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E. I. DU PONT DE NEMOURS & COMPANY
KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

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PIGMENT COLOR RESEARCH REPORT

Final Report

EVALUATION OF CPC/ALUMINUM BENZOATE LAKE (U.S. PATENT 2,327,472), AND PREPARATION OF COUNTERPARTS.

Period Covered: January 1, 1944 - March 14, 1944

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Period Covered: January 1, 1944 - March 14, 1944

SUBMITTED BY: D. B. Killian 4/3/44 DATE SUBMITTED: 3-23-44

APPROVED BY: Alfred Siegel 4-3-44 DATE ISSUED: 4-4-44

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I. INTRODUCTION

Early in 1943, several samples of a non-flocculating copper phthalocyanine lake made by the Harmon Color Works, Inc., were obtained from various sources in the trade. This lake pigment was tested and found to be practically non-flocculating in lacquer and alkyd enamels, when extended with titanium dioxide white. The product was analysed by the analytical laboratory and found to consist essentially of 50% CPC and about 50% aluminum benzoate. With this information, Brizzolara and Reidinger prepared a 50% aluminum benzoate/CPC lake from "Monastral" Blue by precipitation of aluminum benzoate in the presence of the CPC. The aluminum benzoate was obtained by striking a slurried mixture of CPC in a dilute solution of sodium benzoate with alum. The sample prepared in this way in the laboratory was also shown to be non-flocculating in lacquer and alkyd enamels when tinted with titanium dioxide. A sample of the Harmon lake and our experimental match were exposed in lacquer versus controls made from BT-172-D plus alumina hydrate (series 6742), all tinted to the same extent with titanium dioxide. After six months exposure the Harmon product appeared superior to the experimental match in chalk resistance but otherwise the three systems were equal. In addition to these evaluations, the Harmon product was evaluated in the Paint Laboratory under work request CD-5. (January 29, 1943. Notebook 807-192).

A patent issued to the Harmon Color Works covering this aluminum benzoate/CPC lake on August 24, 1943, as U.S. 2,327,472. This patent is directed exclusively to the use of aluminum benzoate to prevent the flocculation of CPC in coating films. The patent specifies that the product must be made by precipitation of the aluminum benzoate in the presence of a slurried CPC, or by a long grinding of CPC paste and aluminum benzoate paste. Furthermore, the specification teaches that mechanical mixtures of CPC and aluminum benzoate are not equivalent to the lake prepared by the preferred procedure, and that less than 30% aluminum benzoate under any circumstances is not as effective as 30% or more aluminum benzoate in the product. The preferred proportions cover the range between 30% and 70% of aluminum benzoate. There are no equivalents listed either in the specification or by inference in examples or claims in this patent for aluminum benzoate. A careful examination of the file history on this patent indicates that no compound of an organic nature other than aluminum benzoate was included in the original or amended specification, with the exception of barium and calcium resinate and also aluminum silicate, all of which are cited as ineffective in preventing flocculation of CPC toners. Evaluation of this patent and a high spot search for equivalents to aluminum benzoate was authorized under the CR-206 project late in December of last year. The work reported herein covers this work and the study of a few aromatic organic acids as equivalents for aluminum benzoate to produce non-flocculating CPC lakes. This work was done between January 1, 1944 and March 14, 1944.

II. PATENT SITUATION

U.S. Patent 2,327,472 (Veeco and Stalzer assignors to Harmon Color Works. Application date 1/3/41; issued 8/24/43) is specifically directed toward the use of aluminum benzoate to prevent flocculation of copper phthalocyanine toner, and a preparation of an aluminum benzoate/CPC lake which is non-flocculating in paint systems. No equivalents are claimed or suggested. Since it seemed unlikely that benzoic acid would be the only aromatic organic acid capable of pro-

