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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

PIGMENTS FROM "PONSOL" RED RL

Period Covered December 1949 to June 1951

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

TITLE: PIGMENTS FROM "PONSOL RED RL

Period Covered: December 1949 to June 1951

Charge: A-II-C-183

SUBMITTED BY: P. H. GRISWOLD

DATE SUBMITTED: April 21, 1952

APPROVED BY : J. H. COOPER

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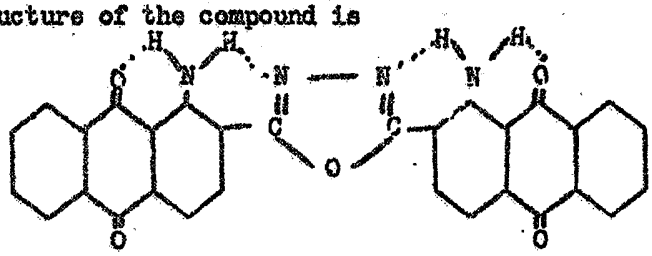
INTRODUCTION

The object of this investigation was to determine the best method of finishing "Ponsol" Red RL for use as a red pigment, and to prepare material for Sales Service evaluation.

"Ponsol" Red RL (formerly referred to as "Vat Red 33") was discovered in Jackson Laboratory during 1947 and investigated as a vat dye, where its excellent lightfastness made it especially interesting (1). This property of lightfastness as well as chemical inertness stimulated interest in it as a pigment.

The structure of the compound is



"Ponsol" Red RL

The stability of the molecule is apparently associated with the high degree of hydrogen bonding possible between the amino hydrogens and their electron deficient neighboring atoms, as well as the lack of reactive groups.

Preliminary tests of "Ponsol" Red RL as a pigment were made by W. S. Struve at Jackson Laboratory and B. J. Godfrey at Newark. The first samples KS-161 and KS-163 were acetone-shot milled and acid pasted respectively. These products were found to have good lightfastness and bleed resistance. The acid pasted material was more interesting because of its bright transparent masstone (2). This acid pasted product and a later sample KS-206 showed serious reactivity in alkyd and lacquer grinds (3) as well as darkening on baking in alkyd. These effects were lessened by autoclaving the acid-pasted pigment and using an aliphatic solvent (VM and P) in place of the more aromatic type (Amsco B) in the paint grinds (4). Examination of materials before and after autoclaving indicated a decrease in average particle size and a decrease in the degree of crystallinity (5). To minimize these undesirable effects of pigments finished by acid pasting, all subsequent samples, so finished, were autoclaved at Jackson Laboratory by W. S. Struve.

The results of these preliminary tests were of sufficient interest to warrant a more complete examination and comparison with other possible finishing methods.

SUMMARY

Tinctorially the best finishing method is acid-pasting and autoclaving because of the strong, intense, yellow hue and dark, intense masstone of the product. Judging by physical behavior the best product is that obtained by acetone shot milling. However, this material is very blue and dull tinctorially with a very milky, brown masstone. The acid-pasted autoclaved product shows considerable reactivity in alkyd systems and tends to bleed in both baking alkyd and vinyl. The acetone milled product has none of these disadvantages.

Dispersion milling yields a product which lies between the two extremes in physical properties found above and is very near the acid pasted material tinctorially, being slightly bluer and duller.

The salt milled product is generally poor, being weak tinctorially and exhibiting excessive reactivity and bleed.

Products made by "HF" - acetone milling are essentially the same as acetone shot milled material in all respects.

Acid(permutoid) swelling yields a very weak and, therefore, uninteresting product.

No great effort has been made to change the fundamental bleed or reactivity behavior of the acid-pasted autoclaved product, nor has the acetone milled product been altered toward the more desirable yellow hue. Accomplishment of either one of these ends would lead to a more desirable pigment.

The acid-pasted autoclaved product was chosen as the most desirable pigment (6) and an order was placed with Orchem (OU-5131) for 100# of this material. This was converted into 10 lbs. of the "Ramapo" ARP-641-D, lot 1372, 28.8 lbs. (solids basis) of the "Ramapo" pulp ARP-643-D, lot 1370, and 327 lbs. of ARL-650-D, S.W. 2645 (a 10% lake of Red RL prepared by extending ARP-643-P with blanc fixe). The products were submitted to Sales Service for evaluation and formulation for sales promotion (7). Since the production of "Ponsol" Red RL is not standardized, this lot was bluer and duller than the lot previously purchased on which all the initial tests had been made.

