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NEWARK PLANT
CHEMICAL DIVISION - COLORS

"LITHOSOL" VIOLET 4RN - SOLVENT-MILLING AND OTHER FINISHING METHODS

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NEWARK PLANT
PIGMENTS COLOR RESEARCH REPORT
FINAL REPORT

TITLE: "LITHOSOL" VIOLET 4RN - SOLVENT-MILLING AND OTHER FINISHING METHODS

PERIOD COVERED: FEBRUARY 1950 - SEPTEMBER 1950

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SUBMITTED BY: F. F. EHRICH DATE SUBMITTED: 7/16/53

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INTRODUCTION:

The original plans for the Pigments Department phthalocyanine plant at Newport called for the eventual manufacture of a red shade of blue similar to that purchased from Orchem, as "Monastral" Fast Blue 2R and which is sold as the barium rosinate lake BP-243-D. Laboratory work was initiated to this end, and considerable interest was developed in the violet pigment itself which is used to shade the CPC to give the redder product. Pressure on this violet work was further intensified by the Ford Motor Company interest in a violet for shading purposes.

At present, acid-pasted "Lithosol" Violet 4RN is purchased from Orchem in pulp form (N-612) for conversion to the barium rosinate lake BP-273-D and to the blanc fixe-extended barium rosinate lake BL-333-D. This acid-pasted violet, although purchased as a standardized product, shows considerable variation in strength and hue when converted to these lakes by standard formulas.

Based on the Pigments Department experience with the solvent milling of phthalocyanine pigments, the solvent-milling of crude "Lithosol" Violet as a means to greater pigment consistency with respect to strength, hue and texture was undertaken.

SUMMARY AND CONCLUSIONS:

"Lithosol" Violet 4RN crude can be solvent-milled in acetone to give products superior to those obtained from the acid-pasted counterpart (N-612). The solvent-milled materials give lakes (BP-273-D, BP-243-D, BL-333-D) superior in strength and texture to the acid-pasted materials and give greater product consistency from lot to lot.

Limited experience with acetone-HF milling suggests that this method may be a satisfactory alternate. Salt and dispersion milling yield inferior products.

Work on solvent-milling and other finishing methods for "Lithosol" Violet 4RN was discontinued due to the decrease in volume of such colors, and the anticipated strong competition from Harmon's Thio Fast Red MV-6606, which appears to offer better money value for the shading of CPC Blue.

DISCUSSION OF RESULTS:

"Lithosol" Brilliant Violet 4RN crude is solvent-milled in acetone in a manner analogous to the solvent milling of phthalocyanine pigments. To a 1.8 gallon steel mill charge:

13,000 gr. 5/32" steel shot
150 gr "Lithosol" Violet crude
1,500 ml. acetone

Grind 72 hours. Screen the milled slurry from the steel shot and dilute to 6 liters with water. Steam distill acetone-free. Add conc. H_2SO_4 (as a 1:1 solution) so as to yield a 3.5% solution. Boil 1/2 hours. Filter hot, wash sulfate-free. Wash on the funnel with a solution of 50 ml. conc. NH_4OH in 1 liter of water. Wash alkali free to Brilliant Yellow. Hold as pulp.

A BP-273-D type "Ramapo" lake prepared from laboratory solvent-milled "Lithosol" Violet 4RN crude was strong (100 parts-140 parts), blue, and sl dull against the control prepared from N-612, (acid-pasted "Lithosol" Violet), and against standard BP-273-D.

The distinct strength advantage offered by solvent-milling as against acid-pasting, in final products such as BP-273-D and BP-243-D, was established using six lots of "Lithosol" Violet 4RN crude received from Orchem. All the products (solvent-milled in 1/2 pint glass jars and evaluated as barium rosinate lakes) were strong and blue against BP-273-D standard. Rubout evaluations of both the solvent-milled toner products and the BP-273-D lakes prepared therefrom indicate some slight strength variation from lot to lot, but far less than that obtained with the use of the acid-pasted counterparts. Some hue variations from lot to lot were indicated.

Six additional lots of crude violet solvent-milled in 1/3 gallon steel mills and converted to the BP-273-D lakes showed greater strength variation than that exhibited by the glass-milled products, and also greater hue variations. The products, however, are all stronger than BP-273-D and are consistently blue against this standard.

PIGMENT TREATMENTS:

There are indications that acid chromate treatment of the finished solvent-ground or acid-pasted (N-612) toner pulps yields a redder, more intense product. Likewise, the use of chromate, or a combination of chromate plus phosphate in the steel mill grind yielded redder products although the materials in these initial trials appeared weaker than corresponding products milled without chromate. All the products, however, are still blue against standard BP-273-D. Alkaline hypochlorite or alkaline peroxide treatment of the finished pulps did not give products comparable to those obtained by chromate treatment. An ammonia wash after chromate treatment appears to offer some advantage.

