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NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

NEWPORT
PHTHALOCYANINE PLANT ASSISTANCE

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NEWPORT PLANT
PIGMENT COLOR RESEARCH REPORT
FINAL REPORT

PHTHALOCYANINE PLANT ASSISTANCE

JANUARY, 1950 - JULY, 1951

SUBMITTED BY: P. D. GRAHAM, JR. DATE SUBMITTED: 10-2-51

APPROVED BY : J. H. COOPER 11/1/51 DATE ISSUED: 11-2-51

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INTRODUCTION

This report is concerned with the work of the Chemical Division Plant Assistance Group at the Newport "Monastral" Plant from January, 1950 to July, 1951 in standardisation and improvement of the processes for manufacture of the three phthalocyanine colors, "Monastral" Blue LB, Blue BG and Green, produced by the Pigments Department. This report represents a continuation of KN-51-39, Phthalocyanine Plant Assistance - January, 1949 - January, 1950.

HISTORICAL

The Newport CPC plant was originally 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 basic synthetic processes were developed by Imperial Chemical Industries and the Organic Chemicals Department; but the current Newport operations include numerous modifications and more features 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 (3.8-4.5%), which is stable to crystal growth in aromatic paint thinners. 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 acid and alkali. 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-chlor phthalic acid is not used in the initial condensation. The crude CPC is chlorinated with sulfur chloride to a chlorine content of 47 - 48.5% at elevated temperatures and pressures, following which the crude Green is extracted, dried and shot milled in acetone.

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

Attempts to use 4-chlorphthalic acid slurry, instead of press-cake, were unsuccessful. The texture of BT-284-D and BT-304-D made from CPC synthesized with 4-CPA slurry was inferior to that made from

4-CPA presscake. Several trials of a revised 4 CPA process, developed by Jackson Laboratory, were made in 1950. The justification for the study was the elimination of chlorine fumes during the filtration operation. Final evaluation showed that the revised (Remington) process gave satisfactory tinctorial properties although slightly weak; however, the fume condition in the operating area had been improved sufficiently by mechanical means to diminish interest in the Remington process.

Blue LB was synthesized at an average rate of 53 syntheses per month. In only two cases was there any difficulty with oxidation of the kerosene in the CPC synthesis. This condition was improved considerably, as compared to 1949, through the use of an anti-oxidant and a control test for oxidation of the kerosene on each batch. The oxidized kerosene was recovered by washing with concentrated sulfuric acid to remove peroxides.

A significant loss of production was incurred by excessive pumping cycles of the synthesis slurries, which were more granular when synthesis temperatures exceeded the specifications (195 $\pm$ 5°C). Although the automatic temperature controls were inadequate, the difficulty was eliminated by an extensive training program and more careful manual temperature control.

The major process improvement in the manufacture of Blue LB was the adoption of the "Kerosene Flotation" (KF) Process in January, 1951, which completely eliminated the formation of pasty CPC that formerly occurred in the basket filtration procedure and reduced the sulfation cycle considerably to bring it in line with the synthesis cycle.

The "Acid Flushing" (AF) Process, which was designed to give a kerosene-free presscake, was evaluated in the plant because no drying equipment was available after the dryer explosion, March 5, 1951. The "AF" trials were not encouraging, since the available plant equipment presented severe limitations. Adaptation of the "AF" process to the plant would necessitate a sizeable capital investment, which cannot be justified.

The seventh plant mill, which was installed in June, 1950, was responsible for a 25% increase in Blue LB production. An increase in the acetone/CPC ratio for solvent milling from 8.7/1 to 10/1 gave some indications of a slight strength improvement.

The final alkaline extraction of Blue LB was eliminated from the process in September, 1950 after several extended plant trials had shown no quality deterioration.

The quality of Newport's production of "Monastral" Blue LB was satisfactory with the exception of a 1-4% average strength deficiency during the first six months of 1951.

B. "Monastral" Blue BG

Three separate campaigns of Blue BG were made between January, 1950 and July, 1951. There were no quality deficiencies, except an average 4% weakness in the first campaign in July, 1950. The third campaign in April, 1951, which represented the first use of KF sulfated crude in BG production, was from a quality standpoint the most successful of any Blue BG produced at Newport to date.

C. "Monastral" Green

During design and installation of fume disposal facilities in the first half of 1950, the Green unit was operated only experimentally. In August, 1950, regular production was resumed.

A significant process improvement was made in April, 1951, when the catalyst, antimony oxide, was replaced with anhydrous aluminum chloride. The violent exothermic reaction, which occurred between antimony oxide and sulfur chloride, was thus eliminated. In addition, the accumulation of solid material in the reflux condenser, was minimized.

Interest in a green toner of jet masstone prompted plant trials involving the use of aluminum chloride in large excess. In the laboratory, it had been demonstrated that such a modification in the chlorination increased the jetness of masstone; however, the plant tests failed to confirm the laboratory findings.

In the extraction of crude Green; Triton X-101 (ex Rohm & Haas), a non-ionic surfactant, was used in place of Turkey Red Oil after January, 1950. A slight tinctorial improvement and a pronounced decrease in foaming resulted.

An increase in drying temperature of crude Green from 100°C to 125°C was made in February, 1951 resulting in approximately a 20% reduction in cycle with no deterioration of quality.

In December, 1950, sodium chromate, which was used in the solvent milling operation, to prevent reduction of the Green CPC, was replaced with sodium nitrite. The latter has the advantage of not forming water insoluble reduction products not easily removed in subsequent extractions.

The average quality of Green CPC throughout the period covered by this report was on the defensive versus standard in intensity; however, the hue and strength were satisfactory, with the exception of a few weak batches in 1950. A major portion of the efforts of the Plant Assistance Group was directed toward elimination of dullness. Most of the process modifications discussed in this report were designed to improve the intensity of Green CPC.

"MONASTRAL" BLUE LB

A. 4-Chlorphthalic Acid

With the exception of two process variations, standard operating procedure was used throughout the period covered by this report for manufacture of 4-chlorphthalic acid.

Based on encouraging results in the Newark Semi-Works trials of 4-chlorphthalic slurry in place of presscake, a series of plant syntheses was started. It was found that additional power was required for the synthesis kettle agitator using slurry as compared to 4-CPA presscake. It was necessary to replace the 10 H.P. agitator motor with a 15 H.P. motor. A second operating difficulty developed during discharging of the kettle. The CPC synthesized from 4-CPA slurry was exceptionally granular, and the pigment slurry could not be pumped easily. This difficulty was believed to result from the presence of an increased quantity of sodium chloride, since the 4-CPA had not been filtered.

Evaluation of the plant trial lots showed that Blue LB synthesized from 4-CPA slurry was inferior in texture when converted to BT-284-D and BT-304-D, and was weak as BL-288-D. Consequently, further study of 4-CPA slurry was abandoned.

