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CHEMICAL DIVISION - COLORS

PIGMENT COLOR RESEARCH REPORT
Progress Report
FINISHING OF PHTHALOCYANINE PIGMENTS IV
"MONASTRAL" FAST BLUE BG

Period Covered: MAY 1, 1948 to MAY 1, 1951

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5 - E. F. Klenke, Newport
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8 - W. J. Clem, Chambers Works
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10 - Extra
11 - Extra

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

FINISHING OF PHTHALOCYANINE PIGMENTS IV

"MONASTRAL" FAST BLUE BG

MAY 1, 1948 to MAY 1, 1951

CHARGE: A-II-C-229
A-I-C-20

SUBMITTED BY: A. J. STRATTON A J Stratton 7/13/53 DATE SUBMITTED: 7/1/53

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INTRODUCTION:

Much of the early work on the finishing of Phthalocyanines by milling was done with chlorine-free CPC. In KN-46-19 it is recognized that these samples are all greener than the previous standard (BT-172-D), but, with a few outstanding exceptions, they were also weak. This weakness was attributed to crystal growth and the greenness was not explained.

Somewhat later, after solvent milling operations were fairly well established, a study of the effect of chlorine content brought to attention the fact that solvent ground chlorine-free CPC exhibited the greenest hue of any of the CPC pigments with a chlorine content no more than that in monochloro CPC. This is in direct contrast to the relatively red shade of the same pigment when acid-pasted or salt milled.

A crystal phase change was suspected and thoroughly confirmed by x-ray studies, which are reported in KN-48-3. The typical red shade acid-pasted product has been called the alpha phase and the green shade solvent milled product has been called the beta phase. In KN-48-3, it is stated that the small particle size material is always in the alpha phase and that the particle size is always larger when the material is converted to the beta phase. However, it is speculated that small particle size beta phase CPC should be a desirable green shade blue pigment.

In this early work, the research efforts were directed toward a red shade CPC and these reversions to an unusually green shade were considered undesirable. However, similar observations at Orchem had attracted the attention of their Sales Group and, in turn, Pigments Department Sales expressed interest in a very green CPC, especially when it was demonstrated that it was crystal stable even though it contained little chlorine.

This report covers laboratory and semi-works development studies leading to the establishment of BT-297-D as a standard and to its improvement thereafter.

SUMMARY AND CONCLUSIONS:

Chlorine-free CPC, when milled in acetone for a sufficient length of time, is completely converted to a small particle size, beta phase CPC which is crystal stable thereafter. The strength obtained is somewhat less than that obtained with CPC-LB, but the product is, nevertheless, considered a valuable pigment. This toner has been standardized as BT-297-D under the name "Monastral" Blue BG, and is now a standard pigment in our line of "Monastral" colors.

The milling step results in two changes which occur simultaneously, but may differ in rate. One is particle size reduction and the other is a phase change. The phase transformation seems to require considerable time for completion; hence, a fairly long milling cycle. Efforts to speed up this phase change with more active solvents have always resulted in weakness. In like manner, treating agents have been ineffective in improving the grinding efficiency.

A later report on more recent work will show that some improvement in strength and milling cycle has been accomplished by using a different crude which is presumably all in the beta phase initially.

PATENT SITUATION:

U.S. 2,486,351, Wiswall - American Cyanamide, has product claims to copper phthalocyanine in the beta phase, with particles below 2 microns in size, BT-297-D comes within this definition, and a license agreement has, therefore, been negotiated with American Cyanamide on all beta phase CPC.

The process of the Wiswall patent is quite different from our solvent milling process. Also our process gives a pigment with a particle size in the range of 0.1 micron. Therefore, a patent application was filed on our behalf and ultimately issued as U.S. 2,556,726 (Lane). This covers the phase change in solvent milling and has product claims similar to those of Wiswall, except for the particle size range of under 0.2 micron.

Since American Cyanamide also sells a beta phase CPC (Cyan Blue Toner GT-3300) which substantially meets the particle size restrictions of Lane, attempts have been made to negotiate more favorable terms under the Wiswall patent. To date, however, these have been fruitless, largely because of a technicality in which it appears that the samples of Cyan Blue GT available to us have been deficient in crystal stability.

No other aspect of this work is believed to be patentable.

DISCUSSION OF DETAILS:

A few experiments recorded in N.B.1187 show the relatively good strength and green hue of chlorine-free CPC when milled in solvents such as isopropanol or acetone. Similar observations are recorded in N.B. 1251-54, 56, 57, wherein solvent milling, salt milling and acid-pasting were compared with both chlorine-free and chlorine-containing CPC. The greenness of the solvent milled chlorine-free CPC was outstanding, and it is commented on in KN-50-19, wherein it is recognized as the beta form. (This report was written about three years after the work was done, during which time the phase changes were recognized).

Shortly after the start-up of the Newport plant in April, 1948, two samples of chlorine-free crude, one steam distilled and the other sulfated, were milled in acetone in the laboratory. Again the very green hue was evident and it was suggested as beta crystal form. These samples were about equal in strength to the then current standard BT-172-D, but they were weaker than could be obtained from CPC-LB.

