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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

"MONASTRAL" BLUE - "AF" SULFATION

Period Covered OCTOBER 1950 - APRIL 1951

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NEWARK PLANT
PIGMENTS COLOR RESEARCH REPORT
FINAL REPORT

"MONASTRAL" BLUE - "AF" SULFATION

PERIOD COVERED: OCTOBER 1950 to APRIL 1951

CHARGE: A-I-C-20

SUBMITTED BY: F. F. EHRICH DATE SUBMITTED: 8/26/53

APPROVED BY: J. H. COOPER 9/2/53 DATE ISSUED:

INTRODUCTION:

Periodic sulfation difficulties at the Newport Plant have affected the production rate of CPC Blue crudes from the time of the plant startup. This bottleneck originates primarily from the variable behavior of the sulfation operation, particularly as it affects the physical characteristics of the sulfated mass. The original plant process is based on the formation and gravity settling from the kerosene reaction slurry of a dense, granular CPC sulfate, and subsequent removal of the kerosene by drainage (8 hour cycle) through the sulfated mass in a basket-type filter.

Optimum process performance depends largely on the sulfuric acid usage. Both the quantity and proper distribution of the acid by agitation etc. are important to insure the formation of a CPC sulfate with physical characteristics which will permit ease of transfer to the sulfation basket and the most efficient removal of the kerosene by drainage without loss of color. The amount of acid required to fulfill the above requirements in practice varies from batch to batch as a result of variations in 4-chlorphthalic acid and blue synthesis and consequently gives rise to unpredictable and often difficult sulfation behavior.

Another important consideration is that the basket presented a very serious source of contamination by virtue of the accumulation of iron rust therein. This was undesirable, because the rust could enter the CPC at this point and result in deterioration of quality in both Blue and Green. Also, the corrosion of the basket necessitated periodic replacement, resulting in production delays and high maintenance costs.

In addition to the above factors, the need for a kerosene-free crude presscake was emphasized by the March, 1951 fire in the Newport Plant crude drying area. The "AF" or acid-flushing process is capable of giving a kerosene-free crude presscake.

SUMMARY AND CONCLUSIONS:

The "AF" or acid-flushing process involves the direct acid-pasting (complete solution) or acid-slurrying of copper phthalocyanine pigment directly from the hot kerosene synthesis mass without the prior isolation of the crude. The products isolated in this manner are strong, intense and green against current standards and exhibit in paint systems the undesirable properties associated with acid-pasted materials as contrasted to solvent-milled products prepared by the standard Newport process. Even after solvent-milling of the "AF" materials, the paint mill-bases are heavy and suggestive of reactivity. Many of the enamels flocculated severely and, though the tinctorial properties had been improved, the working properties had deteriorated.

The following possible advantages in the acid-flushing process in contrast with the standard sulfation process are suggested by the limited experience with its operation.

1. Acid usage as it affects the physical characteristics of the CPC sulfate granules is not critical.

2. The present 8-hour kerosene drainage period is eliminated. No basket-filter equipment is necessary.

3. A substantially kerosene-free material is obtained which offers the following advantages:

a - ease of hydrolysis (no balling etc.)

b - more efficient extraction and filtration of the crude (no kerosene to hinder wetting of the pigment).

c - shorter oven-drying cycle for the oxide (no kerosene present).

d - elimination of fire hazard in crude oven-drying (no kerosene present).

e - absence of kerosene may facilitate solvent-milling in acetone (this possibility has not been investigated).

4. Greater purification of the pigment, approaching and possibly equalling that obtained by the acid-pasting process.

5. Some particle-size reduction inherent in the drowning operation may shorten the grinding cycle (this has not been investigated).

6. Solvent-milling may be eliminated by acid-pasting directly from the kerosene reactor slurry without prior isolation of a dry crude.

The following process disadvantages are indicated:

1. The use of sulfuric acid in quantity greater than that used in the sulfation process will require greater quantities of neutralizing materials either in process or in a separate acid-disposal unit.

2. Additional plant investment.

Equipment limitations in the Newport Plant have prevented a thorough evaluatinn of the "AF" process.