The other process variation was a modification of the chlorination procedure developed in the Organic Chemicals Department by W. R. Remington. Interest in this process at Newport resulted from the need to eliminate a very undesirable fume situation in the 4-CPA area. Incidental advantages of the modification were reduction in sodium chloride and chlorine consumptions and a significant increase in filter press capacity. The Remington process differs primarily from the standard hypochlorite chlorination process in that the disodium phthalate solution is chlorinated at 50-60°C. with no excess of sodium hydroxide.

One plant trial of the Remington 4-chlorphthalic acid process was made in October, 1950. No serious operating difficulties were encountered, with the exception of considerable trouble in pumping the chlorinated slurry to the filter press. However, it was later established that incomplete solution of the phthalic anhydride was responsible and the difficulty could have been avoided by more gradual addition of the phthalic to insure complete solution.

The analysis of the first plant batch of Remington 4-CPA was as follows compared to a standard 4-CPA batch:

	Remington Batch #1	Typical Batch
Solids	68.53%	55.0%
Total Chlorine	20.28%	33.0%
Inorganic Chlorine	6.33%	22.0%
Organic Chlorine	13.95%	11.0%
4-CPA (calc.)	78.7%	65.0%
NaCl (calc.)	10.4%	30.0%
Free phthalic acid (calc.)	10.9%	5.0%

Laboratory grinds of Blue LB synthesized from the Remington 4-CPA were 3-5% weak, green and intense versus controls. When solvent milled in the plant, the LB/CPC using Remington 4-CPA was 102:100 and vvs green versus standard BT-304-D. The chlorine content was 4.12%, which is only slightly lower than average production. The product, when evaluated as BT-304-D and BT-284-D in alkyd, was found to be non-reactive and equal in flocculation behavior and can stability to the BT-304-D and BT-284-D standards. Ink mill evaluation showed the products to be equal to their standards in separation. Hegman texture was essentially equal in the case of BT-284-D, but inferior to standard at 1T pass in BT-304-D, very slightly inferior at 3T and equal at 5T.

Two additional batches of Remington 4-chlorphthalic acid were made in March, 1951 and solvent milled in the plant as three lots. The quality as compared to standard BT-304-D was as follows:

Lot	vs BT-304-D
N 623 - 152	104:100 vs green vs intense
153	101:100 " "
154	102:100 " "

The quality of Blue LB synthesized from Remington 4-CPA appears to be essentially equal to that of normal production, based on the three lots produced in the plant. Since the original justification for study of the Remington process, elimination of fumes,has been satisfactorily corrected by mechanical means (increased ventilation and air-blowing of the filter press), it was decided to abandon any further plant study.

B. Synthesis

Blue CPC was synthesized at an average rate of 53 syntheses per month ranging from a low of 34 to a high of 68 for the period covered by this report. The major reasons for low production in certain months were mechanical items, such as water in the kerosene through faulty decanter operation, failure of kerosene heating tank coils, plugged urea lines, Dowtherm difficulties, repairs to glass lining and shutdowns to remove tools which were accidentally dropped into the synthesis kettle. The Newport Plant Process for the synthesis of "Monastral" Blue LB as of June, 1951 is described in Exhibit (1).

Several other causes of production delays, which pertain to the process rather than the equipment will be discussed in this report.

During the period, January, 1950 through June, 1951, evidence of kerosene oxidation was recorded twice. A sample of kerosene is analysed prior to each synthesis and, if there is any evidence of oxidation as determined by peroxide number, the kerosene is not used.

In both cases in which oxidation had apparently occurred, the kerosene was washed with concentrated sulfuric acid to remove peroxides prior to use. In neither case was the cause of oxidation determined; however, it may be significant that kerosene stocks were low, necessitating complete discharge of storage tanks which contain relatively small quantities of an unidentified sludge and water.

It will be remembered that kerosene oxidation occurred quite frequently during the first two years of CPC operation at Newport. Although the exact mechanism is not understood, it is well established that CPC formation is retarded by peroxide in the kerosene. The use of an anti-oxidant, Paranox 441 ex Esso, which was started in 1949, has largely eliminated the difficulty.

Loss of production was sustained in March, 1950 by a plant trial of LB syntheses using 4-chlorphthalic acid slurry in place of presscake (see Discussion under "Monastral" Blue LB, Section "A"). A loss of approximately four hours per synthesis was incurred, since it was necessary to vaporize large quantities of water from the 4-CPA slurry prior to addition of the other ingredients. In addition, significant delays were encountered discharging the synthesis slurry from the reaction kettle. The pumping difficulties were attributable to the unusually granular character of the pigment slurry, which was believed to be caused by larger than normal quantities of sodium chloride remaining in the unfiltered 4-CPA slurry.

Throughout the period covered by this report until April, 1951, a significant production loss was recorded practically every month because of excessive pumping cycles resulting from the granular character of the CPC. It was found that batches synthesized at temperatures above specifications (195 ± 5°C.), frequently led to discharge difficulties, while those within specifications caused no trouble. The automatic controls, which regulate the temperature, are inadequate and require additional manual control by the operator. After a rather extensive operator training program and several minor modifications to the Dowtherm heating system, the temperature control problem was solved by April, 1951.

C. Sulfation

Sulfation of both "Monastral" Blue LB and chlorine-free CPC was continued through 1950 with no significant process changes. The filtration "basket", screened with "Teflon", was used with moderate success; however, as the demands for additional production increased, it became apparent that a drastic process or equipment change was needed. During the latter part of 1950, the number of batches which could not be hydrolysed properly had been reduced to an average of about three per month; nevertheless, production losses due to manual removal of unhydrolysed presscake or "pelletized" CPC were prohibitive. The best average cycle using the "basket" was approximately 14 hours.

In the fourth quarter of 1950, the Newark CPC Research Group developed the "Kerosene Flotation" process (KF) and, on January 4, 1951, the first plant trial was made at the Newport CPC plant. The "KF" process, which is described in Exhibit (2), differs from the "basket" filtration process in that the CPC synthesis slurry of kerosene is sulfated with 98% sulfuric acid (1600# 98% sulfuric acid per LB synthesis of 1071# phthalic anhydride) and the kerosene is then "floated" to the surface by adding water immediately without agitation. Following decantation of the kerosene, ice, sodium hydroxide solution (50%) and additional water are added to effect hydrolysis of the CPC. The slurry is then adjusted to a pH of 9.0-10.0 with sodium hydroxide solution and extracted by the standard procedure.

The first plant trial of the "KF" process was entirely satisfactory, with the exception of some mechanical difficulty with the steam eductor used for kerosene decantation. After several minor revisions to the kerosene decanting equipment, the "KF" process was used the remainder of January, 1951 for the sulfation of 48 batches, which represented the highest production rate yet achieved in the plant.

In the first week of February, 1951, there was some difficulty with the "KF" process resulting in formation of pellets, which could not be discharged from the sulfation tank. One process modification, addition of 3000# of ice instead of 1500# prior to hydrolysis, corrected the difficulty with pellets. From February 6, 1951 through June, 1951, the plant experienced no difficulty with the process. The overall "KF" cycle was significantly less than the "basket" sulfation cycle and slightly less than the synthesis cycle; and, for the first time in the Newport plant, production of crude CPC was not restricted by the sulfation operation.