SALT AND DISPERSION MILLING

Salt-milling with either NaCl or Na_2SO_4 yielded products blue and weak against the solvent-milled counterparts. Dispersion milling with salt, "Perclene" and Span 80 yielded a product very blue and dull against the solvent-milled products and very blue against the salt-milled products.

HF-MILLING

Acetone HF-milling of "Lithosol" Violet 4RN crude using either borax or sodium chloride as a grinding medium yielded products essentially equal to those obtained by solvent-milling in acetone (see KN-52-13).

A comprehensive weatherometer exposure series (300 hrs.) designed to compare the relative behavior of acid-pasted "Lithosol" Violet, N-612 (in the BP-176-D formula) versus solvent-milled and HF-milled "Lithosol" Violet (in the BP-273-D formula extended to equal the toner content of BP-176-D) indicates the essential equality of the variously finished violets with respect to change on exposure. Six plant lots of BP-176-D, standard BP-176-D and BP-273-D, three solvent-milled lots and one HF-milled lot were used.

A comparison of solvent-milled violet versus Orchem acid-pasted material (N-612), the latter being a better than average material of recent Orchem production, permits the following conclusions:-

a. Regardless of the strength level and method of laking, the solvent-milled material results in a product of better strength by rubout than the acid-pasted product.

b. Without exception, the use of ammonium rosinate in place of sodium rosinate (as in present BP-273-D) results in a product of better strength by rubout.

c. A 50% "Ramapo" type lake reduced with blanc fixe to ABL-333-D gave better strength by Ford rubout than a 75% "Ramapo" lake reduced with blanc fixe to an ABL-328-D type product, where the materials were prepared from acid-pasted dye. However, where the corresponding materials were prepared from solvent-milled dye, no advantage was evident for the product of higher rosination.

BEHAVIOR IN ALKYD ENAMEL

Alkyd evaluations of BP-273-D and ABL-333-D lakes indicate that greater strength may be realized by our testing method from solvent-milled "Lithosol" Violet as against the acid-pasted Violet (N-612). Approximately four pounds of an FBP-273-D lake has been prepared in the Semi-works from solvent-milled Violet for F & F's examination.

F & F, Phila., alkyd enamel evaluation of two experimental BP-273-D type lakes prepared from N-612 (Orchem acid-pasted "Lithosol" Violet) and from Newark solvent-milled "Lithosol" Violet, respectively, indicated the latter to be bright and red in tint (10/90 TiO_2) and 10% strong versus the former. By actual analysis, the solvent-milled

violet lake (F)BP-273-D lot 2424, contains 69.31% of violet toner. Whereas the acid-pasted violet lake, (E)BP-273-D, lot 2417 contains 70.89% of violet toner.

An alkyd enamel prepared from a BP-176-D type lake produced by adjusting a BP-273-D lake (from solvent-ground violet) to the toner content of BP-176-D (12.8%) with blanc fixe was very strong against standard BP-176-D.

Weatherometer exposure (336 hrs.) of a BP-273-D alkyd enamel prepared from solvent milled violet indicated the material to be very slightly inferior to standard BP-273-D and against a control.

A 50% aluminum benzoate lake of either solvent-milled "Lithosol" Violet or its acid-pasted counterpart does not offer any advantage with respect to resistance to flocculation in alkyd enamel compared to standard BP-273-D.

INK MILL EVALUATION

Ink mill evaluation of a BP-273-D lake prepared from solvent-milled "Lithosol" Violet Crude 4RN showed a marked strength advantage over the standard (42 parts = 100 parts) as judged by the five-tight inks. The solvent-milled product was vastly superior to the standard in rate of strength development and in the Hegman gauge texture rating. The product was bluer than the standard. Evaluation in alkyd enamel showed the product to be blue, dull, s. strong and essentially equal in bleed (baked white overstripe).

The ink mill evaluation tabulated below indicates the texture obtained by the use of solvent-milled "Lithosol" Violet crude versus standard BP-273-D. At equal toner content, the solvent-milled product (FBP-273-D) returns greater strength than the acid-pasted counterpart (EBP-273-D).

			1T	3T	5T	7T
EBP-273-D	SW-2417	72% Orchem dye-ammonium rosinate	7	7	7-1/2	7-1/2
FBP-273-D	SW-2424	72% solvent-milled dye-ammonium rosinate	6-1/2	6-1/2	7	7
BP-273-D	SD-90870	standard	1	6-1/2	6-1/4	6-3/4

SEMI-WORKS STUDIES

A plot of the rate of strength development versus time in three 58 gallon solvent mill grinds of "Lithosol" Violet 4RN crude indicates that standard strength (versus a typical laboratory grind) was reached in approximately 4 hours, and maximum strength (ca twice standard) in 24 hours. Maximum toner strength is reached in 12 hours

in the 200 gallon mill. No operating difficulties were encountered. The 93% recovery yield reported was confirmed in the Semi-works in the solvent-milling operation. Typical barium rosinate "Ramapo" products prepared from the finished material compare favorably with the laboratory solvent-milled counterparts.

EXPERIMENTAL DETAILS:

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

NB-1357
NB-1191

jc