-51-39 Phthalocyanine Plant Assistance By: P. D. Graham, Jr. 1/49-1/50

7) ~~Paul Griswold 3/3/82~~
(Newport)

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NEWPORT PLANT

Final Report

PHTHALOCYANINE PLANT ASSISTANCE

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NEWPORT PLANT

PIGMENT COLOR RESEARCH REPORT

FINAL REPORT

PHTHALOCYANINE PLANT ASSISTANCE

JANUARY, 1949 - JANUARY, 1950

P. D. Graham Jr.

SUBMITTED BY: P. D. GRAHAM, JR. DATE SUBMITTED: 6/8/51

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INTRODUCTION

Operation of the Newport CPC plant was started in April, 1948 under the surveillance of a Color Research Group temporarily assigned to this work. This arrangement was continued until January, 1949, at which time a Plant Assistance Group was established for the purposes of improving and standardizing the process, reducing costs and increasing production per unit investment. This report covers the work of the Plant Assistance group for the year 1949.

HISTORICAL

The Newport CPC plant was designed to produce two phthalocyanine pigments, "Monastral" Fast Blue LB and "Monastral" Green, at rates of 22,000# and 15,500#, respectively, per month in a five-day week. The processes are based on developments by Imperial Chemical Industries and the Organic Chemicals Department, as well as numerous modifications and additions resulting from work of the CPC Color Research Group at Newark.

The manufacture of Blue LB at Newport is based on the reaction, in a specially refined kerosene, of phthalic anhydride, urea and copper chloride, catalyzed with ammonium molybdate. A predetermined portion of the phthalic anhydride is replaced with 4-chlorphthalic acid to produce a low chlorine CPC (4-5%), which is stable to crystal growth in aromatic paint solvents. Concentrated sulfuric acid is added to the reaction slurry to sulfate the pigment and facilitate the separation of the kerosene. Following hydrolysis and a weak alkali extraction and drying, particle size of the pigment is reduced by shot milling in acetone to a standard strength level. The milled slurry is distilled to recover the solvent, and extracted with both weak alkali and acid. The finished product is shipped to Newark as a 15% slurry for the manufacture of toners, lakes and dispersed pastes.

In the manufacture of polychlor CPC ("Monastral" Green) the Blue synthesis is essentially the same as for Blue LB, except that 4-chlorphthalic acid is not used in the initial reaction. The crude CPC is chlorinated with sulfur chloride to 47-48.5% chlorine at elevated temperatures and pressures following which the crude Green is extracted, dried and acetone milled.

Provisions were not included in the original plant design for the production of "Monastral" Blue BG, which is solvent milled chlorine-free CPC. It was first produced at Newport in March, 1949, using Blue LB equipment with no revisions. The omission of chlorphthalic acid in the synthesis of Blue BG is the only major difference of operating technique between LB and BG.

SUMMARY AND CONCLUSIONS

A. "MONASTRAL" BLUE LB

The most serious problem encountered in the manufacture of 4-chlorphthalic acid, which is used as an ingredient for synthesis of Blue LB to provide the desired 4.0-4.5% chlorine content, was foaming

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during final acidification. The problem was greatly minimized by adjustment of pH and standardization of the quantity of sodium hydroxide used in preparing the solution of disodium phthalate prior to chlorination.

Production of Blue LB was frequently hampered by oxidation of the kerosene and the resultant failure of the CPC synthesis. The use of an anti-oxidant, such as Paranox 441 ex Esso Standard Oil Company, has been effective in preventing oxidation and is now standard practice. A peroxide number is determined on the kerosene prior to each synthesis and the specification requires that kerosene showing any measurable oxidation should not be used. Several trials, involving the substitution of a cheaper fuel grade of kerosene for the deodorized grade failed, because of operating difficulties.

A significant overall improvement in the sulfation operation was effected during 1949 by standardizing the volume prior to acid addition and adding the acid in 1-1/2 hours. A rather extensive study disclosed the acid requirement to be 1600 pounds 98% sulfuric acid per synthesis of 1071 pounds phthalic anhydride. Several plant attempts to use 93.0% sulfuric acid, which would offer a significant saving, failed because of unsatisfactory pumping and filtering characteristics of the slurry.

The solvent milling capacity was increased in 1949 in three steps to 102.5% of the designed project loading.

The finishing yield (solvent milling through extractions) was improved approximately 5% in 1949 by an intensified personnel training program and standardization of operating procedures.

The quality of Blue LB was satisfactory versus Newport shipping standards as shown in Exhibit (4).

B. "MONASTRAL" BLUE BG

The first plant production of the green shade chlorine-free phthalocyanine, Blue BG, which was made in March, 1949, was essentially equal in quality to the Semi-Works standard, BT-297-D. A total of 28,900 pounds of Blue BG was produced in 1949. A quality deficiency occasionally encountered in subsequent production was found to be due to inadequate cleaning of equipment, which resulted in contamination with Blue LB. A 17% increase in milling capacity was realized in the latter part of 1949 by increasing the mill loading 5% and decreasing the milling cycle from 36 to 30 hours.

