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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: ORGANIC BROWN PIGMENTS

Period Covered: 2/5/46 - 6/30/46

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INTRODUCTION

The purpose of this work was to develop a brown pigment which would be suitable for automotive purposes and satisfy the requirements thereof. The broad outlines of the work are contained in a letter sent by Dr. J. H. Cooper on July 31, 1945 to Dr. D. N. Dawson. The letter states that there were customers who had expressed a desire for brown pigments of better gloss and particularly for better retention of gloss, and who would be willing to pay the prices for organic pigments possessing the desired properties.

No previous work has been conducted at Newark with this specific goal in mind. The only work done previously was that on brown pulp colors in the inorganic field.

Experimental Project #229 was authorized for undertaking this problem.

SUMMARY AND CONCLUSIONS

The following types of pigments were prepared and evaluated:

1. Nitroso-β-Naphthol Metal Complexes.
2. "Naphthanil" Types
   a. "Naphthanil" LB
   b. "Naphthanil" BG
   c. Metallized "Naphthanil" Couplings.
3. α - Naphthol Coupling Products.
4. β - Naphthol Metal Complexes.
5. β - Oxynaphthoic Acid Metal Lakes and Complexes.
6. 2,3-Dihydroxyquinoline Coupling Products.

From the above groups mentioned the following were found to be of interest and larger samples have been prepared for outdoor exposure tests:

I. 2,5-Dichloraniline → "Naphthanil" BB, K-2336 Brown pigment showing good lightfastness and bleed resistance.

II. p - Nitroaniline → β -Oxynaphthoic Acid (Copper), K-2369. Also shows good lightfastness and good bleed resistance.

III. Aniline → β -Oxynaphthoic Acid (Nickel), K-4425. A sample was received from Jackson Laboratories.

IV. Benzidine → 2,4-Dihydroxyquinoline (Copper), K-2387.

All other combinations were found to be of no immediate interest.

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DISCUSSION

1. Nitroso- β -Naphthol Metal Complexes

Pigment Green B is of this type, being the iron complex of nitroso-β-naphthol. Various other metallic complexes of nitroso-β-naphthol were prepared in the hope that they might give browns, especially the copper complex. Two procedures were used: 1. The solution of the nitroso-β-naphthol as the bisulfite ester; and 2. the solution of the nitroso-β-naphthol in acetic acid. The complexes of titanium, chromium, copper, cobalt, and zirconium were prepared. However, none of them was of any interest.

2. a) "Naphthanil" LB Type:

"Naphthanil" LB, which is a carbazole type hydroxycarboxylic acid, is reported to give browns when coupled with suitable first components. However it was found that commercial "Naphthanil" LB contains high amounts of Dextrin, which interfered with the coupling procedure and resulted in highly reactive pigments. An attempt was made to purify the "Naphthanil" LB of all the Dextrin but whatever small amounts of Dextrin remained seemed to interfere with the preparation of strong and non-reactive pigments.

2. b) "Naphthanil" BG Type:

2,5-Dichloraniline was coupled with "Naphthanil BG, which is the dimethoxyanilide of β-oxynaphthoic acid, to produce a brown of good strength and lightfastness. A K ample (K-2386) has been prepared for outdoor exposure.

2. c) Metallized Naphthanil Types:

Couplings of p-nitroaniline and o-nitroaniline with "Naphthanils" ASV, AS, ASG, ASOL, OP, RL, and MX were prepared and treated with ammoniacal copper in an attempt to form copper chelates with the pigments. Some color changes were observed, some very reddish browns being obtained. However a decrease in lightfastness, strength, and oil bleed was observed upon metallization.

3. α -Naphthol Coupling Products

The coupling of p-nitroaniline with α -naphthol was prepared and was found to bleed badly. Couplings p-chloro-o-nitroaniline, o-chloro-p-nitroaniline, and m-nitro-p-toluidine with α -naphthol were also made. The products were characterized by poor strength, poor bake bleed, and poor lightfastness.

Three naphthylamine sulfonic acids, Laurent's Acid, Tobias Acid, and Naphthionic Acid were coupled with α -naphthol. The resulting combinations were found to be highly soluble and could only be precipitated on the addition of large amounts of barium chloride. A coupling of two moles of p-nitroaniline with one mole of α naphthol gave a brown which, however, showed a very high bleed, a very high oil absorption, and extremely weak tetrazole strength. None of these combinations was of any interest.