ducing improvements in flocculation of CPC in paint systems, other aromatic carboxylic acids were studied in similar lakes. As discussed in the following sections of this report, aluminum ortho-chlor-benzoic acid has been found to be practically equivalent to benzoic acid in preventing flocculation of CPC when the corresponding aluminum salt is prepared in the presence of the CPC. Also, aluminum para-isopropyl benzoate gives a CPC lake of the improved flocculation but inferior in lacquer systems either to the lake made from ortho-chlor-benzoic acid or benzoic acid. On the other hand, different simple substituted benzoic acids such as anthranilic acid, sulfanilic acid, salicylic acid, and ortho-benzoyl benzoic acid when used to prepare the corresponding aluminum salt lake of CPC fail to give any appreciable improvement in resistance to flocculation of the CPC lake when extended with TiO_2 in lacquer or alkyd. Also naphthoic acid and phthalic acid were ineffective in preventing flocculation when precipitated as the aluminum salt with CPC toner. The aluminum ortho-chlor-benzoate/CPC lake is considered as an equivalent to the aluminum benzoate/CPC lake of the Harmon patent, but this equivalent does not appear to be general in character since all substituted benzoic acids do not behave in the same way to prevent the flocculation of CPC, and in fact only ortho-chlor-benzoic acid is of much use for this purpose among the various candidates examined to date. For this reason the argument can be advanced that the aluminum ortho-chlor-benzoate lake of CPC is not an obvious equivalent of the Harmon patent and therefore might be claimed as an independent discovery. Since ortho-chlor-benzoic acid is not covered by the Harmon patent, it appears that we are free to manufacture the ortho-chlor-benzoate/CPC lakes.

III. SUMMARY & CONCLUSIONS

1. The results of this work substantiates the claim of the Harmon patent. A 50% CPC/50% aluminum benzoate lake is practically non-flocculating when extended with titanium dioxide in lacquer where extension has not been carried too far, and is non-flocculating even at high TiO_2 extensions in alkyd enamels. This product is important and very interesting in that it is the first non-flocculating copper phthalocyanine product appearing on the market, and is vastly superior to any standard CPC toner in this respect.

2. A high spot search for equivalents to this product not covered by the Harmon patent has been made. Benzoates of other metals than aluminum are not effective in preventing the flocculation of CPC, and the improvement appears to be specific to aluminum salts. Aluminum ortho-chlor-benzoate appears practically equal to aluminum benzoate in inhibiting the flocculation of CPC but the latter lake is still somewhat superior in this respect in lacquer. Both lakes appear non-flocculating in alkyd enamels. A number of other organic aromatic acids have been investigated and found of little, if any, value to prevent flocculation of CPC. However, p-isopropyl benzoic acid gives an aluminum salt lake of CPC which is non-flocculating in alkyd enamels but only slightly improved in this respect in lacquers.

3. No effort was made to determine whether or not the aluminum benzoate CPC lake is a desirable addition to the Newark line. However, this lake does not appear as important now as it did before this evaluation study. Ortho-chlor-benzoic acid is one material which is capable of producing

results practically as good as benzoic acid for this use, and it is likely that a more thorough investigation may uncover other leads of equal merit. Also, the Harmon product is not as flexible in use as the coalesced phthalocyanine pigments, specifically Pigment BX-CR.

4. The aluminum benzoate CPC lake is not as good in its resistance to flocculation in lacquer as Pigment BX-CR. The benzoate lake when reduced 50% with titanium oxide in lacquer shows a very slight flocculation as judged by pour-out tests, whereas Pigment BX-CR fortified with CPC toner to the same color content is free of flocculation. Extension of the benzoate lake with TiO_2 further than 50% reduction shows increasing flocculation as the amount of TiO_2 increases; Pigment BX-CR shows no flocculation even at 1:100 dilutions with TiO_2. The benzoate lake exhibits some tendency to inhibit the flocculation of CPC toner in the presence of TiO_2 in lacquer, but here again Pigment BX-CR is more effective in this respect, i.e. Pigment BX-CR will prevent the flocculation of definitely greater amounts of CPC toner than will the benzoate lake. The benzoate lake when tinted with TiO_2 in lacquer separates on shelf storage but not as badly as a mechanically mixed tint made from straight toner and TiO_2. Pigment BX-CR in lacquer is non-separating after a year and one-half shelf storage. The benzoate lake has been reported to grow crystals in xylene which fact would indicate that it would not be can stable and would show color drift on storage. This is being checked at present. The coalesced phthalocyanine pigments are can stable.

5. It appears that the aluminum benzoate or other organic acid aluminum lakes of CPC made from toner paste are less attractive economically than coalesced pigments.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

The work reported herein can be divided into two parts, namely, evaluation of the Harmon patent U.S. 2,327,472 and a search for equivalents to aluminum benzoate which are effective in preventing the flocculation of CPC. CPC lakes containing 50% aluminum benzoate were made in the laboratory from both Heliogen Blue BV and "Monastral" Fast Blue BK pastes. The process of example 1 of subject patent was duplicated and modified procedures were also employed in the preparation of the benzoate lakes. The effect of colloid milling the CPC paste both with and without the sodium benzoate before precipitation of the aluminum salts was also studied. The benzoate lake was also prepared by a reverse strike procedure from that of the patent example, i.e., addition of sodium benzoate to the CPC slurry containing dissolved alum. All of the benzoate lakes were essentially equal to each other in their resistance to flocculation but there was a slight variation in this respect shown by the various products when extended with TiO_2 in lacquer. In alkyd enamels all of the experimental benzoate lakes appeared equal to each other.