C. POLYCHLORO CPC

The polychloro CPC unit was not operated from February 17 to April 1, 1949, because the process was not standardized and most of the production was exceedingly dull. It was also shut down from September 24 for the remainder of the year because of the inadequacy of fume disposal facilities.

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The quality of polychloro production in 1949 was uniform in strength, but varied considerably in hue and intensity, ranging from blue to yellow and dull to s. intense versus standard GT-486-D. Serious operating difficulties and inadequate control of the chlorination procedure were largely responsible for the fluctuations in quality. It was determined that sulfur chloride reflux during chlorination is necessary to produce the desired yellow shade. A number of chlorinations at pressures significantly below the designed 300 psi resulted in products considerably bluer than standard GT-486-D; however, the reflux condenser was not in service at the time.

A rather violent exothermic reaction in the chlorination step between antimony oxide (catalyst) and sulfur chloride (chlorinating agent), which was extremely difficult to control, resulted in a build-up of solid material in the reflux condenser and occasionally rupture of the autoclave safety disc. This difficulty was partially overcome by very careful addition of sulfur chloride.

A process change involving discharge of crude CPC Green from the rotating dryer directly into a hopper, rather than slurrying with water, resulted in a significant increase in rate of production.

Extraction of crude CPC Green was changed from sodium hydroxide to sulfuric acid and later to a water (actually acid) extraction during 1949. An increase in yield, less thixotropic presscakes and elimination of foaming resulted.

Production equal to goal strength, 83:100 versus GT-486-D, was obtained 85% of the time in 1949. The dullness of Newport production appeared to be associated with solvent milling. It was possible to develop a fairly good correlation between dullness and lack of sodium chromate at the end of milling. An increase in the quantity of chromate resulted in a significant reduction in the number of dull lots.

A sodium hypochlorite extraction, in addition to the standard sulfuric acid and ammonium hydroxide extractions, improved quality significantly; however, it was necessary to discontinue the hypochlorite extraction at Newport, since the equipment was not suitable for such service.

"MONASTRAL" BLUE LB

A. MANUFACTURE OF 4-CHLORPHTHALIC ACID

Chlorphthalic acid, which is used as an ingredient in the synthesis of Blue LB, is prepared at Newport by chlorination of a solution of disodium phthalate. A number of operating difficulties in the manufacture of 4-chlorphthalic acid were corrected during the year 1949.

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The major difficulty, severe foaming during the "salting out" and acidification steps was minimized by adjusting the pH after addition of chlorine to 4.5-4.8 and standardizing the sodium hydroxide solution prior to solution of the phthalic anhydride. The use of two mols excess of sodium hydroxide, measured to ± 3%, was found to decrease the foaming tendency as well as to facilitate filtration of the slurry. The quantity of sodium chloride used for "salting out" the 4-chlorphthalic acid was reduced from 238# to 200# with no apparent loss of yield.

Two attempts to use 4-chlorphthalic acid slurry instead of presscake were made on a plant scale, thus eliminating the filtration step and a very undesirable fume problem. The first attempt failed, since the crude CPC produced by this modification was solvent milled directly after Blue BG, and was seriously contaminated. The second attempt also failed since pellets were formed after sulfation, probably as a result of inadequate removal of kerosene. A number of operating difficulties in addition to the above items indicated the desirability of postponing any further work in the plant on elimination of 4-chlorphthalic acid filtration.

B. SYNTHESIS OF BLUE LB

Blue LB was synthesized throughout the year with no serious operating difficulties, with the exception of several syntheses in which reaction did not occur. It was found that partial oxidation of the kerosene (Sonneborn's "DeoBase" or Esso's "Bayol D") prevented formation of CPC. The molten reactants solidified in the kettle on cooling, and removal had to be done manually. Oxidation of the kerosene was prevented by the addition of an anti-oxidant, such as Paranox 441 ex Esso, and the use of ammonium bicarbonate (later carbon dioxide) to blanket the kerosene. The specification now requires that the kerosene for CPC synthesis shall contain no measurable peroxide.

The yield, as measured by the weight of crude CPC and based on phthalic anhydride input, varied from 71.3% to 79.3% of theoretical for the year 1949, the highest yield being obtained in December. The improvement appears to be the result of intensified joint efforts of Production, Engineering Service Division and the Chemical Division to realize the specified conditions of reaction and minimize mechanical losses.

The substitution of a relatively inexpensive fuel grade kerosene for Esso's "Bayol D" was studied in the plant. Five batches were synthesized with fuel grade kerosene during the year. Although several operating difficulties were encountered, the final plant quality by rubout was essentially equal to normal production. In the first synthesis, severe foaming occurred, perhaps as a result of the use of a larger quantity of kerosene to compensate for the higher losses anticipated with fuel grade kerosene. Filtration of the slurry was found to be significantly slower than slurry made with Bayol D, resulting in inefficient washing since presses were not completely filled. As a result of heavy demands upon LB production, it was necessary to refer the fuel grade kerosene study to the Newark Semi-Works.