DISCUSSION

"Ponsol" Red RL Crude was finished by the following methods:

1) Acid-pasting and autoclaving
2) Acetone-ball milling
3) Dispersion milling
4) Salt milling
5) HF-acetone milling
6) Acid (permutoid) swelling

The products were converted to barium resinate lakes for evaluation. A preliminary comparison of the mode of laking the acid-pasted, autoclaved material through use of ammonium or sodium resinate showed the former to have a slight advantage in texture as indicated by rate of strength development of inks (N.B. 1340-2 and 1340-5). All subsequent "Ramapos" were made from the ammonium resinate emulsion and contain 76.1% dye and 23.9% barium resinate.

The accompanying charts show the comparisons of these finishing methods in rubout, alkyd and vinyl evaluations.

CHART I

COMPARISON OF ARP-641-D TYPE LAKES

Finishing Method	Rubout Evaluation	Alkyd Evaluation: Tinctorial	Flocculation (Pour Test)	Discoloration on Baking	Bleed on Baking	6 Month Exposure
Acid-pasting and Autoclaving (1340-20)	Standard	Standard	OK	Bad	Slight	OK
Acetone-shot milling (1340-12B)	Very blue and dull	Very blue and dull	Slight	OK	None	OK
Dispersion milling (1340-14B)	sl. weak, sl. blue, sl. dull	v.s. weak v.s. dull	OK	Slight	Trace	Inferior
Salt milling (1340-13B)	Very weak	Very weak	OK	Bad	Trace	-
HF-acetone milling (1340-19)	Very blue and dull	Very blue, and dull	Slight	OK	None	-
Acid swelling (1340-23)	Extremely weak	-	-	-	-	-

REACTIVITY IN ALKYD: STORMER METHOD

Finishing Method	Initial Consistency	After One Month Storage	Difference
Acid pasting and Autoclaving (1340-20)	94 KU	125 KU	31 KU
Acetone-shot milling (1340-12B)	68 "	78 "	10 "
Dispersion milling (1340-14B)	67 "	81 "	14 "
Salt milling (1340-13B)	80 "	114 "	34 "
HF-acetone milling (1340-19)	63 "	73 "	10 "

COMPARISON OF ARP-641-D TYPE LAKES

Vinyl Evaluation

Finishing Method	Tint	Masstone	Fadeometer
Acid pasted and autoclaved (1340-20)	Standard	Standard	OK
Acetone-shot milled (1340-28E)	Very blue and dull	Very blue and dull more opaque	OK
Dispersion milled (1340-31A$_2$)	trace blue and dull	slightly dull	OK

MILLING VARIABLE STUDIES

The rates of strength development in acetone shot milling, dispersion milling and salt milling indicated that all reached maximum strength after 96 hrs. milling time. "Ramapos" were made from pigment which had been milled for this length of time, in each case, for the evaluation comparisons. "HF"-acetone milling was carried out for two hours. An additional hour of this type of milling showed a negligible strength increase.

Attempts to oxidize the bluer shade product obtained by acetone milling to a yellower hue were made with chromic acid, hypochlorite and hydrogen peroxide. Chromate gave a very slight advantage in yielding yellower hue, but the other two oxidizing agents produced products even bluer than the control (1340-21).

Acetone milling crude "Ponsol" Red RL in the presence of chromate or chromate with trisodium phosphate did not improve the resulting shade toward a yellower hue. (1340-24).

Grinding crude dye with alkyd vehicle gave excessively blue, dull products of no interest (1340-29).

Solvents other than acetone were examined for shot milling finishing. Methanol, ethanol, isopropanol, methyl acetate, "Celanese Solvent 601", "Cellosolve", dimethyl formamide, dioxane, nitrobenzene, perchloroethylene, and a 3% solution of "Blancol" in water were employed. The organic solvents gave products equivalent to that with acetone except in the cases of nitrobenzene and perchloroethylene which were very weak. The product from the "Blancol" water grind was very dull, but considerably yellower than acetone milled material (1340-26).

Ball milling of crude "Ponsol" Red RL was carried out in water with agents determined to be good wetting and dispersing agents such as "Triton X-100", "Ammonyx AO", SP-717", "Ethomeen C/25", "Ethomeen C/60", "Areskleen 400", "Igepon T", "Duponol G" and "Victowet 12". The products where the "Ethomeens", "Igepon T" or "Duponol G" were used gave rather strong pigments for water grinds and yellower hue compared to the acetone milled product, but were not sufficiently good to warrant further investigation. (1340-30).

Dispersion milling with small amounts of dispersing agent other than "Span 80" such as capric acid, "Duponol G", triethanolamine-C_{12} ester or silicone polymer gave no improvements in strength or hue of the product, nor any benefit in the reactivity behavior in alkyd system (1340-31).