Mechanical mixtures containing various proportions of CPC toner, BT-172-D, and aluminum benzoate were extended by grinding in lacquer with titanium dioxide. None of the systems showed any improvement in flocculation from that obtained with regular toner CPC extended with titanium dioxide. Also, CPC toner paste was mixed in slurry form with a slurry of aluminum benzoate and the resultant product was no better in flocculation than CPC toner without the added benzoate. These results substantiate disclosures in the Harmon patent. Crude CPC was salt milled

with aluminum benzoate for 48 hours and the resultant lake was much better in its resistance to flocculation than standard CPC toner but was not quite equal to the aluminum benzoate lake made by precipitation methods.

Other metals were investigated in place of aluminum for preparation of metallic benzoate CPC lakes. Lakes containing 50% CPC were made with copper benzoate, zinc benzoate, titanium benzoate, chromium benzoate, stanneus benzoate, and lead benzoate. None of these lakes were of much interest as non-flocculating CPC pigments, and show no worth while improvement in resistance to flocculation over the regular toner pigments.

Titanium dioxide was coated with aluminum benzoate and this extended TiO_2 was used to tint CPC toners in lacquer. The resultant lacquer systems were not equal in their resistance to flocculation to the benzoate CPC lake when tinted to the same depth with TiO_2.

The above results agree with the claims made in the Harmon patent. It appears necessary to precipitate aluminum benzoate in the presence of CPC toner to produce a non-flocculating lake. Example 4 of the patent describes the preparation of a non-flocculating aluminum benzoate CPC lake by ball milling a mixture of CPC and aluminum benzoate in the presence of water. This example has not been checked.

A number of other organic aromatic acids have been evaluated as their aluminum salts versus the aluminum benzoate lake to determine whether any of these products are equal to the benzoate lakes in resistance to flocculation. The following acids have been studied: Ortho-chlor-benzoic acid, para isopropyl benzoic acid, salicylic acid, anthranilic acid, sulfanilic acid, ortho-benzoyl benzoic acid, phthalic acid, beta-oxy-naphthoic acid, and alpha and beta naphtheic acids. Also aluminum silicate and aluminum hydrate were evaluated for their effect on the flocculation of CPC. The foregoing acids were added as their sodium salts to a slurry of CPC toner in amounts sufficient to give a 50% aluminum salt lake when struck with alum in the appropriate amounts. These lakes were ground as 50% extensions with TiO_2 in lacquer and compared to the Harmon product as well as laboratory samples of aluminum benzoate lakes. A lake made from ortho-chlor benzoic acid is equal to the benzoic lake in its resistance to flocculation in lacquer. The para isopropyl benzoate lake is better than a mechanical mixture of toner and TiO_2 but is markedly inferior to the benzoate lake in lacquer. However, both these lakes appear equal to the benzoate lake in resistance to flocculation in TiO_2 tinted alkyd enamels. None of the other acids show any significant improvement in their resistance to flocculation in lacquer or alkyd systems over toner controls.

The above listed organic acids were also used to prepare the corresponding aluminum salt lakes of TiO_2. The coated titanium dioxides were not very effective in preventing the flocculation of CPC when tints were made in lacquer. Mechanical mixtures of CPC toner and aluminum salicylate extended with TiO_2 in lacquer show no improvement in flocculation over toner controls. Also, a salt milled lake made from crude CPC and aluminum salicylate is unimproved in its resistance to flocculation. One interesting observation was made in the course of this work that the aluminum salt of beta-oxy-naphthoic acid is a relatively bright greenish yellow. The lakes containing the aluminum salt of BON and CPC are green.

