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E. I. DuPont de Nemours & Company

Jackson Laboratory

May 18, 1942

Pontachrome Flavine A

JLR-43-168, No. 4 Serial Number 18019

E. I. DuPont de Nemours & Company

Jackson Laboratory

Azo Colors Division

S. S. Rossander

Problem Report

May 18, 1942

Pontachrome Flavine A

Work Done By - B. G. Carson, J. H. Trepagnier, S. B. Smith

Reported By - S. B. Smith

Work Started - 1-16-42

Completed - 3-15-42

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Pontachrome Flavine A
(Project 1315)

S. B. Smith

JLR-43-168, No. 4 Serial Number 18019

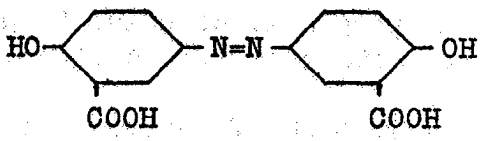
Object of the Investigation:

To find a more economical route to this color.

Period Covered by the Report:

January 16, 1942, to May 15, 1942

Historical Background:

Pontachrome Flavine A 

(azo salicylic acid) has been made since 1936 at the Dye Works by the following route: phthalimide -> anthranilic -> ortho-chlor-benzoic -> 5-nitro-2-chlor-benzoic -> 5-amino-2-chlor-benzoic, coupled to salicylic and hydrolyzed. Since the yields on the nitration and reduction step and the hydrolysis step are poor and since the color will soon be produced on a tonnage basis for use in khaki mixes it was decided to study other possible routes to the color.

The following reports cover related work on Pontachrome Flavine A or its intermediates done at this time by divisions at Jackson Laboratory other than the Azo Division:

JLR-43-168, No. 2; Serial Number 17992
2-Chlor-5-Nitro-Benzoic Acid by V. Weinmayr; Dated 4-3-42

JLR-43-168, No. 3; Serial Number 18009
Pontachrome Flavine A by Hydrogenation by R. B. Scott; Dated 5-18-42

JLR-43-168, No. 5; Serial Number 17825
2-Chloro-5-Nitro-Benzoic Acid by R. F. Deese and L. E. Schniepp - reported by H. A. Bergstrom; Dated 5-21-42

JLR-43-168, No. 6; Serial Number 18007
5-Nitro-Salicylic acid; by H. A. Bergstrom; Dated 5-15-42

Summary and Conclusions:

The present route to the color is the most attractive approach and future work should be along the line of improving yields and reducing operating costs of the present process.

The following routes were attempted in the hope of finding a more economical preparatory route:

1. Direct coupling of 5-amino salicylic to salicylic. Coupling at all pH's including 30% caustic, in pyridine, at various temperatures, acylating, and metallizing the diazo gave principally decomposed diazo.

2. Attempts to carboxylate para-azo phenol or para-azo phenol carboxylic acid were unsuccessful.

3. Reduction of 5-nitro salicylic acid with zinc and caustic or by catalytic hydrogenation would not stop at the azo but went on to form 5-amino salicylic.

4. Catalytic reduction and zinc caustic reduction of 5-nitro-2-chlor benzoic resulted principally in azo and hydrazo body but this could not be hydrolyzed in satisfactory yield to azo salicylic acid.

5. Nitrosation of salicylic acid followed by reduction with disulfide gave a good yield of 5-amino salicylic but this product would not condense with nitroso salicylic to give azo salicylic or with nitro salicylic to give the azoxy. Catalytic reduction of the copper complex of nitroso salicylic to the azo was unsuccessful.

Patent Situation:

None of the developments covered in this report are considered promising enough to warrant patent investigation.

Plans for Future Work:

Nothing further is planned along the line of alternative routes to this color. Future work will be concerned with examination of the present process to give improved yields or more economical handling, which will probably be carried out in the Dye Works.

Experimental:

1. Direct Coupling

5-Amino-2-hydroxy benzoic acid (DW-Para amino salicylic acid Charge 2) was diazotized regularly and direct coupling attempted at various alkalinities ranging from pH 4.0 to coupling in 30% caustic. Various buffers including sodium acetate, sodium bicarbonate, sodium carbonate, caustic soda, caustic potash, magnesium oxide, calcium hydroxide, ammonia, pyridine, and Solvent P were tried. Pyridine was also used as a solvent for the attempted coupling.

Temperature variations from 0°C to 75°C were tried on both caustic and carbonate buffered couplings.

Various attempts to strengthen or stabilize the diazo were made: 2:7 disulfo naphthalene and maleic acid were introduced in the coupling but did not arrest diazo decomposition. Attempted acetylation of the diazo did not improve coupling speed. 5-amino salicylic acid was both coppered and chromed prior to diazotization but this apparently weakened the diazo instead of strengthening it.