DISCUSSION OF RESULTS:

A. Laboratory and Semi-Works

The acid-flushing process can be described in outline as follows:

Sufficient sulfuric acid is added to the hot kerosene reactor slurry so as to form a liquid interface between the lower acid and the upper kerosene layers (sp.g. 1.8 vs. 0.8 approx.). The amount of acid required to effect this stratification is less than that needed to dissolve CPC in the conventional acid-pasting process, but more than that used in the standard sulfation process. It is not necessary to effect complete solution of the CPC in the acid, but merely to suspend it in the excess acid. The acid requirement is lessened by virtue of the high temperature (approximately 150°C) at which this operation is performed. The lower acid-layer is run off or the upper kerosene layer is decanted in such a manner as to yield a substantially kerosene-free acid solution or slurry of CPC. The acid layer is then hydrolysed by the use of ice, or by the conventional acid-pasting process by drip-drowning into water. The latter alternative is preferred inasmuch as some particle size reduction undoubtedly occurs.

Laboratory trial of the "AF" or acid-flushing process indicates that a quantity of acid 3-1/2 - 4 times that currently used in the standard sulfation process is required to form a distinct fluid, acid-pigment layer under the clear pigment-free kerosene layer. This effect can be obtained either by adding the sulfuric acid to the kerosene reaction slurry, or conversely, by adding the kerosene reaction slurry to the concentrated sulfuric acid. In either case, complete transfer of the pigment into the lower acid layer is effected. The lower acid-pigment layer is run off and finished as usual.

The solvent-milled products so obtained are intense, v.v.s. green to equal in hue, and v.s. strong versus the best laboratory LB/CPC control, and 8-10% strong, and intense versus standard BT-304-D. The products are 10% strong and intense vs. Heliogen Blue BA and Orchem's Blue BNC. The masstones are distinctly jet versus standard and versus laboratory controls prepared by the standard process. The extracted crudes proved to be intense, green and 30% weak against the best laboratory LB/CPC solvent-milled materials.

Ink mill evaluation of the toner materials produced by this process indicates the material to be essentially equivalent, texture-wise, and in rate of strength development to the standard process materials and to BT-304-D standard. Ink consistencies are likewise essentially equivalent.

A modification of the "AF" method involving under-the-surface addition of the kerosene reactor slurry to the sulfuric acid with mild agitation proved to be workable in the laboratory. A complete flushing of the pigment from the kerosene to the acid is thereby

effected, the kerosene floating to the surface of the acid layer. Quality equivalent to that reported above was obtained (strong, intense, v.s. green vs. control). The acid (4 parts per part of CPC) can be neutralised in-process after hydrolysis, without any sacrifice in quality.

Whereas the crudes obtained by the standard sulfation process cannot be ground to full strength and tinctorial quality in an alkyd enamel system, the crudes from the "AF" process apparently can be so ground to give products fully equal to their solvent-milled counterparts as regards strength, tinctorial quality, flocculation, and can-stability.

Semi-works trials of the "AF" process using LB/CPC kerosene reactor slurry posed no problems, from an operating standpoint. The process involves pumping of the kerosene synthesis charge under the surface of 98% sulfuric acid (four times the quantity currently used for standard sulfation), whereby the pigment is flushed into the acid layer. The kerosene, completely free of pigment, forms an upper layer. No agitation appears to be necessary to effect the flushing. The lower acid-layer is run out and drowned in boiling water as in the standard acid-pasting process. A small quantity of the acid layer is left behind so as to insure a kerosene-free acid layer. This residue is worked up with the succeeding batch. A CPC pulp so obtained analyzed for 0.6% kerosene (solids basis) before oven-drying, in contrast with standard process (sulfated) crude cakes which contain 15-40% kerosene. The acid employed in the "AF" process is ultimately neutralized in-process, which fact minimizes the waste acid-disposal problem.

The first attempt using Cl-free CPC (kerosene reactor charge at room temperature) yielded a crude product (laboratory drowned) which by flushing was green, intense and s.strong vs ABT-318-D (Pigments Dept. experimental soft powder treated acid pasted chlorine free CPC - "Monastral" Blue R).

The second "AF" attempt using LB/CPC (kerosene reactor charge at 130°C) yielded a crude product (laboratory drowned) by flushing, which was green, intense and equal in strength to BT-284-D standard. The undertone was red and intense against BT-284-D.

Rubber tests of two of the laboratory "AF" materials (solvent-milled) showed them to be satisfactory for such use (oxygen bomb test).

The results of seven Semi-works trials of the "AF" process are summarised on the following page.