As a result of the CPC dryer explosion March 5, 1951, it was decided to evaluate another sulfation procedure modification, "Acid-Flushing" process (AF), since smaller scale evaluations at Newark indicated that relatively kerosene-free crudes could be obtained. Obviously, since no equipment was available for drying CPC, the "AF" process appeared attractive, although complete quality evaluation was not available. Briefly, the "AF" process consists of dissolving the CPC synthesis slurry in 98% sulfuric acid (7 parts acid per part CPC) and drowning the solution in water.

The plant trial of the "AF" process was unsatisfactory, because severe equipment limitations and several operating difficulties prevented a thorough evaluation. Based on the results of the trial, it was concluded that a major expenditure would be required for adaptation of the Newport plant to Acid Flushing. In the meantime, the facilities at Newark were modified to permit drying Newport crude CPC, and the need for complete kerosene removal prior to drying no longer existed. For this reason and subsequent evidence that acid flushed CPC showed reactivity and flocculation in alkyd enamels in several instances, study of the "AF" process was abandoned.

D. Solvent Milling

The particle size reduction operation, shot milling in acetone, was continued throughout 1950 and the first four months in 1951 with no changes in procedure. The milling rate, 362# per 21 hours, is equal to 102.5% of the project design capacity.

The seventh plant mill, which was installed June 29, 1950 increased Blue CPC production by 25% (five mills used for Blue and two for Green CPC). No difficulties were associated with the start-up of the seventh mill.

In May, 1951, the acetone/CPC ratio was increased 15% from 8.7/1 to 10/1 as a result of milling studies at the Newark Semi-Works, which indicated that the new ratio would improve the rate of milling. The study was continued for three weeks in the plant and, at first, there appeared to be a slight strength advantage (1-2%), although considerably less than that realized in the Semi-Works. The average of the entire three week study did not show any marked advantage; however, it is planned to repeat the evaluation.

A second variable study, omission of dilutions, was also made in May, 1951 for a one week period. Normally, 50% of the total acetone used for milling is charged initially, 20% after one hour and 30% after six hours. Based on interpretation of power curves, it appeared that a higher average power and perhaps an improvement in milling would result if all the acetone were charged initially. Unfortunately, most of the study was invalidated by an operating error, mixing of Blue LB and Blue BG; however, in the remainder, there appeared to be a 2-3% strength deficiency, instead of an improvement, even though the power required for milling was higher.

E. Extraction

The extraction procedure for Blue LB, subsequent to solvent milling, on January 1, 1950 consisted of a 2% sulfuric acid extraction followed by a 3% ammonium hydroxide extraction. No changes were made for the period covered by this report.

In February, 1950, a study of omission of the alkaline extraction was initiated. This variable was evaluated simply by comparing quality of plant samples of non-alkaline extracted Blue LB with the final plant product. A number of such evaluations showed no apparent quality deterioration associated with omission of alkaline extraction.

The first plant evaluation of omission of the alkaline extraction was made in March, 1950. The evaluation of six lots of Blue LB in various formulations was as follows:

1. BP-173-D, BT-284-D and BT-304-D products were fully equal in ink mill behavior and Hegman texture to their controls.

2. BT-284-D and BL-282-D products were fully equal to their controls in color and flocculation tested in alkyd.

3. BL-288-D products were very slightly on the defensive strengthwise versus standard by actual linoleum tests.

As a result of the satisfactory evaluation of the above six lots, an additional 12,000# of Blue LB was made in May, 1951 without an alkaline extraction. The quality was entirely satisfactory in all Newark codes tested, with the exception of one lot of BT-284-D, which was inferior in texture to suitable controls.

Additional production of Blue LB without an alkaline extraction was made in July, 1950 for a more complete evaluation as BT-284-D. The average results of six lots of BT-284-D were as follows:

Rubout evaluation	- 1-5% weak vs std.
Ink	- 3% weak on the 5T passes vs. std.
Vinyl	- 5% weak vs. std.
Alkyd	- trace weak vs. std.

In view of these results and the potential savings realisable from omission of the alkaline extraction, a two-month plant trial was started September 29, 1950 to provide data for a statistical evaluation. The results of the two-month trial of elimination of the alkaline extraction showed no significant quality degradation; hence, omission of the alkaline extraction was incorporated into the standard manufacturing procedure.

F. Quality

The quality of Newport Blue LB production is shown as Exhibit (3) averaged by months. The quality was satisfactory for the period covered by this report with the exception of 1-4% average weakness compared to standard BT-304-D in the period, January, 1951 through June, 1951.

From January, 1950 to February, 1951, 524 lots of Blue LB were produced without a single lot outside the strength specification, which is ± 5% of BT-304-D. In February, 1951, several lots, which were 6% weaker than BT-304-D, were produced from the first plant crudes using the "Kerosene Flotation" sulfation procedure. Also, in February, 1951, several lots, which were 6-10% weak versus BT-304-D, were found to contain an appreciable quantity of beta phase CPC, probably indicating contamination with chlorine-free CPC (Blue BG).

In May, 1951, substandard production amounted to six lots, which were 6-9% weaker than BT-304-D. The excessive weakness was found to be attributable to ineffective press washing after the acid extraction, and was corrected by more frequent inspection and replacement of plates and frames.

An extensive study of Blue LB strength was initiated in June, 1951. There are indications that plant solvent milling in the present cycle of 21 hours gives a product whichaverages 100:100 versus standard BT-304-D, when finished in the laboratory. Therefore, attention has been directed to improving the efficiency of the plant finishing to approximate that realizable in the laboratory. Two lots, which were finished on the acid side (pH = 3.1 and 3.7) instead of a minimum pH of 7.0, were 3% stronger by rubout than normal production. Pending evaluation of these lots as BT-304-D, additional study is planned.

G. Yield

The "Monastral" Blue LB yield for January, 1950 through June, 1951 ranged from 74.4% to 81.3% and averaged 77.5% as shown in Exhibit (4). All yields are expressed as percentage of theoretical, calculated on a phthalic anhydride basis.

Two process changes, which are believed to have improved yields, were made in 1950. As a result of data developed in the Newark Laboratory and Semi-Works, the quantity of copper chloride dihydrate used in the synthesis of CPC was increased in May, 1950 from 98% to 103% of the theoretical requirement. The average yield increase for the subsequent thirteen months was 1.5% as compared to the previous four months. It is believed that the major portion of this increase is attributable to the increased quantity of copper chloride dihydrate.

The second process change, regulation of the synthesis temperature within specifications, may be responsible for a portion of the yield increase. According to information from the Organic Chemicals Department, yield increases of 3-5% were obtained by synthesizing CPC below 195°C as compared to 200-210°C. During the latter part of 1950 and the first part of 1951, the number of syntheses at temperatures above 200°C was gradually reduced until April, 1951, when excessive temperatures were eliminated (explained under "Monastral" Blue LB, Section "B").