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C. SULFATION

Several significant modifications to the sulfation operation, which have permitted increased production rates, were adopted in 1949.

Plant experimentation showed that better operating conditions resulted when the synthesis slurry was diluted with kerosene to a specified volume; consequently, the addition of fresh kerosene to a volume of 900 gallons prior to sulfation was adopted as standard practice. The rate of acid addition was varied over a fairly wide range from 3/4 hour to three hours. A cycle of 1-1/2 hours was found to be the optimum period. A lengthy evaluation of the quantity of sulfuric acid showed that 1200-1600 pounds of sulfuric acid per synthesis resulted in fine particles of CPC sulfate, from which kerosene could not be separated easily. When 1600-2000 pounds sulfuric (per synthesis of 1071# phthalic anhydride) were used, the CPC sulfate tended to become progressively "pasty"; however, separation of kerosene was not inhibited, but transfer of the slurry was rendered impractical with existing equipment. As a result of this variable study, 1600# of 98% sulfuric acid per synthesis was adopted as the standard quantity.

At the request of the Production Division, a laboratory evaluation of commercial 93% sulfuric acid for sulfation was made. The use of 93% sulfuric acid offered an ingredient savings in addition to the savings in installation of tank car facilities, since 93.0% acid does not require steam heated storage and transfer equipment as does 98% sulfuric acid. The laboratory studies were sufficiently promising to attempt a plant evaluation. Two plant sulfations with 93.0% sulfuric acid resulted in a number of operating difficulties as compared to 98.0% acid. Since removal of kerosene and ease of pumping, filtering and washing were adversely affected, the idea was abandoned.

In laboratory studies variation of the slurry temperature prior to sulfation indicated that more satisfactory results were obtained at temperatures below 100°C. than at 125-150°C. (temperature of plant sulfation). The CPC sulfate tended to remain in suspension at 80-100°C. during sulfation, while at 150°C., severe settling occurred after addition of approximately half of the acid. The lower temperature of sulfation was not adopted, in the plant, since cooling of the synthesis slurry below 100°C. would be expensive and time consuming.

D. SOLVENT-MILLING

A study, designed to determine the capacity of the solvent milling operation, resulted in an increase in mill loading from 314 pounds to 362 pounds per 21 hours actual milling time, with no detectable degradation in quality. This study was accomplished in 5% increments, followed by a thorough quality evaluation prior to attempting the next increase. This quantity appears to be near the upper limit that can be pumped satisfactorily from a mill, since dilution to the full mill capacity is required at the 362 lb. loading. A similar study

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was attempted in the early part of 1949, but failed, since weakness to the extent of 5-6% versus standard BT-284-D was encountered. The success of the more recent study is believed to be attributable to lower kerosene content of the crude as a result of increased dryer efficiency, higher acetone concentration through improved distillation and several process improvements in extraction and washing of the crude pigment. The milling rate, 362#/21 hours, is equal to 102.0% of project design capacity.

E. FINISHING OPERATIONS AND QUALITY - BLUE LB

The monthly finishing yield for the year 1949 (i.e., from milling through extraction steps) ranged from 91.6% to 98.5% of theoretical with an average of 95.8%. A reasonably steady increase, which was maintained throughout the year, is believed to be attributable to improvements in operating technique of the filter presses and slurry transfer equipment in addition to a reduction of foaming during extraction.

Severe manganese contamination, which ranged from 0.010 to 0.015% of the pigment weight, (specification is 0.001% minimum) was prevalent during the first part of 1949. The contamination was traced to a portion of the water supply, which was obtained from a plant well and mixed with purchased water. Discontinuance of this source of water and replacement of it with purchased water was responsible for a reduction of manganese content to within specifications.

As a result of a customer complaint of grit in finished LB pulp, a study was opened to determine methods of minimizing grit. It was found that mechanical methods, several of which were in use at the Chambers Works, were not entirely successful, but that precautions could be taken to minimize the formation of grit. An intensified campaign was undertaken at Newport to prevent drying of the pigment in process, and the grit content was reduced to the point that a lake prepared for linoleum usage was acceptable to the customer.

The quality of Newport production is shown as Exhibit (4) averaged by months. With the exception of a few weak batches produced in July and August, the quality was satisfactory compared to Newport shipping standards. The weakness of these lots was traced to inefficient washing in the filter presses following acid extraction and was corrected by frequent inspections and repairs of the presses.

"MONASTRAL" BLUE BG

A total of 28,900 pounds of Blue BG was produced in the year 1949. Since the same finishing equipment is used for BG as for Blue LB, production of BG was conducted on a campaign basis, supplying Newark with approximately three months requirements each campaign. The quality of the entire 1949 production of Blue BG is summarized in Exhibit (3).

