223.41

KN 53-20

Serial No. KN-53-20

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NEWARK PLANT
CHEMICAL DIVISION - COLORS

Progress Report

FINISHING OF PHTHALOCYANINE PIGMENTS VI "MONASTRAL" BLUE LB

Period Covered: APRIL, 1948 to MARCH, 1951.

FILE: 223.41

DATE: 8/12/53

223.41

Serial No. KN-53-20

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

FINISHING OF PHTHALOCYANINE PIGMENTS VI "MONASTRAL" BLUE EB.

APRIL 1948 to MARCH, 1951.

CHARGE: A-IC-20

SUBMITTED BY: A. J. Stratton DATE SUBMITTED: 7/17/53

APPROVED BY: J. H. Cooper 8/10/53 DATE ISSUED: 8/12/53

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INTRODUCTION:

A previous report in this series (KN-50-19) covers the work on finishing "Monastral" Blue LB up to about April 1, 1948, when the Newport plant for the manufacture of phthalocyanine pigments began operations. This report completes the discussion of the studies on finishing Blue LB up to about March 1, 1951. Much of this work was done during the early stages of operation of the Newport plant and, to a large extent, comprises work which was designed to assist in the more efficient operation of the plant. This includes a limited amount of work on the synthesis of CPC-LB.

SUMMARY AND CONCLUSIONS:

The work during this period may be summarized under the following six topics:

1. Control Testing

A great many samples taken from various stages of the Newport plant operations were tested at Newark in order to determine whether the Newport plant was operating at the maximum expected efficiency. In general, the quality of the crude synthesized at Newport was excellent; but there was some difficulty in obtaining as good results in the Newport ball mills as could be obtained consistently at Newark. Although no clear-cut solution to the problem was ever attained, it was generally agreed that careful attention to specified details of operation largely overcame this difficulty. Some slight loss in quality was also observed during the further processing at Newport. In spite of these slight deficiencies, the quality was such as to permit the establishment of new standards at Newark, which were markedly superior to previous phthalocyanine standards. A brief study of goal yields indicated that any losses in the ball mills were mechanical, and that yields in excess of 98% of the pigment charge should be readily obtained.

2. Grinding Studies in the Semi-Works

In an effort to improve the efficiency of operation in the Newport ball mills, considerable study of grinding in the semi-works ball mills was carried on at Newark. One factor, which seemed important at the time, had to do with the amount of acetone in relation to the pigment in the mill. Whereas the original specification called for seven parts of acetone per part of pigment, the results of this study led to the suggestion that the mills be originally charged with only five parts of acetone, and that additional acetone be added in two steps, so that near the end of the grinding cycle there would be a total of ten parts of acetone present. Such a cycle gave smoother power curves and seemed to give somewhat improved efficiency in the over-all operation. It would appear now, however, that the original conclusions may not have been altogether valid. Some study of mill loading in the semi-works led to the conclusion that any substantial increase beyond the original specification of 314# per charge would result in increasing the required cycle to such an extent that the pounds of pigment ground per hour would not be increased, and might even be somewhat decreased.

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Discharging the mill through the bed of shot proved difficult at Newport and resulted in a marked variation in the amount of charge remaining in the mills. It was demonstrated in the Newark semi-works that a very uniform retention of charge in the mill could be accomplished by dumping with the outlet at a specified angle from the vertical, so that it was just above the bed of shot in the mill. This was tried at Newport but was not considered practical, and has never been adopted for regular plant operation.

3. Synthesis Study

In view of some difficulties in the Newport plant, certain synthesis studies were undertaken to determine the effect of variables inherent in the plant operation, but not previously well covered in semi-works studies. There was no clear evidence that the addition of the urea in melted form at a temperature of about 140°C gave results significantly at variance with those in the previous semi-works syntheses, in which the urea was added before the charge was heated. The addition of the cupric chloride at temperatures of about 160-180°C was tried without any significant evidence of benefit. Adding this chemical in dry form under these conditions proved very difficult, but it has been successfully done in later work by slurrying in kerosene.

The re-use of the kerosene was, in general, new with the Newport plant; and the use of Newport recovered kerosene was tried at Newark to see whether that could account for any of the difficulties observed. In general, if there has been no significant oxidation of the kerosene, recovered kerosene gives results at least as good and perhaps slightly superior to that from fresh kerosene.

4. Lakes

A substantial amount of the phthalocyanine blue production is converted into three lakes for specialized uses. In no case did the direct use of Newport CPC-LB (N-623) give results exactly comparable to those previously obtained with phthalocyanine pigments manufactured at Orchem. However, suitable modifications were developed, and revised formulas were established for BP-173-D and BL-282-D. The linoleum lake, formerly coded BP-263-D, was modified in a more significant manner to give a definitely stronger lake, which was coded BL-288-D.