H. Spray Drying

In May, 1950, several experimental spray drying tests of crude Blue CPC were conducted at the Experimental Station in cooperation with the Engineering Service Division. Using an inlet temperature of 450°F and an outlet temperature of 200°F, the crude was dried successfully to a very fine powder of kerosene content ranging from 0.5% to 2.0%. Quality evaluation in the laboratory showed that the spray dried CPC was at least equal to suitable controls made from pan-dried CPC.

After the dryer explosion in March, 1951, interest was revived in spray drying both on a custom basis and as a replacement for the damaged plant dryers. Several spray drying companies were contacted and drying was actually started at Spray Drying Service, Inc., Garwood, N.J., but had to be discontinued since their equipment was inadequate for proper dust control.

Arrangements were made at the Experimental Station in April, 1951 to spray dry sufficient crude Blue LB for two plant mill charges (about 1000#). Again, due to inadequate dust recovery equipment, it was necessary to stop drying after only 270# was processed. Consequently, the spray dried product was evaluated in the Newark Semi-Works, instead of the Newport Plant. The conclusions drawn from the evaluation were as follows:

1. Spray dried crude returns a slightly more intense product than tray-dried CPC.

2. Spray dried crude presents the possibility of an increase in mill loading.

3. Solvent milled spray dried crude at the standard loading shows no evidence of a more rapid rate of strength development than tray-dried crude.

4. The apparent advantages of spray dried CPC do not constitute sufficient justification for installation of a spray dryer as compared to P. & S. tray dryers.

"MONASTRAL" BLUE BG

A. Production

A total of 34,045# of Blue BG was produced in three campaigns in the period covered by this report. The first Blue BG campaign in July 1950, 9888#, was milled at a production rate 17% higher than previous campaigns as a result of a decrease in mill cycle from 36 to 30 hours.

The next Blue BG campaign in October, 1950, which totalled 12,699#, was solvent milled in a 30 hour cycle; but the mill loading was increased 5% from 330# to 345# per charge.

The third campaign, 11,458#, was solvent milled in April, 1951 at the same production rate as the previous campaign.

B. Quality

The quality of the July, 1950 Blue BG campaign averaged 104:100 and vs green compared to BT-297-D, SW 373 and showed no indication of Blue LB contamination. Laboratory extraction of a number of plant mill samples resulted in an average quality of 99:100, vs green and s intense. Two batches, N 657-75 and 80, which were 105:100 versus standard BT-297-D, SW 373 as shown in Exhibit (5), were each improved to 100:100 by additional laboratory washing, indicating that inadequate or inefficient plant washing was responsible for the plant weakness.

The Blue BG campaign in October, 1950 averaged 102:100, vs green and vvs intense versus BT-297-D, SW 373. This campaign showed the least contamination from Blue LB of any to date. The quantity of copper

chloride dihydrate used in the synthesis was increased to 110% of theory as a result of laboratory studies, which indicated a significant yield increase. The actual plant yield for subject campaign improved 4% on a phthalic anhydride basis.

In April, 1951, the Blue BG campaign averaged 101:100, vvs green and vs intense versus standard BT-297-D, SW 373 and was considered the best BG campaign produced at Newport from both quality and production standpoints. This campaign represents the first use of crude CPC sulfated by the "Kerosene Flotation" procedure for Blue BG. In-process sampling of a large number of batches showed that the final alkaline extraction of Blue BG does not improve quality. It is planned to eliminate the alkaline extraction following solvent milling in subsequent Blue BG production.

"MONASTRAL" GREEN

A. Chlorination

The chlorination unit was operated on an experimental basis only from January, 1950 through July, 1950 while awaiting design and installation of adequate fume disposal facilities. Twenty chlorinations were made in this period when the prevailing wind was away from the adjacent communities.

After the fume scrubbing towers were installed in August, 1950, normal production of CPC Green was resumed. Between August, 1950 and July, 1951, an average of forty chlorinations per month was produced, ranging from a low of twenty-one in August, 1950 to a high of fifty-seven in May, 1951.

Probably the most important process improvement that was developed in the period covered by this report was the substitution of anhydrous aluminum chloride for antimony oxide as the catalyst in the chlorination step. A rather violent exothermic reaction between antimony oxide and sulfur chloride had been a constant source of difficulty, resulting in an accumulation of solid material in the reflux condenser and an occasional rupture of the autoclave safety disc. It was found by laboratory chlorinations that a polychloro CPC could be produced with aluminum chloride tinctorially equivalent to that with antimony oxide. After April, 1950, anhydrous aluminum chloride was used as the catalyst in the standard process.

There was no evidence of a reaction of sulfur chloride with aluminum chloride in the laboratory chlorinations; however, in the plant, occasionally a temperature rise occurred, which would at times reach 40-50°C. The literature reports complex compound formation of sulfur chloride with aluminum chloride. In the plant, it was possible to correlate dullness of the final product with a temperature rise in the autoclave, presumably resulting from a reaction between the sulfur chloride and aluminum chloride. The frequency of the temperature rises was reduced considerably by a modification of the method of addition of

of ingredients. The aluminum chloride was "sandwiched" between the crude CPC Blue and the agitator rotated one complete turn prior to addition of sulfur chloride. In June, 1951 a second revision in the method of adding ingredients was responsible for complete elimination of such temperature rises. The entire quantity of sulfur chloride was charged to the autoclave, to which had been previously added crude CPC Blue and anhydrous copper chloride. The anhydrous aluminum chloride was then "drowned" rapidly without agitation into the sulfur chloride with no detectable reaction.

In March, 1950, two chlorinations were made with antimony trichloride in place of antimony oxide as the catalyst. As a precaution against possible reaction violence, the batch sizes were reduced to 25% and 50% of normal. The reflux condenser was cleaned before the two chlorinations and inspected afterwards. Only one tube was found clogged, although a sizeable quantity of solids was found at the vapor entrance to the condenser. By laboratory milling, both products were strong, intense and equal in hue versus GT-674-D, lot 430.

The use of anhydrous copper chloride in the chlorination was started in January, 1950 in the Newport Plant. It was demonstrated in the laboratory that the presence of copper chloride provided insurance against the possible bad effects of inorganic iron contamination, and appeared to offer a substantial tinctorial improvement over controls.

Several plant experiments were made using 10 and 20% anhydrous copper chloride on CPC Blue basis. Both quantities appeared to enhance quality significantly; however, there was no advantage in the larger quantity. The use of 10% anhydrous copper chloride on the pigment basis was adopted as standard practice.

Three chlorinations were made in January, 1951 using crude Blue CPC, which had received an acid extraction in addition to the usual alkaline extraction. Solvent milling of these, both in the plant and laboratory, showed no tinctorial advantages for the batches which received both extractions.

Anhydrous aluminum chloride, transferred from Edge Moor (ex Ohio Apex), was used successfully in August, 1950 in place of the more expensive and less readily available anhydrous aluminum chloride (pulverized) from the Mallinckrodt Chemical Company. The use of the Ohio Apex product was continued as standard practice with substantial savings.

In December, 1950, a slight leak around the main flange of the autoclave body was observed. An inspection of the joint revealed serious corrosion (about 70 pits) of the nickel-clad flange. The surface was refaced with nickel and operated satisfactorily. In June, 1951, it was necessary to reweld several small pits during a scheduled shutdown.

