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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

TITLE PIGMENT GREEN B

Period Covered JANUARY, 1953 - MAY, 1954

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NEWARK PLANT

CHEMICAL DIVISION - COLORS

FINAL REPORT

TITLE: PIGMENT GREEN B TONER

PERIOD COVERED: JANUARY, 1953 - MAY, 1954

CHARGE: 1101-11-22

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SUMMARY & CONCLUSIONS:

Pigment Green B Toner, GT-646-D, has been found to be on the defensive in certain properties relative to three competitive products in several specific fields of application, although superior in tinctorial properties, i.e., yellowness and intensity. The three competitive products and their reported points of superiority are Imperial's Chippewa Green (strength and strength development), Eakins Velvetized Pigment Green (texture and grit) and Sherwin-Williams' CP-1106 Green (cure resistance or heat stability).

Studies leading to laboratory products with improved strength development and texture (grit elimination) at some sacrifice of tinctorial properties were completed in the laboratory. These experimental laboratory products were found to be superior to GT-646-D in cure resistance and additional studies to develop a product equal to the Sherwin-Williams Green in color and cure resistance were continued.

A laboratory product, essentially equal in color and cure resistance to the Sherwin-Williams' Green was prepared and coded GT-756-D. Plant trials of the (A)GT-756-D process were not successful in duplicating the laboratory results and the pigment green program has been closed out in favor of other more urgent problems.

DISCUSSION:

Reports from the paint trade to the effect that Imperial's Chippewa Green showed higher strength than GT-646-D in an alkyd flat paint prepared by roller mill grinding were confirmed by tests of Sales Service and the Chemical Division. The poor grinding character of this product was immediately evident (Hegman gauge texture 0-1, first pass) and subsequent reports indicated that Eakins Velvetized Pigment Green was far superior (Hegman guage texture 5-7, first pass) to the Imperial or du Pont product in this property.

Chippewa Green by rubout was found to be 10% strong versus GT-646-D, (90-100) but blue and dull in tint; the strength difference in alkyd was approximately 25% but the rate of strength development on the roller mill was equal to that of GT-646-D. The Eakins product was equal in strength, blue and dull versus GT-646-D by rubout but developed more strength with less grit after one pass on the roller mill. Initial studies were carried out in the laboratory to modify either current GT-646-D or GT-76-P to improve the texture and wetting in the alkyd paint system without markedly altering the color properties of the Newark product.

Treatment of pigment presscake or slurry with a large number of different types of surface active agents showed that improvements in

rate of strength development and texture (grit elimination) could be obtained, but at the expense of color intensity. Among the agents which appeared to be of interest were daxad, sodium soaps of fatty acids, petroleum sulfonic acid, diglycol stearate, and Sotex C. Of this group, the cationic material, Sotex C, seemed to offer the greatest potential based on earlier pigment green studies with the incorporation of organic amine type materials into the product. The substitution of Sotex C for the potassium laurate currently used in GT-646-D process resulted in weak dull products, tinctorially, but with markedly improved strength development. A study of the combined use of both agents in the process resulted in a product with improved color, the laurate in close to formula quantities being absolutely essential, and improved grinding properties. The optimum ratio of laurate to Sotex C for this type of product was of the order of 2:1.

Evaluation of the Sotex containing product by a special varnish drier rubout with high cobalt drier and at very weak extensions (1:100) showed it to be far superior to standard GT-646-D in heat stability, approaching the stability of Sherwin-Williams' CP-1106 Green in this property. This competitive product was found to be superior in color retention to GT-646-D in a special rubber tile formulation several years ago, GT-646-D fading from a green to a brown during the curing cycle. Earlier work at Newark had shown that a similar effect could be obtained in linoleum at low pigment concentrations or by the accelerated rubout procedure cited above; under conditions of higher pigment concentrations either in composition or rubout, this observed fading of GT-646-D is not apparent. At Sales' request, a decision was made to alter the research program and point towards a suitable counter-offering for the Sherwin-Williams' Green in both color and cure resistance.