The second lot of "Ponsol" Red RL manufactured by Orchem was finished by acid-pasting and autoclaving, acetone milling, and dispersion milling. In all cases the same relative tinctorial comparisons of these methods held true. All products were bluer and duller than the similar products made from the previous lot. This dye is not made by a standardized plant procedure and evidently the method of manufacture affects the final tinctorial properties. (1340-34, 38, 39, 40).

"PONSOL" RED RL LAKES

An attempt was made to produce a high strength lake from crude dye by reducing a slurry of the crude in the presence of barium sulfate with sodium hydrosulfite, followed by air oxidation. The product was very weak compared to a lake made by simple mixing of acid-pasted and autoclaved pigment paste with blanc fixe. (1340-24).

Linoleum lakes of BL-288-D and BL-237-D types were made from a paste of acid-pasted, autoclaved Red RL. The very weak, dull tinctorial properties of the products showed them to be of no interest in the linoleum field. (1340-3 & 4).

A BL-282-D type lake of acetone-milled material was made in the hope of reducing the flocculation tendency observed on use of the "Ramapo" of this type of finished product in alkyd. A very definite improvement in flocculation resistance was obtained when this lake was used. (1340-28B).

A BT-284-D type product was made from acetone milled "Ponsol" Red RL and found to have better texture than the untreated pigment, although weaker. The "Ramapo" was better in texture than either as judged by rate of strength development on the 3-roll ink mill. (1340-28C).

A lake consisting of 15% "Ponsol" Red RL (finished by acid-pasting and autoclaving) and 85% barium sulfate was made by both slurry mixing the components or precipitating the barium sulfate in the Red RL slurry. No noticeable differences were found in the strength or texture of the products prepared by these methods. The finally accepted method for making such a highly extended lake was to slurry the paste of the resinated acid-pasted autoclaved "Ponsol" Red RL with "blanc fixe" to form a product containing 10% toner (ARL-650-D).

EXPERIMENTAL:

Acid Pasting "Ponsol" Red RL N.B. 1325

Done by W. S. Struve at Jackson Laboratory: 2560 gms. of 96% sulfuric acid charged to kettle and cooled to 5°C. 256 gms. Ponsol Red RL crude added slowly keeping temperature below 10°C. Stirred until dissolved (2-4 hours). Added over an hour period to 5600 gm. ice and 20,000 gms. water agitated. Stirred an additional hour, pressed and washed acid free to Congo Red paper.

Autoclaving the Acid-Pasted Ponsol Red RL N.B. 1325

Done by W. S. Struve at Jackson Laboratory: 1706 gms. of acid-pasted Ponsol Red RL paste 256 gms. solids basis) charged to autoclave. 854 gms. water added and stirred to a smooth paste. Neutralized with 5 gm. ammonia. Autoclave closed and heated to 150°C. for one-half hour under autogenous pressure. Cooled to 75°C. pressed and washed once.

"Ramapo" Formulation ARP-641-D (N.B. 1340-34)

1176.5 gms. of acid-pasted, autoclaved "Ponsol" Red RL paste (solids basis 200 gm.) weighed into 20 liter jar and volume made up to 2500 ml. The following ammonium resinate emulsion prepared and added with good agitation:

To 366 ml. water in 4 liter beaker were added 62.7 gms. of freshly pulverized "K Wood resin". 40 ml. of conc. ammonium hydroxide added and heated to dissolve and disperse the resin. Heated to boil and held until pH

was 9.2 and the emulsion was stable. This emulsion was added to the pigment slurry through a 60 mesh screen over a 5 minute period. A solution of 31.34 gm. barium chloride dihydrate in 167 ml. water was added dropwise in a 5 minute period. Agitation continued for 5 min. then heated to the boil and held 30 minutes. Flooded to 15 liters, filtered and washed free of chloride. Dried at 140°F. Yield 263.3 gms.

Composition: "Ponsol" Red 76.1%, Barium resinate 23.9%.

Extended "Hamapo" ARL-650-D S.W. 2645

59 lbs. ARP-643-P (11.5 lbs. of ARP-641-D dry basis) made up to 50 gallons. 76 lbs. Blanc Fixe added over 30 minutes through recirculating draft tube. Draft tube allowed to recirculate for 60 minutes. Pressed with agitation, dried at 140°F. for 48 hrs. Pulverized at regular speed. Yield 82 lbs.

Composition: "Ponsol" Red RL 10%, Barium resinate 3.12%, Blanc Fixe 86.88%.

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