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Blue BG was produced for the first time in the plant in March, 1949. The quality of the initial production, which consisted of two mill charges or 375# commodity weight, was 100:100 and vvs green versus the goal standard, BT-297-D, SW 373. No operating difficulties were encountered in this production.

The second production of Blue BG, eight mill charges or 2203#, was made in April, 1949. Quality evaluation showed that the first 40% of this campaign was contaminated with residual Blue LB as the result of inadequate cleaning of equipment. The quality of the remainder of the campaign compared favorably with standard BT-297-D, SW-373.

The third BG campaign in July, 1949, which resulted in 2920#, was less successful than the second from a quality standpoint as indicated by the red hue and relatively high chlorine content (1.5 to 0.3%) versus BT-297-D, SW 373. Some weakness, 2-6% versus standard, was encountered and could not be explained; however, based on in-process sampling, it was shown that the desired strength was developed during milling, but apparently not realized in the subsequent extraction steps.

The fourth and fifth campaigns, which were made in August and December, respectively, yielded 10,409 and 12,993 pounds, and both were significantly more successful than the preceding campaign. However in the latter half of the fourth campaign, weakness to the extent of 4-8% was again encountered and could not be explained, although the weakness is believed to be associated with variations in production of the crude CPC. Three lots were milled an additional 12 hours (48 vs 36 hours), but did not result in any significant improvement in quality.

Two variables, shorter cycle and increased mill loading, were studied during the fifth BG campaign. A 5% capacity increase was realized for 78% of the campaign with no apparent quality deterioration. The cycle of six mill charges was reduced from 36 to 30 hours and quality essentially equal to normal production was produced. A combination of these two variables, which will be used in future campaigns, amounts to a 17% increase in capacity, based on the original standard procedure.

POLYCHLORO CPC

A. CHLORINATION

Polychloro CPC was produced at Newport on a production basis the first part of 1949, but was discontinued February 17, 1949, to prevent an accumulation of large stocks of substandard color. Two chlorinations, Cl-104 and Cl-105, were made in March to provide the Newark Semi-Works with crude Green for variable studies. Starting in April, the chlorination equipment was operated on a controlled experimental basis under the direct surveillance of the Chemical Division until August, 1949, at which time the responsibility for operation

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was accepted by the Production Department. The chlorination operation was discontinued 8/24/49, since a serious community fume problem had been created as a result of inadequate fume disposal facilities.

The operating performance and quality by laboratory finishing methods of the chlorinations made under Chemical Division Supervision in 1949 are shown as Exhibit (1).

A review of Exhibit (1) shows that unusual difficulty of operation and frequent equipment failures prevented a controlled evaluation of variables under study in the majority of the chlorinations. However, considering only the chlorinations which were made under satisfactory conditions of operation, the quality as finished by standard laboratory procedures ranged from 80;100 to 91:100, blue to vs yellow and dull to intense versus standard GT-486-D.

The sulfur chloride reflux system attached to the autoclave was a constant source of difficulty, particularly during the periods of intermittent operation. After numerous inspections of both the reflux (Andale) and tail condensers in 1948, which showed the condensers to be almost entirely plugged with solidified material, it was agreed to operate with refluxing. Chlorinations C1-109 through C1-122 sere made accordingly, but were all significantly blue versus standard GT-486-D. Consequently, the reflux condenser was reinstalled 6/17/49, and an improvement in hue became very obvious as can be seen in Exhibit (1) starting with batch C1-123.

The reflux condenser, which was inspected and cleaned after 27 chlorinations (C1-123 through C1-149), was found to have 59 of its 61 tubes completely blocked with a granular material, which was found by analyses to contain large quantities of antimony, ammonia, chlorides, sulfates and iron. (This difficulty was essentially eliminated in 1950 by the substitution for antimony oxide (catalyst) of aluminum chloride, which greatly reduced the blockage in the reflux condenser.)

Chlorination operating conditions were varied throughout the year in search of optimum conditions. Although the results of these trials are undoubtedly inconclusive, it is evident that as the pressure and temperature are increased, an increase in chlorine content and a subsequent yellower hue are obtained, at least, within the range of conditions studied. Insofar as pressure alone is concerned, it appears that the most desirable products were made in the 250-300 psi range. All products synthesized at 165 and 200 psi were considerably bluer than standard GT-486-D. However, this may not be significant, since the reflux condenser was not in service during the lower pressure runs.

The temperature variable was not studied further to any great extent in 1949, since in the earlier work at the Newport plant, it was demonstrated that temperatures of 170°C. or higher were required to produce the desired tinctorial properties. Although it would

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appear desirable to study temperatures in excess of 178°C., the Newport plant is limited by the available plant steam.

Five chlorinations were made using pulverized crude Blue, but did not appear to offer any tinctorial improvement compared to suitable controls with regular lump crude.