5. Soft Powder Treatments

The simple drying out of N-623 as received at Newark, gave a product which exhibited excellent strength, but which was distinctly poor in the usual test for texture, and particularly in a rather serious separation on the first pass over the ink mill. In spite of such deficiencies, this product has been coded BT-304-D, and has enjoyed substantial sales to certain customers. Nevertheless, the soft powder toner was required for general sales purposes, and a number of specialized treatments were tried in developing this product. The process finally adopted involved the addition of 10% of carbon tetrachloride, based on the weight of dry pigment in the slurry, to the diluted N-623, followed by vigorous agitation, and

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either pan drying directly or drying after the removal of some of the water by filtration. This product was coded BT-284-D, and exhibited a slight deficiency (perhaps 5%) in strength as compared to BT-304-D.

6. Miscellaneous Experiments

A so-called waste solvent from the Polychemicals Department (largely Methyl Acetate) was proposed for use in place of acetone on the basis of a markedly lower cost. In simple laboratory tests it gave results substantially equivalent to acetone, but offered no advantage. The limited water solubility was judged a definite disadvantage, and the fundamental value as Methyl Acetate could involve a higher cost than that of the acetone involved. It was not deemed desirable for further study.

Salt milling and dispersion milling were shown to be acceptable methods of finishing phthalocyanine pigments in place of acetone milling, but were not considered attractive operations.

Fluid energy milling of phthalocyanine crude and finished pigments did not significantly alter their properties.

DISCUSSION OF EXPERIMENTAL RESULTS

1. Control Testing

A great many samples of materials taken at various points in the Newport operation were transported to Newark and tested in the laboratory under conditions previously established for optimum operation in the Newark semi-works and laboratory. For instance, the Newport crudes were brought to Newark and tested both as lump and as pulverized crude in both laboratory and semi-works mills. At no time was any significant advantage observed in milling the pulverized product as compared with the lump. In general, all of the crudes tested were of excellent quality, although there were a few notable exceptions. It is believed that most of these exceptions resulted from syntheses known to be unusual in one way or another.

Many samples were taken from the Newport ball mills and tested at Newark in the same way that semi-works mills had been samples previously. In general, the grinding curves were quite normal, but many of the ball mill charges failed to develop the strength which was reasonably expected from the previous observations. Most of these difficulties were never clearly pointed out, but it was the general consensus that they resulted from careless operation of the mills. Some improvements were also observed as the result of new techniques which were proposed, following some of the studies at Newark.

Extraction of samples taken at various points subsequent to the ball mill operation indicated that the Newport plant suffers slight losses at almost every point of handling, but that these losses were substantially in line with losses in color strength frequently observed in similar operations. No improvements in these operations were proposed.

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Generally speaking, control testing of the finished products from Newport, shipped to Newark as N-623, was not done in the laboratory. Such work as was done, however, confirmed the Control Laboratory indications that the products were quite uniform and of acceptable quality.

A limited amount of work on goal yields to be expected in the ball milling operation indicated that any losses observed in this operation were purely mechanical, and that yields in excess of 98% of the pigment charged, when considered as pure pigment, should be anticipated.

2. Grinding in the Semi-Works

Observation of the power requirements in ball mills, both at Newark and at Newport, demonstrated that there was generally a very sharp drop-off in power after a significant perior of grinding. If additional acetone were added at the point where this drop-off occurred, it could be largely prevented or, if the acetone were added after the power had dropped off, a large increase in power consumption would be noted. This suggested first that more acetone should be used throughout the grind, but trial of this technique indicated that the grinding rate during the early part of the cycle was frequently reduced in such an operation. On the other hand, when the amount of acetone at the beginning of the charge was less than normal, the grinding rate appeared to be rapid up to the point of power drop off. These observations led to the proposal that the charge be started with a relatively small amount of acetone, and that it be diluted at previously determined points through the cycle to maintain as uniform a consumption of power as possible. The original specified loading called for seven parts of acetone per part of pigment, and the cycle ultimately adopted called for starting the charge with five parts of acetone, diluting to seven parts after about two hours, and to ten parts of acetone after about six hours of milling. This cycle was adopted and used for several years, but there is now some doubt as to the over-all validity of these results.

A limited study of mill loading was carried out both in the semi-works mill and in the Newport mills, and it appeared that increasing the mill load always increased the required time to achieve the desired strength to such an extent that there was no over-all increase in production from the mill. As far as CPC-LB is concerned, these results still hold, although markedly different techniques now make it possible to use larger charges in the mill.