Several laboratory preparations of the aluminum ortho-chlor benzoate lakes were made. These experimental products varied in their resistance to flocculation depending upon the method used in preparing them. Thus a lake made by precipitation of the ortho-chlor benzoate salt in the presence of regular "Monastral" Blue BK paste was practically equal in its resistance to flocculation in lacquer to the Harmon benzoate lake. However, a lake made by a similar process except using CPC paste previously colloid milled was less resistant to flocculation than the former lake. These results indicate that physical conditions of manufacture of these benzoate lakes or the ortho-chlor benzoate lakes are likely to influence the nature of the products obtained. No thorough study has been made of this aspect of the problem. However, it appears likely that the aluminum ortho-chlor benzoate lake can be prepared to equal the aluminum benzoate lake in its resistance to flocculation in lacquer and alkyd enamels.

It is interesting to compare the properties of the Harmon product against those of our experimental non-flocculating CPC pigment, Pigment BX-CR. After one and one-half years shelf storage of a lacquer pigmented with Pigment BX-CR no visible separation has occurred in the lacquer systems and the stored lacquer is just as uniform as after grinding. A sample of the Harmon lake extended to the same extent with TiO_2 in lacquer shows considerable separation of TiO_2 from the colored pigment shortly after grinding. The Harmon lake is superior in this respect, however, to mechanically mixed CPC toner and TiO_2 in lacquer. Technical Laboratory has reported that the Harmon lake grows crystals in xylene. This fact would lead one to suspect that the Harmon product would not be very stable in paint on shelf storage. This property is being tested at present with the Harmon lake but results are not yet available. The coalesced phthalocyanine pigments are very stable. The Harmon product extended 50% with TiO_2 in lacquer shows a very slight flocculation by pour-out tests whereas Pigment BX-CR fortified with CPC to the same color content shows no flocculation at all. Further extension of the Harmon lake with TiO_2 produces increasingly greater flocculation. Pigment BX-CR can be extended to 1 to 100 TiO_2 without any flocculation being evident by the pour-out test. A lacquer system pigmented with 50% of the Harmon benzoate lake, 12.5% BT-172-D and 37.5% TiO_2 shows a noticeable flocculation by pour-out tests whereas a similar system pigmented with 50% Pigment BX-CR and the other components the same is non-flocculating. This result indicates that the Harmon product is not as good as Pigment BX-CR in inhibiting the flocculation of CPC toner when extended with TiO_2 in lacquer. The aluminum benzoate lake is non-flocculating when extended with TiO_2 even to relatively weak shades in alkyd enamels, and in this respect is equal to Pigment BX-CR.

The Harmon aluminum benzoate CPC lake is an important and interesting product because it is the first sample of a non-flocculating CPC pigment which has appeared in the trade. In those applications of CPC where flocculation is a serious problem the Harmon product undoubtedly would be a more desirable material to use than regular CPC toners or lakes. However, ortho-chlor benzoic acid has given lakes of similar properties and this acid is not covered by the Harmon patent. These facts as well as the development of experimental coalesced phthalocyanines appear to lessen the importance of Harmon's aluminum benzoate lake. It appears that any of the aluminum salt lakes of CPC made from regular toner pastes are not likely to be as economically attractive as the coalesced phthalocyanine pigments.

V. EXPERIMENTAL DETAILS

Preparation of Aluminum Benzoate CPC Lakes

Notebook 1045-41, 42, 1085-19, 23, 26

Evaluation of the Aluminum Benzoate Lakes in Lacquer and Alkyd

Lacquer - 1045-37, 1085-6, 1027-25, 1027-28 (Exposure Series 6742)

Alkyd Enamels - 1061220, (Exposure Series 6826, Rezyl 807-1)
1085-30

Organic Acids other than Benzoic

(See above evaluation tests for the benzoate lakes for grind of these products in lacquer and alkyd).

Ortho-chlor Benzoic Acid

1085-4, 1085-19, 1085-25

Para Isopropyl Benzoic Acid

1085-22

Naphthoic Acids

1085-4, 1085-19

Phthalic Acids

1085-4, 1085-19

Benzoyl Benzoic Acids

1085-19

BON

1085-4

Anthranilic Acid

1045-46

Sulfanilic Acid

1045-46

Aluminum Silicate Lakes

1085-4

Aluminum Hydrate Lakes

1085-4

MISCELLANEOUS EVALUATIONS

Salt milled CPC and Aluminum Benzoate

1045-47

Salt milled CPC and Aluminum Salicylate

1045-47

Preparation of Aluminum Benzoate and Aluminum Salicylate

1045-34

TiO_2 coated with various Aluminum Organic Acid Salts

1085-12

Metallic Benzoate Lakes other than Aluminum

1085-24