The standard extraction procedure for preparation of the crude Blue prior to chlorination consisted of an alkaline extraction with 3% sodium hydroxide solution at 95°C. for two hours. Five chlorinations, which were made from crude Blue that received an acid extraction with 2% sulfuric acid in addition to the standard alkaline extraction, exhibited no advantage in tinctorial properties as compared to normal production.

B. REACTION VIOLENCE

The reaction between the catalyst, antimony oxide, and sulfur chloride proceeds rapidly, converting antimony oxide to antimony trichloride. In a number of cases, this reaction could not be adequately controlled in the plant and resulted in excessive pressure in the autoclave. The problem was solved by a revision in plant procedure which permitted the antimony oxide to react with a small quantity of sulfur chloride prior to introduction of the remaining quantity of sulfur chloride to the autoclave.

A second reaction, the introduction of the first eight mols of chlorine into the phthalocyanine molecule, also proceeded rapidly in plant equipment and, in a number of cases, resulted in rupture of the autoclave safety disc. This problem had not been encountered on a laboratory scale, since an oil bath was used for heating the laboratory autoclave and permitted excellent control of heating rates. However, the plant autoclave was heated with high pressure steam. The reaction violence was reduced to a point which permitted satisfactory operation by specification of a maximum allowable heating rate. Nine chlorinations, Cl-152 to Cl-160, inclusive, were made under the specified conditions prior to the plant shutdown with no significant reaction violence.

C. SULFUR CHLORIDE REMOVAL

The rotating dryer, which is designed to remove sulfur chloride from the CPC Green slurry by distillation, was operated with increasing success in 1949. The major difficulties, which were largely mechanical, were overcome to the extent that a satisfactory cycle was obtained for the existing production rate.

One of the most serious problems was severe leakage of the rotating dryer packing glands, both process and steam. The situation was improved considerably by several mechanical revisions, improved type of packing and realignment of the rotating dryer.

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Near the end of 1948, the method of discharge of the crude pigment was changed from a "wet" to "dry" procedure. A water slurry of pigment and Turkey Red Oil (as a wetting agent) could not be completely discharged (pumped) from the dryer, since adequate dispersion of the slurry was not realized with the relatively slow rotation of the dryer. In addition, the use of water in the rotating dryer complicated the procedure, since it was imperative that the dryer be dried completely prior tc charging the following batch. Consequently, the "dry" pigment discharge method was adopted and used successfully.

D. EXTRACTION OF CRUDE POLYCHLORO CPC

The alkaline extraction of the crude Green pigment prior to solvent milling was troublesome from both quality and operating standpoints. The procedure as used in January, 1949, consisted of an alkaline extraction of the pigment with sodium hydroxide and Turkey Red Oil for one hour at 95-100°C. At completion of the extraction period, ammonium sulfate was added to a pH of 6.0-6.5 to facilitate filtration. The major objections to such a procedure were foaming of the charge, considerable yield loss and thixotropy of the presscake. Consequently, a rather comprehensive study of the extraction procedure was started in the laboratory. The first plant change in procedure, substitution of sulfuric acid for ammonium sulfate, improved plant operation to some extent in that less thixotropic presscakes were formed and there was no difficulty in reaching the specified pH, in contrast to previous experience with ammonium sulfate.

Additional laboratory and Semi-Works investigation showed that an acid extraction or simply water (acidic from hydrolysis of the residual sulfur chloride in the pigment) resulted in quality at least equal to that obtained with the alkaline extraction. On the basis of this work, the plant procedure was revised in April, 1949, to include a water extraction with Turkey Red Oil. The major problems of extraction appeared to be solved with the exception of foaming as the temperature reached 95°C. Extraction at 90°C. did not affect quality and decreased foaming, compared to extraction at 95°C.

E. SOLVENT MILLING AND QUALITY

A compilation of all lots of Newport synthesized Polychloro CPC and quality compared to standard GT-486-D are shown as Exhibit (2). The most serious tinctorial problem in the year 1949 was the inability of the plant to obtain consistently pigment of satisfactory intensity. Although practically all of the lots in Exhibit (2) appear strong versus standard GT-486-D, the goal strength of 83:100 was obtained in only about 85% of the production.

The standard milling conditions for Green at the beginning of 1949 specified 400 lbs. crude pigment and 360 gallons of acetone milled for 24 hours. As a result of an apparent satisfactory rate of strength development, six batches were milled in January, 1949, for 36 hours using a 628 lb. loading. Satisfactory strength was obtained, but rub-out evaluation indicated the products to be duller than expected from laboratory control grinds. Consequently, the charge and cycle were both reduced to the original conditions.