A series of chlorinations, produced in January, 1951, resulted in very dull products. The dullness was found to be attributable to rechlorination of CPC, which had been recycled with the sulfur chloride

as the result of the vapor outlet line being removed from the rotating dryer. Analyses of the sulfur chloride in the system showed a pigment content of 2-4%. After distillation of the contaminated sulfur chloride to effect removal of the pigment, Polychloro CPC of satisfactory quality was produced.

A 10% batch size increase was tried experimentally in October 1950 for four chlorinations, C1 239 to 242, inclusive. Tinctorial evaluation showed no detectable quality deterioration compared to suitable controls. An additional series of twenty chlorinations with the 10% increase confirmed the preliminary tests. On 11/9/50, the increased batch size was adopted as standard practice. In December, 1950, six chlorinations with a second 10% increase in batch size were made successfully; but the quality evaluation was completely invalidated by the introduction of other variables in subsequent operations.

The Newport plant process for the chlorination of CPC as of June, 1951 is shown as Exhibit (6).

B. Reflux Condenser

The Andale condenser, which is used for refluxing sulfur chloride during the chlorination, contains sixty-one 5/8" nickel tubes. In the early work when antimony oxide was used as the catalyst, flow was frequently stopped in the condenser by the accumulation of solids. After replacement of antimony oxide with aluminum chloride, some blockage of the condenser occurred, but to a much lesser extent.

The frequency of tube blockage and analyses of the "solids" removed from the Andale condenser are shown as Exhibit (7).

When anhydrous aluminum chloride was substituted for antimony oxide (starting with chlorination #C1-169), the amount of tube blockage was significantly less. The unusually severe stoppage after chlorination #C1 561 (57 tubes) is believed to be caused by pressure surges that occurred in this period rather than gradual accumulation.

As shown in the table of "Analyses", Exhibit (7), the nickel content increased significantly. This is probably caused by the presence of hydrochloric acid, which is a product of hydrolysis of sulfur chloride and also a by-product of the chlorination of CPC. The aluminum content ranged from 0.33% to 2.0%, in contrast to antimony which had been as high as 12.5%. It is interesting to note that the antimony content was 10.3, 1.99 and 1.13% respectively, on the three analyses after its usage was stopped. It is believed that residual antimony in the sulfur chloride, which is recycled, is responsible.

Inspection and cleaning of the reflux condenser requires about eight hours. It is planned to clean the condenser in the future after every 100 chlorinations.

C. Masstone

The majority of Newport production the first seven months of

1950 was solvent milled from Orchem's eutectic crude Green. The masstone of solvent milled eutectic Green is considerably darker than that produced by the sulfur chloride process. The need for a darker masstone Green became apparent when the trade experienced difficulty in matching certain standards with the lighter masstone Green supplied in the latter part of 1950.

In the laboratory, it was demonstrated that a dark masstone could be produced if aluminum chloride in excess of catalytic amounts were used in the chlorination. Two chlorinations, Cl 503 and 504, were made in the plant 4/16/51 and 4/17/51, respectively, using 25% aluminum chloride on a CPC basis. For some unexplained reason, the yields were unusually low on both chlorinations as well as the control chlorinations, Cl 505 and 506; however, sufficient crude was obtained for single mill charges. When evaluated at Newark, the masstone was slightly darker than that of the controls, but considerably lighter than that of the goal standard GT-674-D, lot 430, which is solvent milled eutectic Green. In view of the yield deficiencies, two chlorinations with 25% aluminum chloride were scheduled 5/5/51. During addition of the sulfur chloride to the autoclave containing the CPC Blue and anhydrous aluminum chloride, which had been partially dispersed by one rotation of the agitator, the pressure rose to 130 psi and the temperature to 112°C. The batch was very dull by both laboratory and plant processing, in conformity with past experience. In view of the apparent "violence" of this technique, the second scheduled chlorination was cancelled.

On 5/15/51, two chlorinations, Cl 559 and 560, were made with 50% aluminum chloride on a CPC basis using the modified procedure of charging the aluminum chloride to the sulfur chloride, which had been used successfully with no reaction with the normal quantity of aluminum chloride (6%). There were no operating difficulties associated with these chlorinations, with the exception of the liberation of an excessive quantity of hydrogen chloride fumes that could not be handled during the water extraction. The evaluation of Cl 559 and 560, after solvent milling, as GT-674-D in lacquer, unfortunately, did not give a dark masstone compared to standard GT-674-D, Lot 430, although it was slightly darker than the controls. The inability of the plant to match laboratory performance could not be explained and the dark masstone problem was referred to the laboratory for further study.

D. Extraction of Crude Green

The only significant modification in the extraction procedure in the period covered by this report was the substitution of Triton X-101 (alkyl phenol polyglycol ether ex Rohm and Haas), a non-ionic surface active agent, for Turkey Red Oil. In concentrations of 0.5% on a CPC weight basis, Triton X-101 gave a more intense and yellow polychloro CPC than TRO in the laboratory. In January, 1950, Triton X-101 was evaluated in the extraction of Green crude and found to be essentially equal, if not slightly better, from a quality standpoint. In addition, the foaming tendencies of the slurry were much less pronounced than with TRO. Consequently, the use of Triton X-101 was adopted as standard practice.

E. Drying of Crude Green

The drying temperature of crude Green was raised experimentally from 100°C to 125°C for four batches, C1 407-410 inclusive, in February, 1951. Since there was no deleterious effect on quality, a drying temperature of 125°C for 48 hours was adopted as standard practice for the CPC plant dryer #4.

After the dryer explosion in March, it became necessary to use the Ti-Tint dryer at Newport for Green crude. It was found that an endpoint of 1.0% moisture could be obtained in 24 hours as compared to 48 hours in #4 dryer even though the Ti-Tint dryer temperature was only 104°C. The more rapid drying was believed to be attributable to better air circulation.

In June, 1951, the air circulation of #4 dryer was improved to the point where crude Green containing 1% or less moisture could be obtained in 40-44 hours at 125°C. A maximum of 46 hours was required to maintain the desired production rate.

F. Solvent Milling

The standard milling conditions for Green at the beginning of 1950 were:

400 # crude pigment
40 # trisodium phosphate
40 # sodium chromate
360 gals. acetone (minimum purity-98.5%)
Mill 24 hours

These conditions were used throughout the year until in December 1950, the sodium chromate was replaced with an equivalent quantity of sodium nitrite. The replacement was made as a result of a laboratory study, which showed that sodium nitrite prevented reduction of the pigment as well as sodium chromate and, in addition, did not present the possibility of forming water insoluble compounds that could not be readily removed in subsequent extractions.

During the first nine months of 1950, most of the crude Green solvent milled at Newport was purchased from Orchem as shown in Exhibit (8).