At about this same time Orchem obtained a similar product by salt milling a chlorine-free crude in the presence of an active solvent, such as xylene or "Perclene", and they submitted it to us as a potentially new product for sale. Comparison with our own solvent milled products of the same type demonstrated a pronounced superiority in strength for the solvent milled product. Based on this comparison, two charges of an Orchem crude was milled in acetone in the Newark semi-works. These products were shown to be in the beta phase and crystal stable by ordinary accepted tests. (Apparently, all products of this type will grow crystals on prolonged heating in high boiling solvents such as TCB). Although relatively good in strength, they were still inferior to the best laboratory products from Newport crudes, and a third semi-works charge was made (S.W.373) using Newport sulfated crude. This product was established as a temporary standard for BT-297-D and is still looked upon as the goal standard for semi-works production.

A production campaign of 6 lots was made at Newport early in March, 1949, with a 36 hour grinding cycle. Samples from one mill charge were examined by X-ray for crystal phase with the following results:

Sample	beta phase
Crude Lot 233	55%
6 hr. mill sample	60%
12 hr. " "	70%
18 hr. " "	70%
24 hr. " "	80%
30 hr. " "	80%
36 hr. " "	100%
S.W. 373	100%

It thus appeared that a 36 hour milling cycle was necessary for complete phase conversion.

Attempts to speed up this phase conversion by the addition of xylene or "Perclene" to the acetone have been unsuccessful and have nearly always resulted in weakness. It was also demonstrated that a small amount of TCB could cause weakness. Since the Orchem crude had a strong odor of TCB, this was generally accepted as the reason for its poor performance in solvent milling.

When the various lots of the first plant campaign were examined, it was found that the first lot was somewhat red and contained an appreciable amount of chlorine. This emphasized the importance of a thorough clean up to remove all CPC-LB from the crude system and from the ball mills, since the small amount of chlorine-containing pigment remains in the alpha phase.

Studies with various solvents in the milling operation demonstrated that alcohols, in general, were poor solvents for promoting phase conversion, with substantially no conversion realized in methanol. On the other hand, even acetone failed to convert a strong, acid-pasted, alpha phase chlorine-free CPC to the beta phase.

At one time there seemed to be evidence that the addition of NaCl to the acetone grind gave a superior product, but the good results were not consistent and this modification was abandoned. Studies on extraction of the crude also failed to provide any clues for improvement of the process.

Examination of samples taken from the mills gave evidence that there was considerable variation in behavior of various charges during the milling. In some charges, there is a relatively rapid development of strength with little phase conversion, followed by a slow phase conversion and some loss of strength. Other charges appear to carry on the phase conversion and particle size reduction simultaneously. It was also observed that there was a wide variation in the tinctorial properties of the crude pigments made at Newport and in the Newark semi-works. Some charges of crude were green in hue and relatively strong, whereas others were weak and red. No good correlation between the quality of the crudes and their behavior in the milling operation was ever established conclusively; but there was some evidence to support the thesis that the red, weak crudes gave the best final products and that the simultaneous phase conversion and strength development was to be preferred. Since no means of control has been found, such a conclusion would be largely academic in any case.

Some evidence in Jackson Laboratory had indicated that reducing agents inhibit phase change, whereas oxidizing agents promote it. Benzaldehyde, organic peroxides and nitrobenzene were used in acetone grinds without any observed beneficial effect on the phase conversion.

Sodium benzoate as a treating agent in the acetone mill gave some evidence of benefit, but it could not be confirmed on a semi-works scale. Arquad 12 was without value as an agent in the mills.

A rather extensive study of chlorine-free synthesis was made in the semi-works primarily from the standpoint of yield. No pronounced quality differences could be accounted for by these variables. Increasing the mill load reduced the rate of milling, so as to reduce the over-all production rate.

Neither soaking a crude in acetone prior to the milling cycle, nor allowing the ground pigment to stand in acetone prior to steam distillation, had any significant effect on quality.

One rather disturbing observation on the possible instability of finished products was never satisfactorily resolved. A container of lot S.W.349 (Orchem crude, milled at Newark) was found after several months standing to be stratified in color with a layer of red shade material on top and the typical green shade beneath. This had stood through a period of hot weather and high humidity and it was feared that the beta phase material had reverted to alpha phase. Experiments with the green shade material from this same container and with other lots were never able to bring about such a change; nor has it been observed with any other lot. The conclusion was reached that there must have been contamination in this container, but this was never proved conclusively.

The use of crude which had been spray dried and, hence, was in the form of a very fine powder, did not affect the course of the milling operation in any significant manner.

EXPERIMENTAL DETAILS:

The studies reported herein are recorded in detail in the following experiments:

N.B. 1187-66
N.B. 1251-54, 56, 57
N.B. 1275-81
N.B. 1286-68
N.B. 1321-14, 22, 24, 28, 30, 33, 44, 53, 61, 81, 82, 89, 91.
N.B. 1190-2, 3, 10, 13, 16, 19, 20, 21, 24, 26, 32, 36, 39, 67, 68, 69, 72, 73, 76, 91.
N.B. 1191-17, 18, 20, 51, 61, 67/
N.B. 1345-1, 2, 3, 5, 6, 8, 10, 15, 17, 18, 19, 21, 32, 53, 60, 64, 67.
N.B. 1383-5
N.B. 1393-41, 48, 55, 56

MPH