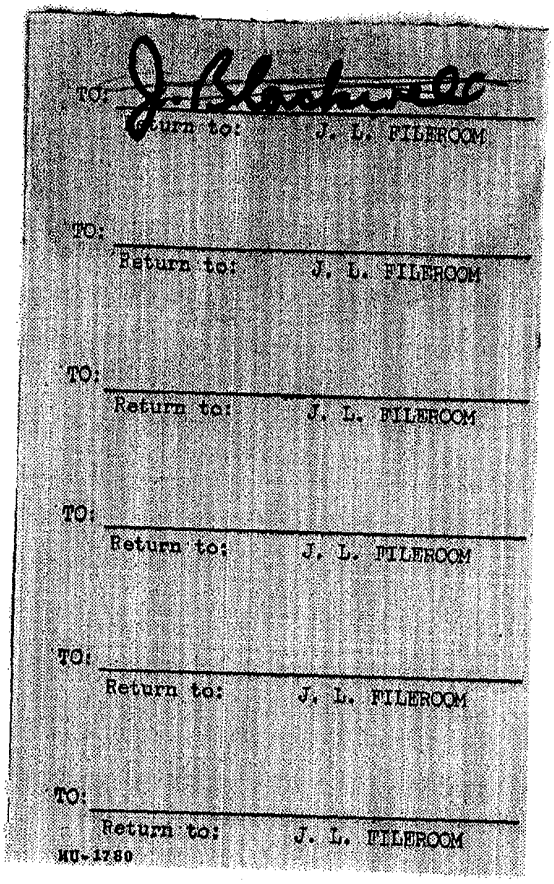
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JLR-43-462, No. 1
Serial Number 18835

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E. I. DuPont de Nemours & Company

Jackson Laboratory

May 5, 1944

New Chromate Brown J-43-P-224
Duplication of Anthracene Chromate Brown EBA (General)

Progress Report

B. G. Carson

C. E. Sparks
Division Head

Serial Number 18835
JLR-43-462, No. 1

DUP050041215

New Chromate Brown J-43-P-224
Duplication of Anthracene Chromate Brown EBA (General)
(Project 2450)

B. G. Carson

JLR-43-462, No. 1 Serial Number 18835

Object of the Investigation:

To help establish the constitution of Anthracene Brown EBA (General) and to prepare a preliminary sample duplicating this color.

Period Covered by the Report:

September 4, 1943, to December 10, 1943.

Historical Background:

It was found early in 1943, by the Sales Division that Anthracene Brown EBA (General), selling for the same price as DuPont Chromate EBN, had a metachrome strength of approximately 120% of that of our product, though the two products are of approximately equal strength dyed after chrome. Jackson Laboratory was asked to complete the preliminary investigation of the competitive product. It was agreed by the Sales Division that the exact duplication of the shade of Anthracene Brown EBA was of minor importance. What was first desired was a chromate brown with the metachrome-topchrome ratio of the competitive product.

Summary and Conclusions:

It has been found that Anthracene Chromate Brown EBA is a mixture of approximately equimolecular parts of the monazo dye 4-nitro-2-aminophenol diazotized and coupled (->) to m-phenylenediamine and the disazo dye 4-nitro-2-aminophenol -> m-phenylenediamine <- Laurent's Acid. This confirms for the most part the results obtained earlier by the Azo Area Laboratory.

A preliminary sample (J-43-P-224) of this constitution has been submitted to the Technical Laboratory, who has recommended

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the preparation of a final sample and the development of a workable process for the production of the color. This work has been authorized.

Patent Situation:

See AN-108 and AN-1602.

DuPont Chromate Brown EBN and its prototype Chromate Brown EB have been on the market many years. DuPont Chromate Brown EBN is known to contain a small amount of the monazo combination because of incomplete coupling of the Laurent's Acid. Changing the ratio of monazo to disazo dyes does not change the patent status; so it is considered that the new product is not patentable and that we are free to manufacture and to sell it.

Plans for Future Work:

The preparation of a final sample duplicating Anthracene Chromate Brown EBA and the development of a tentative Semi-Works process for the manufacture of this dye will be finished shortly.

Experimental: (See JLNB-4053-80-89, 140-152)

Separation of Monazo from Disazo Dyes

A. Anthracene Chromate Brown EBA (JLNB 4053-80)

Thirty grams of Anthracene Chromate Brown EBA was dissolved in about 2500 cc. water and placed in a large-capacity continuous liquid-liquid extractor with an extraction chamber about forty inches in length. Ether was used to extract the monazo dye present. At the start of t he operation, acetic acid was added to the dissolved dye until it was neutral (The dye is standardized with approximately 25% soda ash.). After three days more acetic acid was added to make the solution acid to litmus. Extraction was very slow. After a week, no color was evident in the ether layer; so the extraction was stopped. The ether solution was run into a weighed flask and distilled from the dye after which the dye was dried at 100°C. for two hours. The monazo dye (4053-80A) weighing 9.2 grams was dyetested and turned over to H. W. Daudt for analysis. It proved to be the dye 4-nitro-2-amino-phenol -> m-phenylene-diamine.

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The disazo dye left in the water layer was converted to the free acid dye by the addition of HCl at the boiling point. Filtration of the free acid dye was slow, but the filtrate was colorless. After repeated washings of the precipitated disazo dye it was dried at 100°C. This product weighing 10.9 grams, designated as 4053-80B, was also dyetested and given to H. W. Daudt for identification. It proved to be the dye 4-nitro-2-aminophenol -> m-phenylene-diamine <- Laurent's Acid.