G. Extraction of Solvent Milled CPC

The only process changes in the final alkaline and acid extractions were omission of the sodium chromate in the acid extraction and elimination of heels. The omission of sodium chromate was tried experimentally as a result of an extensive laboratory and Semi-Works investigation at Newark and appeared to give a slight tinctorial improvement. In December 1950, the omission of sodium chromate in the acid extraction was adopted as standard practice.

Also, in December, 1950, process "heels" were eliminated in the alkaline and acid extractions by a more accurate determination of the number of frames required for filtration and actual "washing" of the residual contents of a tank into the press. The change, which was prompted by the idea that extended extractions of a portion of each lot may be harmful to quality, appeared to result in a very slight improvement in tinctorial properties, as judged from a statistical average of quality.

H. Quality

As shown in Exhibit (8), the tinctorial properties of Green varied considerably throughout the period covered by this report. The quality evaluation of the major portion of Green production during the first eight months of 1950, which was solvent milled eutectic Green purchased from Orchem, is not included in the attached quality summary.

The strength of Green production averaged 103:100 versus goal standard GT-674-D, lot 430 from January through December, 1950, but improved to 100:100 versus standard for January through June, 1951. This improvement appears to be attributable to the elimination of sodium chromate in the solvent milling and acid extraction steps, as well as improvement in filtration and washing techniques of the two extractions.

The hue of Green production for the period covered by this report averaged slightly on the blue side of GT-674-D, lot 430. Of a total of 210 lots, 164 were within the vs blue - vs yellow specifications, twenty-four were s blue, nineteen were blue and three were s yellow. The intensity of Green production varied widely from dull to intense versus standard GT-674-D, lot 430; however, the majority of production was on the dull side. Of the 210 lots, 112 ranged from s dull to s intense, ninety-four were dull and four were intense versus standard.

In the early part of April, 1951, a new standard for Newport, GT-674-D, SW 2609, which was made at Newark from Newport synthesized Green, replaced the previous standard GT-674-D, lot 430, which was made from solvent milled eutectic Green. The major difference between the two standards was masstone, the masstone of GT-674-D, SW 2609 being light vs GT-674-D, lot 430.

The most serious tinctorial problem in 1950 was the inability of the plant to obtain consistantly CPC Green of satisfactory intensity. Most of the plant experiments and changes in standard operating procedures discussed in the other sections of this report under "Monastral" Green were designed toward improvement in intensity.

EXHIBIT (1)

NEWPORT PLANT PROCESS FOR SYNTHESIS OF "MONASTRAL" BLUE LB AS OF JUNE, 1951

To the glass lined 1500 gallon reactor add:

7800 lbs. (1200 gals.) of "Deo Base" or Bayol D" Kerosene.

Start agitator.

3 lbs. Paranox 441 (name recently changed to WS 1936 concentrate) (Note 1).

Sample kerosene and determine peroxide number. If any measurable oxidation exists, do not use. (Note 2).

Close manhole and heat to 110°C with Dowtherm.

One batch chlorphthalic acid (Note 3).

835 lbs. phthalic anhydride.

300 lbs. copper chloride dihydrate (Note 4).

2.5 lbs. ammonium molybdate. (Note 5).

Heat charge to 130°C.

Then add:

1500 lbs. molten urea.

Heat charge to 195°C and hold for four hours at 195±5°C.

Pump entire slurry to the sulfator.

NOTES

1. The purpose of the anti-oxidant is to inhibit oxidation of the kerosene.
2. If a measurable peroxide number is found, the kerosene should be washed with concentrated sulfuric acid.
3. One batch of chlorphthalic acid, which is synthesized at Newport from 236 lbs. phthalic anhydride is the proper quantity to give the specified 4.0-5.0% chlorine in Blue LB/CPC.
4. This quantity was increased from 285 lbs. as a result of Semi-Works study which showed a higher yield with an excess of copper chloride.
5. Use J. T. Baker's Technical Grade on an "as is" basis.

EXHIBIT (2)

NEWPORT PLANT PROCESS FOR SULFATION OF "MONASTRAL" BLUE LB BY THE "KEROSENE FLOTATION" (KF) PROCEDURE AS OF JUNE, 1951

After pumping one synthesis charge of Blue LB to the sulfator, add while agitating:

1560 lbs. 98% sulfuric acid in 1-1/2 hours.

Stop agitator

Start siphon and decant kerosene.

Add 700 gals. water.

Let settle one hour.

Start siphon and decant all kerosene floated to surface.

Add 3000 lbs. ice.

Start agitator.

Add 50% sodium hydroxide solution to pH of 7.0-8.0.

Pump charge to extraction tank for alkaline extraction.

EXHIBIT (3)

QUALITY OF "MONASTRAL" BLUE LB

Date	Packed Lots	Average Quality vs BT-304-D, Lot 90719
January, 1950	N623-523 to 559	100:100 s green
February, 1950	N623-560 to 596	101:100 s green
March, 1950	N623-597 to 637	101:100 s green
April, 1950	N623-638 to 681	100:100 vs green
May, 1950	N623-682 to 728	99:100 vs green vvs dull
June, 1950	N623-729 to 764	99:100 vvs red vvs dull
July, 1950	N623-765 to 799	100:100 vvs red vvs dull
August, 1950	N623-800 to 849	100:100 vvs green vvs dull
September, 1950	N623-850 to 889	100:100 vs green vs dull
October, 1950	N623-890 to 920	101:100 vvs dull
November, 1950	N623-921 to 966	101:100 vs green
December, 1950	N623-967 to 2	101:100 vvs green vvs dull
January, 1951	N623-3 to 45	102:100 s green vs intense
February, 1951	N623-46 to 79	104:100 s green vvs intense
March, 1951	N623-80 to 97	104:100 s green vs intense
April, 1951	N623-98 to 104	102:100 vs green s intense
May, 1951	N623-105 to 147	103:100 vs green vs intense
June, 1951	N623-148 to 185	103:100 vs green vs intense

EXHIBIT (4)

YIELD OF "MONASTRAL" BLUE LB

Month	Year	Yield*
January	1950	77.0%
February	1950	76.0%
March	1950	75.0%
April	1950	76.0%
May	1950	80.6%
June	1950	78.5%
July	1950	78.1%
August	1950	76.0%
September	1950	74.4%**
October	1950	78.1%
November	1950	77.6%
December	1950	76.6%
January	1951	76.2%
February	1951	76.1%
March	1951	81.3%
April	1951	80.3%***
May	1951	77.2%
June	1951	76.0%

*Expressed as % of theoretical based on phthalic anhydride consumption.

**1.2% low due to one synthesis, which was discarded, because a scraping knife fell into the glass lined kettle.

***1.2% low due to one synthesis, which was discarded, because a steel nut fell into the glass lined kettle.

EXHIBIT (5)

QUALITY OF "MONASTRAL" BLUE BG

Packed Lot	Date	Quality vs BT-297-D, SW 373
N 657 -63	July, 1950	99:100 vs red
-64	"	105:100 s green
-65	"	105:100 s green
-66	"	105:100 s green
-67	"	102:100 s green
-68	"	106:100 s green
-69	"	106:100 s green
-70	"	104:100 s green
-71	"	104:100 s green
-72	"	105:100 s green
-73	"	102:100 s green
-74	"	104:100 s green
-75	"	105:100 vvs red vvs dull
-76	"	106:100 vs red
-77	"	104:100 vs dull
-78	"	105:100 vvs red vvs dull
-79	"	105:100 vvs red vs dull
-80	"	105:100 vs dull
-81	"	103:100 s dull
-82	"	103:100 vvs green vvs dull
-83	October, 1950	100:100 vvs green
-84	"	100:100 vvs green
-85	"	101:100 vvs green
-87	"	102:100 vvs green
-88	"	101:100 vs green
-89	"	102:100 green s intense

EXHIBIT (5) (CONT'D.)