The consistency of the charge at the end of grinding, and even after dilution with a substantial amount of acetone, is such as to make the draining, through the bed of shot to an outlet at the bottom of the mill, a slow and somewhat uncertain operation, so that the amount of charge retained in the mill was quite varied in amount. It was suggested that this might be overcome if the point of discharge were just above the bed of balls, and this was

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demonstrated on the Newark mills by dumping with the outlet at a substantial angle from the vertical, so that it was above the bed of balls. A very uniform retention of charge could be achieved in such a manner, and the discharge from the mill was quite rapid. The technique was tried on the Newport plant, but the arrangement of the mills was such as to make it very difficult of practical operation, and the advantages were not deemed sufficient to justify its use in a regular manner.

3. Semi-Works Synthesis

There are no details of significance to add in addition to those given in the conclusions above.

4. Lakes

Generally speaking, the strength of lakes prepared from N-623 by standard formulas was deficient when compared to products made by the same formulas from phthalocyanine pigments previously purchased from Orchem. In the case of "Ramapo" Blue, BP-173-D, this was substantially overcome by making a slightly higher toner content lake, but this lake exhibited some dullness in comparison with the original standard. In spite of this slight deficiency in color, a new standard was adopted and has continued in fairly successful operation. In other respects, the "Ramapo" Lake shows most of the expected advantages, although its superiority over BT-284-D is much less than had been the superiority of the former standard over the old toner (BT-172-D). The experience with the non-flocculating benzoated lake, BL-282-D, was very much the same with respect to color, but a satisfactory strength in paint, where this color is important, was readily obtained.

The manufacture of an acceptable linoleum lake presented some difficulty and it was ultimately decided to standardize on a significantly higher toner content (about 25%), and to recode the former BP-263-D to BL-288-D. Once established, this lake has enjoyed rather successful operation.

5. Soft Powder Treatment

It was recognized even before the Newport plant started operation that marked improvement in texture of the dry toner would be required. Many modifications of previously accepted techniques for soft powder phthalocyanine pigments were tried, as well as some new ideas. For instance, most of the treatments which were successful with acid pasted pigments, such as treatment with naphthalene, proved useless with the solvent milled pigment. Treatment with ammonium naphthenate, and vigorous agitation to give a foam-like mass, gave a superficially soft product, but it did not prove to be actually as good in texture as it appeared. At one time, it was believed that treatment

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with a long chain amine as its acetate salt, gave a significant improvement. The product was reasonably soft in texture, but was almost always weak, and the process was abandoned. Various emulsions of volatile organic liquids, such as mineral spirits or carbon tetrachloride, were tried with somewhat mixed results, but many of them promoted weakness in addition to some improvement in texture. It was finally observed that the simple addition of carbon tetrachloride to the paste, followed by vigorous agitation and drying, gave a marked improvement in texture with a minimum loss in strength. Substantial variations in the amount of carbon tetrachloride could be used, and the use of 10% based on the pigment was the final choice. This process was adopted and continues in use to this day in the manufacture of BT-284-D, which exhibits a slight deficiency (perhaps 5%) in strength as compared to the simple dried out N-623, which is coded BT-304-D.

6. Miscellaneous Experiments

Since it was known that the crudes at Newport varied considerably in the amount of kerosene present, some tests were made to determine the effect of this kerosene on the milling operation. Although the results were not conclusive, it is believed that the presence of the kerosene is not particularly harmful if the acetone is of normal high purity.

A solvent, under the designation Solvent 89, was proposed by the Polychemicals Department as a replacement for acetone, since it was said to be available in substantial quantities as a waste material. This solvent consisted largely of methyl acetate. Tests in conventional ball mill operations indicated that it was substantially equivalent to acetone in properties, but offered no significant advantage, and its limited water solubility posed some potential problems in its use. Furthermore, its actual value as methyl acetate would be in excess of the cost of the acetone in regular use, and it was not deemed desirable to pursue its study further.

Since salt milling and dispersion milling operations were being conducted in connection with CPC Blue BG, and with CPC Green, a limited amount of experimental work was done to determine the value of these operations with CPC-LB. The results indicate that products of excellent quality can be obtained by such means, but there was no evidence of significant economic advantage in their use, and the work was not pursued further.

A special type of a fluid energy mill was proposed by a supplier for milling operations at Newark, and experimental work was done on the supplier's machine with both CPC-LB crude and finished products. There was no evidence in this work of any significant particle size reduction in the fluid energy milling operation. This is in line with observations at Newark and in the Orchem laboratories that no simple grinding operation will significantly affect the tinctorial strength of phthalocyanine crude pigments.

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Samples of pigment derived from a study of spray drying of CPC-LB crude were milled and gave no evidence of any improvement in ultimate quality resulting from this method of drying the crude pigment.

EXPERIMENTAL DETAILS

The experimental work covered in this report is recorded as follows:

N.B. 1275 - 61, 63, 64, 65, 66, 67, 71, 72, 73, 75-85.

1286 - 16-39, 41-45, 49, 53, 56, 59-65, 67, 71,72, 74, 77-83.

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1191 - 24

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1383 - 7

1393 - 43

1404 - 9, 10

MPH

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