2610	Cl-free	25°C	0.6	green, intense, s.strong vs. ABT-318-D
2626	LB	130°C	0.4	green, intense, v.s.strong, vs. BT-284-D
2629	LB	150°C	0.90	green, intense, equal strength vs. BT-284-D
2630	LB	195°C	0.50	green, v.s.intense, vvs.str. vs. BT-284-D
2636	LB	150°C	0.80	-----
2638	Cl-free	150°C	1.2	-----
2639	LB	150°C	0.95	-----

Approximately 6 parts of acid per part of CPC was used for lots 2610 and 2638 (Cl-free CPC). For the LB/CPC trials 7 parts of acid was employed, except in 2639 where 5 parts of acid was used.

No difficulty was experienced in the "AF" processing nor in the drowning operation, except in 2639 (5 parts acid), where cooling of the pigment-acid solution in transfer gave rise to some CPC sulfate crystallization. Maximum particle size reduction will depend on maintaining optimum conditions at this point. The only serious operating problem encountered with the "AF" process results from the copious evolution of HCl fumes, indicating the necessity for providing adequate fume disposal facilities.

A 1.8 gallon acetone mill grind (48 hrs.) of dried lump LB/CPC "AF" crude (lot 2626) gave a product 5-6% strong and essentially equal in hue versus BT-304-D standard by varnish drier rubout.

A Semi-works 58 gallon acetone mill grind of dried lump LB/CPC "AF" crude (lot 2636) gave full strength against standard BT-304-D in 14 hours. The product was green and intense against this standard and had a jet masstone.

Analyses of six typical "AF" products indicate that they contain from 6.2 - 10.2% sulfur expressed as the CPC monosulfonic acid. Undoubtedly some sulfonation occurs during the "AF" processing. Standard BT-304-D analyses for 0.43% sulfur expressed as the monosulfonic acid.

A BL-282-D type lake prepared from a solvent-milled "AF" LB/CPC was s. green, intense and approximately 12% strong versus

standard BL-282-D by varnish drier rubout.

A BP-173-D type lake prepared from a solvent milled "AF" LB/CPC was s. green, intense and 5-6% strong vs. standard BP-173-D.

A BL-237-D type lake (containing ca. 25% CPC) and a BL-288-D type lake prepared from a solvent-milled "AF" LB/CPC were both strong versus standard BL-388-D by the Armstrong rubout procedure.

BT-284-D type products prepared from solvent-milled "AF" LB/CPC by both the carbon tetrachloride and naphthalene treatments were weak against standard BT-284-D.

1.8 gallon mill acetone grinds (48 hrs.) of several "AF" crude both LB and chlorine-free yielded products strong, green and intense against the appropriate standards. The BT-297-D products derived from the "AF" process were essentially equal to the standard in texture and rate of strength development. In alkyd enamel systems, there was no evidence of heavy mill base or other undesirable rheological behavior. Flocculation resistance was essentially equivalent to that of standard BT-297-D.

The BT-284-D and BT-304-D materials derived from acetone-milled "AF" crudes were inferior to the respective standards in texture, rate of strength development and rheological properties. In alkyd enamel heavy mill bases suggestive of reactivity were observed as well as severe flocculation in several instances. Some products, however, were fully equal to standard in the latter respect.

A Semi-works 58 gallon solvent-milling of an LB/CPC "AF" crude pulp yielded a product of essentially full strength after 18 hours of milling. The product was green and intense versus standard BT-304-D and gave a jet masstone. The grind was conducted in the equivalent of 72% acetone (i.e. based on water content of the pulp).

Laboratory chlorination of chlorine-free crudes (2) manufactured in the Semi-works by the acid-flushing ("AF") process yielded products essentially equal to the control, although s. dull vs. GT-674-D (lot 430).

B. Plant Trial

On April 10, 1951, one plant trial was made of the "AF" process to accumulate operating data and to determine the limitations of present equipment for sustained "AF" processing. Based upon the experience gained during this plant trial (see detailed report, P. D. Graham to J. H. Cooper, 4/13/51, and E. F. Klenke to F. C. Evans, 4/5/51), it appears that a number of major equipment changes and installations would be necessary to permit continued operation.

EXPERIMENTAL DETAILS:

The work summarized in this report is recorded in the following notebooks:

NB 1365
NB 1382

Patent considerations are discussed in letter, A. J. Stratton to J. N. Tully, 4/9/51, included herein.

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