In most of the above cases the amount of Flavine A formed was negligible. In the case of the 30% caustic coupling possibly as much as 10-15% azo salicylic was formed based on capillary tests but it was so contaminated with decomposition products that purification was not feasible. (3648-159, 173)

2. Carboxylation of p-Azo Phenol and p-Azo Phenol mono Carboxylic Acid

Preparation of para azo phenol was attempted by the following routes: 1. p-amino phenol -> phenol; diazo too weak to couple

2. PNA -> phenol, reduced, diazotized, and decomposed in hot (80°C) 10% sulfuric; this gave a good yield (3648-162 = 93.5% theory) with reasonably good analysis (Kjeldahl nitrogen 12.75%, Azo nitrogen by $TiCl_3$ 12.36% theory for para azo phenol 13.98%) but was dark brown in color and was not easily purified further.

3. p-Chlor Aniline -> phenol followed by hydrolysis according to the Flavine A process; 3648-178 gave approximately 30% hydrolysis. This lead was not followed up by more strenuous contitions.

4. Sulfanilic -> phenol + caustic fusion; Literature reports decomposition above 215°; so fusion was tried at 190° without success.

5. Benzene sulfonic ester of p-amino phenol -> phenol, hydrolyzed. When purified this sample (Carson 3735-122) had MP-195°C. - Lit MP-216°C.

Attempts to make para azo phenol monocarboxylic acid by substituting salicylic acid for phenol in methods 2,3,and 5 above gave comparable results. (3648-161, 167 and 3735-121)

Carboxylation experiments (Trepagnier 3706-42,50,60, 63, 65) on the material prepared from PNA and Benzene sulfonic ester of p-amino phenol (methods 2 and 5) indicated that neither para azo phenol or para azo phenol mono carboxylic acid could be carboxylated by the methods tried. Conclusions are based on shade and fastness properties of chromed dyeings on wool vs. the original samples and vs. Pontachrome Flavine A.

3. Reduction of 5-Nitro Salicylic Acid to Azo Salicylic Acid

Schniepp succeeded in separating the 3 and 5 nitro salicylic isomers through the difference in solubility of their potassium salts. On reduction of the 5 isomer with zinc and caustic the product was 5 amino salicylic acid. (3722-154)

Scott attempted the catalytic reduction of the mixed 3 and 5 isomers but got no azo body. His product was the mixed amino salicylic acids.

4. Reduction of 5-Nitro-2-Chlor Benzoic Acid Followed by Hydrolysis of the Chlorine to Give Azo Salicylic Acid

Scott (JLR-43-168, No. 3; Serial Number 18009) was able to reduce this compound catalytically to give principally azo and hydrazo body with some intermediate reduction products and some 5-amino-2-chlor benzoic. However, the hydrolysis did not go well, and a capillary indicated that the mono hydroxy, dihydroxy and dichlor bodies were all present as well as a large amount of brownish color which evidently was decomposed dye. Although he was able to effect improvement, a clean product was never secured.

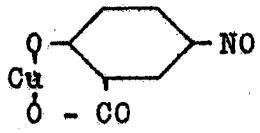
Schniepp was able to get the azo chlor benzoic mixture similar to the above by means of zinc-caustic reduction (3722-155). No hydrolysis was attempted.

This general method for the preparation of Flavine A is the subject of Swiss patent 164,196.

5. Condensation of 5-amino salicylic acid with 5-nitroso Salicylic acid to give Flavine A

This condensation was attempted in glacial acetic, in a mixture of absolute alcohol and glacial acetic, and in monohydrate using both nitroso salicylic and the copper complex of nitroso salicylic. A trace of azo salicylic was obtained in all cases but the method is not attractive. Solubility is too low in the case of the organic solvents and the reaction very slow even at 60°C while the monohydrate chews up the color even in the cold.

The nitroso salicylic was made according to the method of Gulinov (CA 1928) which treats a mixture of sodium nitrite and sodium salicylate at room temperature with copper sulfate. Yields were good 70-75% theory. Analysis showed a purity of 98.2 by copper and 96.4 by Dumas nitrogen as



(3648-172). Reduction of this material with sodium disulfide indicates that it yields principally 5-amino salicylic acid. It was coupled to H acid along with Chg. 2 p-amino salicylic (actually 5 amino) and diazo salicylic. It actually contains less of 3 amino salicylic than Chg. 2 (based on capillary) (3648-168). A $TiCl_3$ value for the color formed was determined in order to know the % theory yield from salicylic to 5-amino salicylic -> H acid. It is 50.6% theory overall. (There was no isolation until the isolation of the final color.)

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ajm
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