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Although the reason for dullness of Newport production was not firmly established, it appeared to be associated with plant conditions of solvent milling. Sodium chromate, which was used to the extent of 5% of the pigment weight during solvent milling to prevent reduction of the pigment, could not be detected at the end of milling on a number of plant charges. A reasonably good correlation was developed between dullness and lack of sodium chromate at the end of the cycle; however, dullness existed in a number of plant grinds even though an excess of chromate was found. The quantity of sodium chromate was increased to 7-1/2% of the pigment weight with a subsequent reduction (but not elimination) of the number of dull lots.

Since the ultimate plant quality appeared to be unpredictable from the observed operating conditions during manufacture of the crude, a sample of each crude batch was solvent milled in the laboratory prior to plant processing. The crude batches which appeared unsatisfactory in the laboratory were processed in the plant on a campaign basis, thus minimizing the amount of dull sub-standard material produced.

Operation of the Newport chlorination unit was discontinued 8/24/49 as a result of numerous complaints from the adjacent communities of fume conditions, which were a result of inadequate waste disposal facilities. Consequently, in order to continue a supply of polychloro CPC to the Pigments Department customers, Orchem eutectic crude Green was purchased and solvent milled at Newport during the latter portion of 1949. Lots N-624-108-113, 122-163, and 173-202, produced in 1949, were solvent milled eutectic Green.

The average quality of Lots N-624-108 through 113 and 122 through 163 was 83:100, s intense and vs yellow compared to standard GT-486-D. On November 16, 1949, a new standard goal GT-674-D, lot 430, which was made from solvent milled eutectic Green and, obviously, much more realistic for comparison with eutectic production, was established. Compared to the original standard GT-486-D, the new standard/ was yet in masstone, 83:100, s yellow and s intense. Plant production during the latter part of 1949 (N-624-173 through 202) averaged 103:100, vvs intense and vs yellow versus standard GT-674-D, lot 430.

G. EXTRACTION OF SOLVENT-MILLED GREEN

The standard extraction procedure subsequent to solvent milling consisted of an extraction at 85°C. for two hours in 3% ammonium hydroxide solution followed by an extraction at 95°C. for two hours in a 2% sulfuric acid solution. Following each extraction, the slurry was filtered and washed to a conductivity endpoint of 2000 mhos. In the acid extraction, sodium chromate, equal to 3.5% of the pigment weight, was added prior to the extraction.

This procedure was used throughout the year with no significant changes; however, in view of the extreme dullness of a number of finished lots, an additional extraction with sodium hypochlorite was used starting in April, 1949. The hypochlorite extraction, which was first tried on

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lot N-624-75, consisted of frequent additions of sodium hypochlorite and sodium hydroxide solutions as required to maintain the pH above 9.0 during a nine hour extraction period at 45-50°C. The slurry was then acidified with sulfuric acid to a pH of 5.3, boiled for an hour, filtered and washed both chloride and sulfate free. As judged from hourly in-process samples, a very significant improvement in quality occurred progressively as the hypochlorite extraction was continued.

The hypochlorite extraction, with several revisions, reduction in extraction period to four hours and use of a final pH of 2.0 instead of 5.3, was continued as necessary (determined by in-process quality evaluation) as shown in Exhibit (1). In June, 1949, the regular inspection of the acid extraction tank, which had been used for hypochlorite extractions, revealed that the brick lining was severely damaged as a result of using hypochlorite. Consequently, since no other equipment was available in the CPC plant for service with hypochlorite, subsequent sub-standard production was shipped to Newark for extraction. A total of 9378# of N-624 (dry basis) and 2593# green CPC toner GT-674-D was recovered by hypochlorite treatment at Newark on a campaign basis. After June, 1949, hypochlorite extraction of sub-standard green production was continued at Newark as necessary.

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EXHIBIT (1)

CHLORINATION

OPERATING DATA AND QUALITY

	Lot	Press. psi	Temp. °C	Hrs.at Temp.	Operating Performance	Laboratory Finished Quality vs GT-483-D
Cl	109	175	170	3-1/2	Unusually long autoclave cycle (36 hrs.)	84:100 blue dull
	110	165	160	3-1/2	O.K. Performance	83:100 blue intense
	111	165	160	3-1/2	Rapid pressure rise to 260 psi	83:100 blue intense
	112	200	173	3-1/2	Ruptured scale tank safety disc	80:100 blue s intense
	113	200	175	4-1/2	Low chlorine in SCl_2 (57.8%)	83:100 very blue
	114	200	173	5	Lost pressure to 150 psi	83:100 very blue
	115	200	173	4	O.K. Performance	80:100 blue
	116	200	175	3-1/2	Rapid reaction to 220 psi	80:100 blue s intense
	117	200	175	3-1/2	O.K. Performance	80:100 blue intense
	118	200	175	3-1/2	Rapid reaction to 320 psi	83:100 blue vs dull
	119	200	175	3-1/2	Long autoclave cycle (20 hrs.)	80:100 blue s dull
	120	300	175	3-1/2	O.K. Performance	83:100 blue dull
	121	300	175	3-1/2	O.K. Performance	83:100 blue dull
	122	200	176	3-1/2	O.K. Performance	83:100 blue
	123*	300	170	3-1/2	Lost pressure to 170 psi	86:100 yellow
	124	300	170	2-1/2	Lost pressure through packing gland	83:100 dull
	125	250	170	2-1/2	Lost pressure through autoclave discharge valve	86:100 s intense
	126	250	172	3-1/2	Lost pressure to 210 psi	83:100 s blue dull
	127	250	175	3-3/4	Lost pressure to 160 psi	855100 blue duol
	128	200	173	3	Violent reaction	83:100 vs dull