N 657 -90	October 1950	102:100	green intense
-91	"	104:100	s green vvs intense
-92	"	105:100	vs green vvs intense
-93	"	105:100	s green vvs intense
-94	"	102:100	s green s intense
-95	"	106:100	vvs green vvs intense
-96	"	105:100	s green
-97	"	104:100	s green
-98	"	103:100	s green vs intense
-99	"	101:100	s green vvs intense
-100	"	103:100	s green vvs intense
-101	"	103:100	vs green vvs intense
-102	"	103:100	vs green vvs intense
-103	"	103:100	s green vs intense
-104	"	103:100	vs green vvs intense
-105	"	104:100	vs green vvs intense
-106	April, 1951	103:100	vs red vs dull
-107	"	102:100	vs red vs dull
-108	"	100:100	vvs green
-109	"	101:100	vvs green vvs intense
-110	"	100:100	vvs intense
-111	"	100:100	vvs intense
-112	"	101:100	vvs green vvs intense
-113	"	101:100	vvs green vvs intense
-114	"	100:100	vvs green vvs intense
-115	"	101:100	vs green vs intense
-116	"	101:100	s intense
-117	"	102:100	vs intense

EXHIBIT (5) (CONT'D.)

N 657 -118	April, 1951	101:100	vvs intense
-119	"	100:100	s intense
-120	"	103:100	s intense
-121	"	102:100	s intense
-122	"	100:100	vs intense
-123	"	102:100	vs intense
-124	"	101:100	vs intense
-125	"	101:100	vs intense
-126	"	102:100	s intense
-127	"	100:100	vvs intense
-128	"	101:100	vvs red

EXHIBIT (6)

NEWPORT PLANT PROCESS FOR CHLORINATION OF CPC AS OF JUNE, 1951

To the 400 gallon nickel-clad autoclave add:

244 lbs. chlorine-free crude Blue CPC (dried to kerosene content below 1%)

24 lbs. anhydrous copper chloride.

3400 lbs. sulfur dichloride (of minimum chlorine content of 67.5%)

15 lbs. anhydrous aluminum chloride. (Note 1)

Close manhole and bolt securely.

Start agitator.

Set automatic pressure regulating valve at 265 psi.

Check that cooling water is flowing through the reflux (Andale) condenser and brine through the tail condenser.

Start hot water flowing from mixer through autoclave jacket.

An initial reaction will occur at approximately 70°C. The rate of heating is most critical. The following rates should not be exceeded under any conditions. (Note 2).

Temperature Rise	Elapsed Time
25-50°C	20 minutes
50-60°C	15 minutes
60-65°C	15 minutes

After the reaction has occurred, heat with steam to 265 psi and 175°C.

Hold 4 hours above 175°C.

Cool to 125°C and discharge sulfur chloride slurry to the rotating dryer for distillation. (Note 3).

NOTES

1. Ohio Apex Co. aluminum chloride (anhyd.) pellets are used. Aluminum chloride is added through the manhole and "drowned" in the sulfur chloride rapidly.

2. If specified heating rate is exceeded, hot water flow should be stopped immediately and cold water started through the Autoclave jacket.

3. Autoclave should be flushed with 500 lbs. sulfur chloride to remove pigment which may interfere with operation of flush bottom discharge valve.

EXHIBIT (7)

ANALYSES OF "SOLIDS" REMOVED FROM REFLUX CONDENSER

Date Cleaned	Number of Chlorinations	Number of Tubes Plugged	For Analyses, see Table Below
1-24-50	Cl 161-3 (3)	55	A
3-30-50	Cl 164-8 (5)	4	B
7-18-50	Cl 169-79 (11)	16	C
9-20-50	Cl 180-219 (40)	30	D
10-30-50	Cl 220-268 (49)	13	E
11-28-50	Cl 269-320 (52)	3	Not Analyzed
2-22-51	Cl 321-429 (109)	8	"
5-17-51	Cl 430-561 (132)	57	F
6-23-51	Cl 562-618 (57)	6	G

ANALYSES

	A	B	C	D	E	F	G
Antimony,%	12.5	12.5	10.3	1.99	1.13	None	None
Nickel	3.8	1.5	1.0	8.89	6.53	8.5	6.8
Iron	0.9	0.8	0.5	3.28	3.70	1.2	4.0
Ammonia	17.9	16.9	8.6	8.64	7.48	8.2	8.0
Sulfates	4.8	--	Trace	28.3	38.4	26.5	13.0
Sulfur	2.0	1.3	5.8	10.96	17.1	0.1	0.7
Extracted Solids	2.5	--	35.1	5.78	9.8	4.1	6.2
Aluminum	--	--	0.33	1.53	0.9	2.0	1.2
Chlorides	52.0	49.6	40.8	29.9	20.8	25.5	22.8

EXHIBIT (8)

*QUALITY OF POLYCHLORO CPC PRODUCED AT NEWPORT JANUARY, 1950 - JUNE, 1951

Packed Lot	Month - Year	Quality vs. Standard GT-674-D, Lot 43
N-624 -225	Feb., 1950	99:100 blue vs intense
-226	" "	99:100 blue vs intense
-244	March, 1950	102:100 blue s dull
-245	" "	98:100 blue dull
-246	" "	101:100 s blue vvs intense
-313	August, 1950	100:100 intense
-314	" "	104:100 intense
-315	" "	100:100 vvs blue intense
-316	" "	103:100 vs yellow s dull
-317	" "	104:100 dull
-318	" "	102:100 dull
-332	September,1950	101:100 vs dull
-333	" "	104:100 vs dull
-335	" "	102:100 vs dull
-336	" "	100:100 s dull
-350	" "	107:100 vs blue vs dull
-351	" "	107:100 vs blue vvs dull
-352	" "	106:100 dull
-353	" "	105:100 s blue s dull
-354	" "	104:100 vs blue s dull
-355	" "	105:100 s blue s dull
-356	October, 1950	104:100 blue s dull
-357	" "	105:100 blue s dull