The observed behavior of GT-646-D, in compositions and cobalt containing varnish drier rubouts upon heating to 180°F or higher, pointed to the possibility of some form of oxidation playing a role in the degradation of the pigment. Several experiments were designed to check this point using the rubout procedure: (1) baking in a nitrogen atmosphere or in vacuo; (2) baking on glass rather than on metal panels, to observe the under surface not exposed to the surrounding atmosphere; and (3) the incorporation of known available anti-oxidants with the normal GT-646-D by dry mixing. The results of the above experiments may be summarized as follows: baking in nitrogen or in vacuo at 180°F for 40 minutes showed a lesser color change than a corresponding bake under normal conditions in an air-circulating oven; baking on glass in an air-circulating oven showed only a change on the outer surface, the surface in contact with the glass remaining unchanged; simple dry addition of aromatic amine or phenolic type anti-oxidants showed a definite and significant improvement in heat stability as compared with the "as is" pigment.

Of the series of anti-oxidants screened by the rubout procedure N, N' diphenyl-p-phenylene diamine was selected for further study. Incorporation in the modified GT-646-D process containing Sotex C at

various points in the process, resulted in products duller than the Sherwin-Williams' Green with approximately equal cure resistance. Additional process and composition studies designed to improve the color, maintaining the level of heat stability were carried out. Oxalic acid was introduced to complex any ferric iron present and other metals such as zinc and aluminum were incorporated to form other metallic soaps with the pigment. These changes were introduced on the basis of analytical evidence for the presence of a significant quantity of aluminum in the competitive pigment, and evaluation of U.S.P. 1,993,971 (MacQueen) which incorporated zinc or aluminum in one of the early du Pont patents on dry pigment green toners. The product made by the process in the above patent was considerably duller and weaker than GT-646-D but outstanding in cure resistance, equal to the competitive.

Studies incorporating zinc oxide with Sotex C, and N,N'diphenyl-p-phenylene diamine on the basic GT-646-D process were carried out leading to a laboratory product essentially equal to the Sherwin-Williams' Green in color and cure resistance. This product was coded GT-756-D and plant development studies were initiated. The material resulting from the plant trials showed a significant improvement over GT-646-D in cure resistance; however, it was considerably inferior to the best of the laboratory GT-756-D samples in color and cure resistance. Efforts to determine the reasons for the failure of the laboratory process in the plant have proven futile. A comparison of plant and laboratory raw materials was of no avail; laboratory and plant procedures for the formation of the nitroso, and nitroso ester showed practically no differences; the emulsification and incorporation of the diamine could pin-point no differences although there was some evidence that all of the diamine used in the plant process was not retained by the finished pigment. Laboratory studies on the pigment green toner problem have been discontinued.

GLOSSARY:

Pigment Green B	Iron complex of nitroso-beta naphthol.
GT-646-D	Newark manufacture - dry toner.
Imperial Chippewa Green X-2191	C#-54984, 55343
Eakins Velvetized Green	C#-55058
Sherwin-Williams' Permans Green, CP-1106	C#-54214, 55358
GT-756-D	Newark code for modified GT-646-D.
DPPD	N,N' diphenyl-p-phenylene diamine
Sotex C	Cationic surface active agent manufactured by Synthetic Chemicals Corp.

RUBOUT TESTING METHOD:

Pigment evaluations were carried out in a special formulation containing cobalt drier at weak extension levels. The detailed procedure is as follows:

Pigment	1.0g	Vehicle #1	
Vehicle #1	2.0g	#1 Trans. varnish	200g
Mills	4x50	Cobalt Naphthenate (6%)	40g
Ink	.180g	Vehicle #2	
Vehicle #2	10.0g	Zinc Oxide White Seal	60g
Cobalt Naphthenate (6%)	0.5cc	#1 Trans. varnish	40g

Mount extensions on bare aluminum.
Cut into two (2) strips; retain one (1) for control; bake one (1) 40 minutes at 180°F. Compare baked and control panels for degree of color change.

REFERENCES:

Sales Service W/R 912-52 11/7/52
Sales Service W/R 107-53 5/6/53
Research Notebooks 1409429,-50) incl.
1473-1, 33) incl.
Plant batches 60601, 61154.

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