steps have been considered necessary in the isolation of the finished dry pigment from the ground slurry, namely the removal of the solvent, extraction of water soluble impurities in an acid medium and extraction in an alkaline medium, preferably ammonia. Whenever the solvent has been removed by simple evaporation to leave a dry product which is then slurried in water and given an acid and an ammonia extraction, the products have had, in general, entirely satisfactory strength but they have been distinctly dull both in tint and, more pronouncedly, in undertone. This type of pigment is characteristically greener than BT-172-D but the product finished in the way just described seems to be even more green than corresponding acid pasted products.

An alternative method for removing the solvent is that of steam distillation and it has the practical advantage of leaving the product in a water wet form and avoiding a rather nasty operation of wetting up a dry pigment.

The conditions under which the steam distillation of either kerosene or mineral spirits from the solvent ground paste is carried out appear to have a pronounced effect upon the quality of the resulting pigment. Simple removal of the solvent without the addition of any treating agent has not given results materially better than those obtained by removal of the solvent in an oven. However, if certain treating agents are added at the beginning of the steam distillation, or not later than the beginning of the acid extraction immediately following, the tendency to dullness has been, for the most part, completely eliminated. In the tentatively adopted process 5% each of $TEAC_{18}$ ester and Glyceryl Monoricineoleate have been used and added at the beginning of the steam distillation. There is some evidence that both agents are not necessary and that their presence during the acid extraction is all that is necessary but these points remain to be clarified in subsequent work. Whether the amount used is optimum and whether these are, in fact, the best agents for the purpose also remains to be clarified.

When steam distillations are carried out as described above, the operation is very unsatisfactory from a purely mechanical point of view because the first action of water and agitation on the hydrocarbon paste is to thicken it materially and then tends to break up into rather large balls and to stick badly to the sides of the container and the agitator. This results in a relatively small surface from which the solvent can evaporate and an extremely slow rate of solvent removal from the mixture. In those products ground in kerosene it is very doubtful if complete removal of kerosene has ever been obtained during the steam distillation step. Furthermore, the presence of the treating agent mentioned above seems to accentuate the difficulties of the operation and the dilemma is faced in which the more difficult operation gives the better result. Recently, however, it has been shown when the steam distillation is carried out in the that,

presence of a strongly alkaline suspension, as in the presence of caustic soda, many of these difficulties are overcome. Under these conditions there is very little tendency to ball up and there is no tendency to stick to the sides of the container or to the agitator. In the early stages, the product appears emulsified with a much greater surface for evaporation of the solvent and, in the later stages, much of the pigment appears to be completely dispersed in the suspension so that it does not settle out at all. Products made by this method have been excellent in quality, and, in view of the better operating conditions, it appears probable of adoption in the near future.

As pointed out above, under the Summary & Conclusions, it is believed that the details of this step of removing the pigment from the solvent paste and giving it the necessary chemical extraction remain as the most important unsolved problem in the development. This study is going forward rapidly and will probably be the subject of a separate report at a later date. Few, if any, of the water pastes obtained to date have been deemed satisfactory for many purposes for which a water paste is required and the preparation of such satisfactory pastes is also a part of the problem of satisfactorily separating the pigment from the solvent.

It should also be noted at this point that the details of the grinding step have not been given sufficient study to state with certainty that they are in any way optimum. It seems probable, however, these details will be much less critical than the steps of removing the solvent.

X-RAY STUDIES

Some attention has been given to the x-ray patterns obtained from CPC prepared in different ways and this has developed good evidence that two distinct patterns can be demonstrated. For purposes of convenience they have been arbitrarily designated as Pattern A & Pattern B and the following table indicates the conditions under which each appears to be obtained.

Treatment of Pigment	Cl Free CPC 0% Cl	Semi-Chlor from PN 2.6% Cl	Blue LB 4.4% Cl	Monochlor from PN 6% Cl
Crude	A	A	B	B
Acid Pasted	B	B	B	B
Salt Milled	B	B	-	-
Solvent Ground	A	A	B	B

The ultimate significance of these results is not now apparent but it is obvious that there is ground for much more study.

THE TENTATIVE PROCESS

Grinding

1/2 pint glass jars

600 gms steel shot
20 gms dry pigment (or 16 gms CPC in kerosene cake)
1 gm naphthenic acid (or 0.8 gms)
100 cc mineral spirits (or kerosene)
Grind for approximately 100 hours
Add 25 cc solvent and mix well
Strain from balls

"Attritor" (See KN-46-19)

1/3 gallon container with paddles or other device for agitation.
6000 gms steel shot
120 gms CPC in kerosene cake
6 gms naphthenic acid
500 cc mineral spirits (or kerosene)
(with an open container it is necessary to replace solvent lost by evaporation)
Grind approximately 50 hrs.
Dilute with solvent to suitable consistency and strain from balls.

Note

No detailed study has been made of the optimum ratio of pigment to balls, of the optimum viscosity of the paste nor of the optimum loading of the ball mills.

Steam Distillation

To a pigment paste containing 20 gms CPC is added approximately 500 cc water containing 10 gms NaOH, 1 gm $TEAC_{12}$ ester and 1 gm Glyceryl Monoricinoleate. Steam distillation is started and continued

until apparently solvent free (4-6 hours). In recent laboratory work simple vigorous boiling with a steam sparger in an open container in a well ventilated room has been used. At this point much of the pigment is in a highly dispersed condition and probably could not be filtered.

The mixture is then acidified with H_2SO_4 to approximately 3% concentration on the total slurry volume and boiling continued for 30 minutes. It is then filtered and washed acid free.

The filter cake is reslurried in 1000 cc water and NH_4OH added to give approximately 3% concentration (approximately 100 cc conc. NH_4OH). This slurry is boiled about 10 minutes, filtered and washed and the filter cake dried at a temperature of at least 200°F.

Note

No detailed study has been made of the optimum concentration of NaOH in the steam distillation nor of the optimum concentrations of acid or ammonia in the extraction. It seems highly probable that the treating agents are hydrolyzed by the boiling alkali and that a better and more economical combination can be developed.

The high temperature drying is necessary to remove residual solvent not removed in the steam distillation.

Evaluation of the Products

All evaluations have been made by the standard rubout procedure using a ratio of 1 part pigment to 2 parts lithographic varnish, ground 5 times 50 revolutions on a Hoover Muller. Extensions are made at a ratio of 1 to 100 in zinc oxide.

The best products by the above procedure have been from 15% to 20% stronger than BT-172-D and very slightly green. The masstones have varied considerably, some being lighter and some darker than BT-172-D. There is reason to believe that this variation is related to the use of the treating agents but the point has not yet been controlled. Undertones have seemed to appear greener than would be expected from the tint. Although the best products have not been significantly dull in undertone many samples have tended in this direction.

Texture evaluations indicate that these products are at least as good as BT-172-D in both grit and strength development and there is some evidence of superiority. It is noteworthy that the inks are definitely softer than BT-172-D, approximating "Ramapo" Blue BP-173-D in that respect.

Can stability tests indicate these products to be at least as good as BT-172-D and there is some evidence of superiority.

EXPERIMENTAL DETAILS

Complete experimental details and records of the evaluations of the products can be found in the following notebooks:-

NB-1186 - Exps. 1 - 75 inclusive
Pages 8 - 188 inclusive

NB-1206 - Exps. 1 - 58 inclusive
Pages 8 - 161 inclusive