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Lot	Press. psi	Temp. °C	Hrs.at Temp.	Operating Performance	Laboratory Finished Quality vs GT-486-D
Cl 129	300	172	3-1/2	Rapid initial reaction. Lost pressure to 220 psi	86:100 dull
130	300	170	4-1/2	Lost pressure to 170 psi	85:100 dull
131	260	172	4	O.K. Performance	85:100 dull
132	250	175	3-3/4	O.K. Performance	90:100 dull
133	250	178	3	O.K. Performance	91:100 vs yell vs dull
134	250	173	2-1/4	O.K. Performance	85:100 dull
135	250	175	2-1/2	O.K. Performance	85:100 dull
136	250	175	3-1/2	O.K. Performance	80:100 blue dull
137	300	175	4-1/2	Slight pressure loss	84:100 intense
138	250	175	4	Lost pressure to 150 psi	85:100 blue dull
139	300	175	3-1/2	O.K. Performance	85:100 blue dull
140	250	175	3-1/4	O.K. Performance	85:100 blue dull
141	300	175	5	O.K. Performance	86:100 vvs yellow
142	300	175	5	O.K. Performance	85:100 dull
143	300	179	4	Lost pressure to 230 psi	83:100 blue intense
144	300	178	5	O.K. Performance	80:100 s blue intense
145	300	177	4-1/2	O.K. Performance	83:100 dull
146	300	175	5	O.K. Performance	80:100 blue s intense
147	300	183	3-1/2	O.K. Performance	80:100 blue s intense
148	300	183	5	Autoclave gasket blown	80:100 blue intense
149	300	175	1/2	Ruptured disc	83:100 blue intense
150	300	176	5	O.K. Performance	86:100 vs blue intense
151	300	176	5	Violent reaction to 335psi	85:100 dull
152	300	176	5	O.K. Performance	83:100 blue intense
153	300	176	5	O.K. Performance	85:100 blue intense
154	300	179	5	O.K. Performance	87:100 blue intense

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	Lot	Press. psi	Temp. °C	Hrs.at Temp.	Operating Performance	Laboratory Finished Quality vs GT-486-D
- Cl	155	300	178	5	O.K. Performance	83:100 s blue intense
	156	300	175	5	O.K. Perfrrmance	87:100 s blue intense
	157	300	177	5-1/2	O.K. Performance	83:100 blue intense
	158	300	176	5-1/4	O.K. Performance	83:100 blue intnnse
	159	300	177	5-1/4	O.K. Performance	83:100 blue intense
	160	300	---	0	Ruptured disc	85:100 very blue

* Reinstalled (Andale) reflux condenser.

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EXHIBIT (2)

QUALITY OF POLYCHLORO CPC PRODUCED AT NEWPORT IN 1949

Packed Lot		Quality vs Standard GT-486-D
N624-	43	80:100 vs blue vvs intense
	44	81:100 vs blue vvs intense
	45	88:100 blue
	46	86:100 blue
	47	83:100 blue
	48	84:100 blue
	49	84:100 s blue
	50	87:100 vs blue
	51	89:100 vvs blue vvs intense
	52	89:100 vvs blue
	53	85:100 yellow dull
	54	84:100 s yellow s dull
	55	84:100 s yellow dull
	56	86:100 yellow dull
	57	86:100 yellow dull
	58	83:100 vs dull
	59	92:100 yellow
	60	83:100 vvs yellow
	61	84:100 vvs yellow vvs intense
	62	82:100 vvs; dull
	63	82:100 equal
	64	82:100 vvs yellow
	65	83:100 vs yellow vs dull
	66	83:100 vvs yellow s dull
	67	82:100 vvs yellow vs dull
	68	83:100 vvs yellow vs dull
	69	83:100 vvs yellow vs dull
	70	85:100 vs yellow s dull
	71	83:100 vvs yellow vs dull
	72	84:100 vs yellow vs dull
	73	86:100 dull
	74	83:100 vvs yellow vvs intense
	75*	105:100 blue s dull
	76	83:100 vs dull
	77*	83:100 vvs blue vs dull
	78*	89:100 vvs yellow s dull
	79*	94:100 vs blue vs dull
	80*	93:100 vs blue dull
	81	84:100 vs blue vvs dull
	82	82:100 blue
	83	83:100 blue
	84	81:100 blue
	85	83:100 blue
	86	80:100 v blue
	87	82:100 v blue
	88	80:100 v blue