N-624	-358	October, 1950	105:100 s blue s dull
	-359	"	106:100 vs blue vvs dull
	-360	"	104:100 s blue vvs dull
	-361	"	106:100 vs blue s dull
	-362	"	106:100 vs blue s dull
	-363	"	106:100 vs blue s dull
	-364	"	109:100 s blue s dull
	-365	"	105:100 s blue dull
	-366	"	105:100 vs blue dull
	-367	"	107:100 vs blue dull
	-368	"	107:100 dull
	-369	"	104:100 s blue dull
	-370	"	104:100 s blue dull
	-371	"	105:100 s blue s dull
	-372	"	111:100 blue vs dull
	-373	"	106:100 s blue s dull
	-374	"	102:100 blue vvs dull
	-375	"	105:100 vs blue vs dull
	-376	"	105:100 vs blue vs dull
	-377	"	107:100 blue
	-395	November, 1950	106:100 dull
	-396	"	103:100 dull
	-397	"	103:100 s dull
	-398	"	103:100 dull
	-399	"	105:100 dull
	-400	"	103:100 dull
	-401	"	101:100 dull
	-402	"	101:100 dull
	-403	"	101:100 dull

N-624	-404	November, 1950	101:100 dull
	-405	"	101:100 dull
	-406	"	104:100 dull
	-407	"	102:100 dull
	-408	"	104:100 dull
	-409	"	106:100 dull
	-410	"	104:100 dull
	-411	"	101:100 s dull
	-412	"	101:100 s dull
	-413	"	106:100 dull
	-414	"	103:100 dull
	-415	"	103:100 dull
	-416	"	102:100 dull
	-417	December, 1950	102:100 dull
	-418	"	106:100 dull
	-419	"	102:100 dull
	-420	"	101:100 dull
	-421	"	101:100 dull
	-422	"	105:100 dull
	-423	"	104:100 dull
	-424	December, 1950	101:100 dull
	-425	"	103:100 dull
	-426	"	102:100 dull
	-427	"	105:100 dull
	-428	"	104:100 dull
	-429	"	103:100 dull
	-430	"	104:100 dull
	-431	"	102:100 dull

N-624	-432	January, 1951	104:100 dull
	-433	"	104:100 dull
	-434	"	104:100 dull
	-435	"	99:100 blue vs dull
	-436	"	99:100 blue s dull
	-437	"	100:100 blue s dull
	-438	"	100:100 blue vs dull
	-439	"	102:100 s blue dull
	-440	"	101:100 s blue dull
	-441	"	102:100 s blue dull
	-442	"	110:100 intense
	-443	"	108:100 blue vs dull
	-444	"	104:100 dull
	-445	"	103:100 dull
	-446	"	106:100 blue
	-449	"	102:100 dull
	-450	"	106:100 dull
	-451	"	106:100 dull
	-452	"	94:100 blue vs intense
	-453	"	103:100 dull
	-454	"	102:100 dull
	-455	"	102:100 dull
	-456	"	101:100 s blue dull
	-457	"	98:100 dull
	-458	"	98:100 dull
	-459	"	101:100 dull
	-460	"	96:100 vs blue dull
	-461	"	100:100 dull
	-462	"	101:100 vs blue dull

N-624	-463	January, 1951	104:100 dull
	-464	February, 1951	103:100 dull
	-465	"	98:100 s blue dull
	-466	"	101:100 s blue s dull
	-467	"	102:100 vs blue dull
	-468	"	101:100 vs blue dull
	-469	"	101:100 vs blue s dull
	-470	"	100:100 vs blue s dull
	-471	"	100:100 s blue s dull
	-472	"	100:100 blue s dull
	-473	"	100:100 blue s dull
	-474	"	101:100 s blue s dull
	-475	"	100:100 vs blue s dull
	-476	"	100:100 vs blue s dull
	-477	"	100:100 vs blue s dull
	-478	"	100:100 vs blue dull
	-479	"	101:100 vs blue s dull
	-480	"	102:100 vs blue s dull
	-481	"	100:100 s blue s dull
	-482	March, 1951	101:100 vs blue dull
	-483	"	100:100 s blue s dull
	-484	"	101:100 blue s dull
	-485	"	100:100 blue vs dull
	-489	"	103:100 s blue vs dull
	-490	"	102:100 vs blue vs dull
	-491	"	101:100 vs blue vs dull
	-492	"	100:100 vs blue
	-493	"	101:100 s blue vs dull
	-494	"	100:100 vs blue s dull

N-624	-495	March, 1951	102:100 dull
	-496	"	101:100 dull
	-497	"	102:100 dull
	-498	"	101:100 vvs blue dull
	-505	April, 1951	101:100 vs dull
	-506	"	102:100 s dull
	-507	"	103:100 dull
	-508**	"	103:100 s yellow
	-509	"	100:100 vs yellow
	-510	"	101:100 s yellow
	-511	"	101:100 s yellow
	-512	"	101:100 vs yellow
	-513	"	100:100 vs yellow
	-514	"	100:100 vvs yellow vs dull
	-515	"	103:100 dull
	-516	"	101:100 dull
	-517	"	100:100 s dull
	-518	"	100:100 dull
	-519	"	99:100 dull
	-520	April, 1951	98:100 dull
	-521	"	97:100 dull
	-522	"	97:100 dull
	-523	May, 1951	96:100 dull
	-524	"	97:100 s dull
	-525	"	100:100 vvs yellow vs dull
	-526	"	100:100 vvs intense
	-527	"	100:100 vvs yellow

N-624 -528	May, 1951	100:100	vvs intense
-529	"	99:100	s intense
-530	"	99:100	s intense vvs yellow
-531	"	100:100	vs yellow
-532	"	99:100	vs intense
-533	"	97:100	vs yellow
-534	"	99:100	vs yellow vvs intense
-535	"	99:100	vs intense vvs yellow
-536	"	98:100	vs intense
-537	"	102:100	vs yellow vs dull
-538	"	99:100	vvs blue s dull
-539	"	100:100	vs dull
-540	"	103:100	dull
-541	"	100:100	dull
-542	"	100:100	dull
-543	"	101:100	dull
-544	"	103:100	dull
-545	"	100:100	dull
-546	"	100:100	dull
-547	"	100:100	dull
-548	"	93:100	blue dull
-549	June, 1951	94:100	vs blue dull
-550	"	98:100	vs blue vs dull
-551	"	103:100	dull
-552	"	97:100	s blue s intense
-553	"	95:100	dull
-554	"	98:100	vs blue vs dull

N-624 -555	June, 1951	96:100	vvs blue vs dull
-556	"	97:100	vvs blue vvs dull
-557	"	99:100	vs blue vs intense
-558	"	97:100	vvs blue vs dull
-559	"	97:100	vvs dull
-560	"	100:100	s dull
-561	"	99:100	vs blue vs dull
-562	"	97:100	vs intense
-563	"	94:100	vvs intense
-564	"	97:100	vs intense
-565	"	97:100	vvs yellow
-566	"	97:100	vs yellow vs dull
-567	"	98:100	dull
-568	"	98:100	dull
-569	"	97:100	s dull
-570	"	98:100	vvs yellow vvs dull
-571	"	98:100	vs yellow vs intense
-572	"	99:100	vs yellow

* Lots N-624-203 through 224, 227 through 243
247 through 312, 319 through 331,
337 through 349 and 378 through 386 were
milled from Orchem eutectic crude green CPC.

**Started using new reference standard GT-674-D, SW 2609.