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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

PREPARATION AND EVALUATION OF COUNTERPARTS FOR
ALUMINUM BENZOATE IN NON-FLOCCULATING LAKES OF
"MONASTRAL" PIGMENTS

Period Covered: June, 1949 - April, 1950

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INTRODUCTION

The preparation of aluminum benzoate lakes of copper phthalocyanine (HL-282-D type lakes) is covered by a Harmon patent (U.S. 2,327,472, issued August, 1943). This patent covers the preparation of aluminum benzoate lakes of copper phthalocyanine pigments which are flocculation resistant when used in coating films. The patent specifies an aluminum benzoate content greater than 30% on the pigment; below 30% the flocculation resistance is not significant. The aluminum benzoate may be precipitated on to the pigment in slurry form, or it may be incorporated by co-milling it with the pigment paste. There are no equivalents for aluminum benzoate listed in this patent either in the specifications or by inference in the examples or claims.

The current effort to circumvent the patent involved a laboratory study of extenders other than aluminum benzoate. In the work reported herein, lakes were prepared of metallic salts of benzoic acid other than aluminum, and aluminum salts of organic acids other than benzoic.

SUMMARY AND CONCLUSIONS

The Harmon patent refers to aluminum benzoate specifically as the agent which confers non-flocculating properties on the pigment. In an evaluation of this patent in 1944, Dr. Killian found that benzoates of metals other than aluminum are ineffective in preventing flocculation of CPC enamels. He also found that o-chlorobenzoic acid is equivalent to benzoic in inhibiting flocculation of CPC, but that other acids, such as anthranilic, salicylic, and phthalic, are not.

The current search for extenders other than aluminum benzoate revealed that the only materials which are as effective as aluminum benzoate in preventing flocculation of CPC pigments are the aluminum salts of certain substituted benzoic acids: o-chlorobenzoic acid, p-nitro benzoic acid, and o-benzoyl benzoic acid. The aluminum salts of the aliphatic and inorganic acids studied, as well as the benzoates of metals other than aluminum, are completely ineffective in inhibiting the flocculation of CPC pigments.

However, despite the 13¢ /lb. royalty penalty under the Harmon patent, aluminum benzoate still is the best extender for a non-flocculating lake on the basis of both cost and quality.

In the course of this work the following samples have been prepared:

1. A 5 lb. sample of a 48% lake of "Monastral" Blue LB extended with 24% aluminum benzoate and 24% precipitated barium sulfate. This material, AEL-326-D, Lot 2271, is slightly inferior to HL-282-D in flocculation, slightly more intense in hue.
2. Two 4.5 lb. samples of lakes of "Monastral" Blue BG. Lot 2171 is a 48% aluminum benzoate lake; Lot 2177 consists of 24% aluminum benzoate and 24% precipitated barium sulfate. Both are virtually free of any sign of flocculation in alkyl enamel.

3. A 4 lb. experimental sample of a 48% aluminum benzoate lake of solvent-milled eutectic Green and containing 1% H-657 (Blue BG pulp). This material, AQL-709-D, Lot 2276, is completely free of flocculation in alkyl enamel or lacquer.

DISCUSSION OF EXPERIMENTAL RESULTS

1. Salts of benzoic acid other than aluminum benzoate were precipitated on the pigment. The calcium, barium, nickel, and zinc salts are somewhat water soluble and gave low yields. The copper, lead, and iron salts were satisfactory in yield, but did not impart flocculation resistance to the pigment.

2. The calcium, barium, copper, zinc, lead and aluminum salts of benzoic acid were wet-milled with the CPC paste in porcelain mills. The products appeared to be as uniform as those made by the precipitation technique. However, only the lake of the barium salt showed as little flocculation as the aluminum benzoate control. The preparation of barium benzoate lakes is not too practical, because of the water solubility of the salt.

3. 50% lakes containing all $\text{Ni}(\text{OH})_2$ or 1:1 $\text{Ni}(\text{OH})_2$ -aluminum benzoate precipitated on the pigment were prepared and evaluated. Pigment N, $\text{Ni}(\text{OH})_2$, has no apparent effect on the flocculation of the pigment. Flocculation is not reduced, although the pigment may be coated with precipitated $\text{Ni}(\text{OH})_2$.

4. Acids other than benzoic were also investigated. The proportions of acid and alum added were adjusted to give approximately 50% lakes. Those acids, of which the sodium salts were not readily available, were dissolved in an equivalent amount of caustic soda prior to addition to the pigment slurry. These acids were of three types: inorganic, aliphatic, and aromatics related to benzoic acid.

Among the simple acids tested for flocculation resistance as their aluminum salts were: phosphoric, boric, and oxalic. They had no apparent effect on the flocculation of the pigment.

5. The aliphatic acids tested were: malic, stearic, citric, and lactic. None contributed any flocculation resistance. The aluminum salts of malic, citric, and lactic acids are somewhat water soluble and yields of the lakes were low.

6. All derivatives of benzoic acid can be considered to come within the scope of the patent, if all of them are as effective as benzoic acid in reducing flocculation of CPC toners. However, if some benzoic acid derivatives are found to be ineffective, then it is reasonable to assume that the patent claims must be restricted to aluminum salts of benzoic acid only. As long as some substituted benzoic acids are useless in inhibiting flocculation, any other derivatives that are effective are not equivalents but independent discoveries.

Two benzoic acid derivatives which are useless in preventing flocculation of CPC toners in paint films are o- and tere-phthalic acids.

On the other hand, the aluminum salts of o-chlor benzoic acid, p-nitro benzoic acid, and o-benzoyl benzoic acid yielded lakes which are as free of flocculation as those made with benzoic acid. However, all of these acids are more expensive than benzoic. o-Benzoyl benzoic acid is the cheapest of the three, but it still cannot compete economically with benzoic acid in our HL-282-B formula, despite the potential savings on the royalties.

7. The aluminum salts of malic and o-phthalic acids were wet-milled with the CPC paste. The products, although uniform, showed as much flocculation as untreated CPC toner.

8. One of the patent claims is that aluminum benzoate effectively inhibits flocculation of a pigment in a paint system only when used in amounts greater than 30%. In an effort to circumvent this claim, lakes containing 25% aluminum benzoate and 25% precipitated barium sulfate were prepared in the laboratory and evaluated. These were almost as free of flocculation and more intense than the 48% aluminum benzoate lakes. One batch of AEL-326-B, Lot 2271, containing 24% barium sulfate and 24% aluminum benzoate, was prepared in the Semi-works for testing and sampling.

The aluminum benzoate content cannot be reduced below 25% without seriously impairing flocculation resistance. However, it may be claimed, with reason, that the barium sulfate is merely extender, although it is precipitated with the aluminum benzoate.

9. All the orientation work reported herein was carried out on Newport Blue LB paste (B-623), except in the cases of Blue EG and Green. The products were evaluated for flocculation resistance in alkyl enamel tints by the rub and/or pour-out tests (TF 1601-1).

REFERENCES

D. B. Killian: Evaluation of CPC/Aluminum Benzate Lake,
and Preparation of Counterparts.

Howark Report EN-44-22.

Experimental Details: Notebook 1342, Expts. 1-8.