B. DuPont Chromate Brown EBN (JLNB 4053-83)

This dye in the form of a composite of crudes from Charges 302, 303, 308, 309, 310 and 311 was separated into monazo and disazo constituents by the above method. From a 30-gram sample only 2.2 grams of ether soluble material was extracted. The free acid disazo dye from this extraction was designated as 4053-83-B. Its dyetest is reported later.

Synthesis of Probable Constituents

(a) 4-Nitro-2-aminophenol -> m-tolylene-diamine (4053-84

(b) 4-Nitro-2-aminophenol -> m-phenylene-diamine (4053-85)

In synthesizing dyes (a) and (b) the 4-nitro-2-aminophenol was dissolved in dilute HCl and the solution filtered, diazotized and the diazo compound filtered off and reslurried in water. The slurry was added slowly to a concentrated solution containing 50% excess of the diamine. The coupled dye was filtered off without salting and was freed from the excess diamine by washing with water until a few cubic centimeters of the filtrate collected from the funnel gave no Bismarck Brown with acid and nitrite.

(c) 4-Nitro-2-aminophenol -> m-phenylene-diamine <- Laurent's Acid

This dye was prepared by the Dye Works Process for the manufacture of DuPont Chromate Brown EBN, leaving out the m-toluylene diamine and substituting an equivalent amount of m-phenylene-diamine. The monazo combination was purified before being coupled to the Laurent's Acid and at the end of the second coupling the dye was isolated and any excess monazo dye extracted by the method used for Anthracene Chromate Brown EBA.

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Dyetest Comparisons

The dyes described above were dyetested as direct, metachrome, and after-chrome colors. In the monazo combinations the dye prepared from m-tolylene diamine was much redder than that from m-phenylene-diamine whether dyed on wool direct, metachrome, or top-chrome. The dye synthesized from m-phenylene-diamine resembled in every respect the monazo combination extracted from Anthracene Chromate Brown EBA. The disazo dye prepared from m-phenylene-diamine resembled the disazo dye obtained from Anthracene Chromate Brown EBA. However, the disazo dye obtained from DuPont Chromate Brown EBN was only slightly redder than that containing only m-phenylene-diamine as a middle coupling component. It was reasoned, however, that if m-tolylene-diamine were not present in the monazo combination it would be illogical to expect it in the disazo combination since such a mixture as the one being studied would almost certainly be manufactured in one continuous operation rather than as the result of mixing two dyes prepared in separate operations.

Capillary Comparisons

Ordinary capillary methods failed to give bleed-outs from Anthracene Chromate Brown EBA and the purified dyes. It was found, however, that capillary bleed-outs run in closed tubes about twenty inches long using alcohol as a solvent gave bleed-outs which appeared to be significant. The bleed-out of the purified monazo dye from m-phenylene-diamine and that of the monazo combination extracted from the competitive dye were similar and were much less red than the bleed-out from the m-tolylene-diamine dye. No bleed-out could be obtained from the disazo dyes.

It was concluded from the above work and from the analyses by H. W. Daudt that the monazo dye present in Anthracene Chromate Brown EBA contained only m-phenylene-diamine as a coupling component and that the disazo combination probably contained only this coupling component.

Shade Build-up from Pure Dyes

Dyetests were made with mixtures of the purified monazo dye from m-phenylene-diamine and the corresponding disazo dye. Shade comparisons were made on direct, metachrome, and topchrome dyeings

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vs. Anthracene Chromate Brown EBA. It was concluded that Chromate Brown EBA represented approximately an equimolecular mixture of the monazo and the disazo dyes since less than 50-mole percent of the monazo gave dyeings redder and more than 50-mole percent yellower than the competitive product.

Preparation of Preliminary Sample J-43-P-224
(JLNB 4053-151, 2)

0.2 Mole of 4-nitro-2-aminophenol, purified, was diazotized and coupled to 0.2 mole of m-phenylene-diamine following the Dye Works process for the manufacture of DuPont Chromate Brown EBN. Excess nitrite in the diazo solution was destroyed by the addition of a small amount of sulfamic acid before the diamine was added. A very faint excess of the diazo was present at the end of the coupling. Just before adding 0.1 mole Laurent's Acid diazo prepared by the same process 0.3 mole NaOH as a 30% solution was added to the monazo dye. This completely and quickly dissolved the dye, and the solution was iced to 0°C. The Laurent's Acid diazo was added rapidly (10 minutes). The test for Laurent's Acid diazo became negative almost instantly. After about thirty minutes the temperature of the solution was raised to 75°C., and 0.45 moles of HCl (10 Normal) was added slowly. The dye was filtered without salting from the acid (one-half spot on Congo Red paper) liquor. Filtration was fairly rapid. To the wet presscake was added 25 g. of soda ash. After puddling the mixture to a homogeneous mass the dye was dried at 60°C.

The crude dye weighing 122.5 grams exactly matched Anthracene Chromate Brown EBA in direct shade, metachrome shade, and afterchrome shade with a strength of 1:1.

In a second coupling similar in all respects to the above, the use of sulfamic acid to destroy the excess nitrite was inadvertently omitted. Presumably at least a small amount of Bismarck Brown was introduced into the final color, but no difference in shade was detected in the dyetesting.

The Technical Laboratory reported J-43-P-224 as being trace bright, equal in direct strength and metachrome strength, 95:90 in afterchrome strength, and appreciably superior in solubility vs. Anthracene Chromate Brown EBA. Shading with 2% DuPont Alizarine Blue Black B corrected the brightness to duplicate the competitive dye. The preparation of a final sample was recommended.

Submitted for Typing - 5-27-44
Typed - 11-17-44
Ardith M. Messick