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Packed Lot	Quality vs Standard GT-486-D
N624- 89*	80:100 blue s dull
90	80:100 blue s dull
91	83:100 blue s dull
92*	83:100 blue vvs dull
93	84:100 s blue vs dull
94	93:100 s blue s dull
95	90:000 s blue dull
96	91:100 s blue dull
97	91:100 dull
98	85:100 vvs yellow dull
99	85:100 vs blue dull
100	87:100 vvs yellow dull
101	86:100 dull
102	83:100 v dull
103	80:100 v dull
104	80:100 v dull
105	80:100 v dull
106	80:100 v dull
107	83:100 v dull
114**	83:100 s blue dull
115	83:100 vs blue vvs dull
116	80:100 s blue s dull
117	80:100 s blue dull
118	83:100 vs blue s dull
110	81:100 vs blue dull
120	81:100 blue s dull
121	83:100 blue
164**	82:100 blue s intense
165	82:100 blue s intense
166	84:100 blue intense
167	81:100 blue s intense
168	83:100 blue vs intense
169	83:100 vs blue vvs intense
170	85:100 blue vs dull
171	81:100 v blue
172**	84:100 v blue

* Extracted with sodium hypochlorite.

** Lots N624-108 through 113, 122-163 and 173-202 were produced from eutectic crude green in 1949.

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EXHIBIT (3)

QUALITY OF "MONASTRAL" BLUE BG PRODUCED AT NEWPORT IN 1949

Packed Lot	Month Produced	Quality vs Standard BT-297-D. S.W. 373
N657- 1	March	100:100 vvs green
2	April	95:100 s red vvs dull
3	"	99:100 vs red vvs dull
4	"	100:100 equal
5	"	100:100 equal
6	"	105:100 vvs dull
7	July	98:100 red vvs dull
8	"	99:100 vs red
9	"	102:100 equal
10	"	105:100 vvs red
11	"	104:100 equal
12	"	106:100 vvs intense
13	August	100:100 vvs green vvs intense
14	"	102:100 equal
15	"	101:100 vvs green vvs intense
16	"	101:100 equal
17	"	101:100 vvs green
18	"	102:100 vvs green
19	"	106:100 vs green vvs intense
20	"	100:100 vs green vvs intense
21	"	100:100 vs green vvs intense
22	"	100:100 vs green vs intense
23	"	106:100 vs green
24	"	105:100 vs green vvs intense
25	"	105:100 vs green
26	"	105:100 vs green
27	"	101:100 vs green
28	"	106:100 vs green
29	"	104:100 vs green vvs intense
30	"	105:100 vs green vs intense
31	"	106:100 vs green vvs intense
32	"	107:100 vs green
33	"	104:100 vs green vs intense
34	"	108:100 vs green vvs intense
35	"	107:100 vs green
36	December	98:100 vs green
37	"	100:100 vs green vvs intense
38	"	102:100 vs green vs intense
39	"	103:100 vs green vvs intense
40	"	102:100 vs green vs intense
41	"	97:100 s red dull
42	"	100:100 vs green vs intense
43	"	100:100 vs green vs intense
44	"	102:100 vs green vs intense
45	"	102:100 vs green s intense
46	"	101:100 s green vs intense

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Packed Lot	Month Produced	Quality vs Standard BT-297-D, S.W. 373
N657- 47	December	101:100 s green vs intense
48	"	101:100 s green vvs intense
49	"	98:100 s green s intense
50	"	100:100 vs green
51	"	98:100 s green s intense
52	"	98:100 s green s intense
53	"	98:100 s green s intense
54	"	102:100 s green s intense
55	"	102:100 green vs intense
56	"	103:100 green vvs intense
57	"	104:100 green s intense
58	"	99:100 green vvs intense
59	"	104:100 vs green s intense
60	"	103:100 green vs intense
61	"	102:100 s green vs intense
62	"	103:100 green vs intense

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EXHIBIT (4)

QUALITY OF "MONASTRAL" BLUE LB
PRODUCED IN 1949 AT NEWPORT

Month	Packed Lots	Average Quality vs Standard BT-284-D
January	N623-185 to 218	100:100 vs red
February	N623-219 to 258	99:100 vs red
March	N623-259 to 299	99:100 vs red
April	N623-300 to 329	98:100 vs red
May	N623-330 to 350	100:100 vs red
June	N623-351 to 373	100:100 vs red
July	N623-374 to 394	103:100 vvs red vvs intense
August	N623-395 to 408	103:100 vvs red
September	N623-409 to 426	101:100 s red vvs intense
October *	N623-427 to 468	99:100 vvs green
November*	N623-469 to 503	99:100 vs green
December*	N623-504 to 522	99:100 s green

* Replaced BT-284-D with BT-304-D as a Newport shipping standard.

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