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4. β-Naphthol Metal Complexes:

Couplings of β-Naphthol with p-chlor-o-nitro-aniline, O-chlor p-nitroaniline, and m-nitro -p-toluidine were made and metallized with ammoniacal copper, similar to the method of preparation of TT-5-D, which is p-nitroaniline coupled with β-naphthol and metallized with ammoniacal copper. No change in color was observed. The same type of metallization was carried out with "Lithosol" Red 2B, using copper, iron, nickel, and chromium. Color changes occurred but no browns were obtained. However, since the colors showed good lightfastness and good strength they might be of interest as reds.

5. β-Oxynaphthoic Acid Metal Lakes and Complexes:

The manganese, copper, and nickel lakes and complexes of p-nitro-aniline - β-oxynaphthoic acid were prepared. Variable studies on the method of coupling and method of metallization were carried out. It was found that the sodium acetate-acetic acid type of coupling gave products of highest strength and highest bleed resistance. The best method of metallization was by the use of an ammoniacal copper solution. Pressing and reslurrying of the pigment before metallization was not found necessary.

Couplings of 2,5-dichloraniline, p-nitro-o-toluidine, p-chlor-o-nitroaniline, o-chlor-p-nitroaniline, and m-nitro-p-toluidine with β-oxynaphthoic acid were prepared and metallized as above. However the p-nitroaniline product metallized with copper was the only brown of any interest. A K sample has been prepared (K-2369) for outdoor exposure.

The copper, iron, nickel, and chromium toners of p-chlor-aniline-m-sulfonic acid coupled with β-oxynaphthoic acid were prepared. They were somewhat soluble and bled badly. However, none of them was a brown.

The nickel toner of aniline coupled with β-oxynaphthoic acid (D-4425) which was prepared at Jackson Laboratory was received and evaluated. It was a reddish brown and showed good lightfastness and strength. Panels will be prepared for outdoor exposure.

6. 2,4-Dihydroxyquinoline Coupling Products:

p-Nitroaniline, p-nitro-o-toluidine, m-nitro-p-toluidine, benzidine, 3,3'-dichlorbenzidine, and p-chlor-aniline were coupled with 2,4-dihydroxyquinoline and the resulting products metallized with both copper and nickel, following the "Lithosol" Yellow Part 32D procedure. The only brown produced was the copper complex of the benzidine → 2,4-dihydroxyquinoline product. This combination was previously reported by Jackson Laboratory as being of good lightfastness. A K sample (K-2387) has been prepared for outdoor evaluation.

EXPERIMENTAL DETAILS

Exp.	Subject
1199-1,2,11,16,24,25	Pigment Green 8 type - metal complexes.
3	4-chlor-2 amino anisole → N-40-LB.
3,12,19	2,5 dichlor-aniline → N-66-LB.

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Exp.	Subject
3,12	PCONA → N-AS-LB
4,5	Vat dye browns
6	PCONA, OCPNA, MNPT → BN, Cu
7	PCAMEA → BON metal complexes.
8	"Lithosol" Red 2B metal salts.
9	PNOT → N-AS-DG
9,13,26	2,5 dichlor-aniline → N-AS-DG
10	Aniline - BON - Nickel
12	2 methoxy - 5 chlor-aniline → N-AS-LB
14,31	PNA → α naphthol, Cu
15	PCONA, OCPNA, MNPT → α naphthol
17	ONA → N-ASD, N-AS, N-2S, N-ASE, N-ASOL, N-OP, N-RL, N-MX, Cu
18,20	PNA → N-ASD, N-AS, N-2S, N-ASE, N-ASOL, N-OP, N-RL, N-MX, Cu, Ni
19	2, 4 dihydroxy-quinoline-aniline-metals
21, 30, 32, 35	PNA → BON, metals
22	Broenner's Acid, Tobias Acid, Naphthoinic Acid → α naphthol, metals
23	1 amino-2 naphthol-4 sulfonic acid → AAPNA, metals.
27,28	PNA → BON, Cu
27	2,5-di chlor-aniline, PNOA, PCONA, OCPNA, MNPT → BON, Cu.
29	2,5 di chlor-aniline → N-AS-DB
29	Para-chlor anisidine → N-AS-DB
33,34	PNA → 2,4 dihydroxy quinoline Ni and Cu
1199-33	PCONA and MNPT → 2,4 dihydroxy - quinoline Ni + Cu
33,37	Benzidine → 2,4 dihydroxy-quinoline Ni + Cu
33	Di chlor-benzidine and, para-chlor aniline → 2,4 dihydroxy quinoline - Ni + Cu.
36	Analysis of Zinsser's browns.

REFERENCES

Letters July 31, 1945 (J. K. Cooper to D. H. Dawson)

Exposure series S-7936.

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