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Serial Number 18018

E. I. DuPont de Nemours & Company

Jackson Laboratory

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JLR-38-A, No. 94

New Naphthanils

N40779

JLR-38-A, No. 94 Serial Number 18018

E. I. DuPont de Nemours & Company

Jackson Laboratory

Azo Colors Division

S. S. Rossander

Progress Report

July 20, 1942

New Naphthanils

Group Leader - C. E. Sparks

Work Done By - L. Spiegler
C. E. Sparks

Reported By - C. E. Sparks

Work Started - 12-10-41

Completed - 5-15-42

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New Naphthanils
(Project No. 608)

C. E. Sparks

JLR-38-A, No. 94 Serial Number 18018

Object of the Investigation:

To prepare new 2,3-hydroxy-naphthoyl derivatives of aryl-amines and to evaluate the same in Naphthanil colors.

To prepare arylides of citrazinic acid-mono-butyl-ether and evaluate the same in Naphthanil colors.

To prepare arylides of substituted salicylic acids and evaluate the same in Naphthanil colors.

To prepare an anilide of a substituted salicylic acid which possesses the same apparent oxidation potential as Naphthanil AS and to evaluate the same in Naphthanil colors.

Period Covered by This Report:

December 10, 1941, to May 15, 1942.

Historical Background:

There is considerable need in our line of Naphthanils at the present time for products which possess excellent substantivity and produce bright shades of excellent fastness properties when coupled with our standard Naphthanil bases. It is the policy of the laboratory to prepare 2,3-hydroxy-naphthoyl derivatives of arylamines as they become available with the hope that some coupling component of interest might be obtained.

It has been suggested (letter of M. A. Dahlen to S.S.Rossander, dated 10-10-41) that citrazinic acid derivatives be investigated as Naphthanil coupling components.

It has been suggested that it may be possible to prepare derivatives of arylides of salicylic acid which would be of interest in Naphthanil colors by the introduction of various groups into the salicylic acid ring. It was also suggested that, if the anilide of substituted salicylic acid possessing the same apparent oxidation potential as Naphthanil AS were evaluated, it might show promise in Naphthanil colors.

Summary and Conclusions:

No new arylides of 2-hydroxy-3-naphthoic acid have been obtained which show promise. Naphthol AS-KR Supra (BON of cresidine) is termed of no interest at present for possible addition to our line.

The anilide and dianisidide of citrazinic acid-mono-butyl-ether are of no interest due to poor fastness properties of the combinations with standard Naphthanil bases.

Several arylides of substituted salicylic acid have been prepared and evaluated. None are of interest.

The anilide of 2-hydroxy-4,5-dimethyl-benzoic acid possesses approximately the same apparent oxidation potential as Naphthanil AS. The product upon evaluation with standard Naphthanil bases is of no interest due to poor fastness properties.

Patent Situation:

No products have been prepared during the period covered by this report which show sufficient merit to warrant patent protection.

Plans for Future Work:

We shall continue to prepare 2,3-hydroxy-naphthoyl derivatives of arylamines as they become available in the laboratory.

We plan no additional work on derivatives of citrazinic or salicylic acids as Naphthanil coupling components at this time. When times become normal, the question of preparing additional derivatives of salicylic acid will be reopened.

Experimental Work:

See Jackson Laboratory Notebooks 3628, 3766, 3727, 3853, and 3778.

The 2,3-hydroxy-naphthoyl derivatives reported here were prepared by the conventional methods, using toluene as a solvent, an arylamine and PCl_3 as the condensing agent. The products were purified by isolation in toluene suspension and subsequently redissolving and purifying. The following table summarizes the products prepared and their properties. For details.

as to the preparation of any specific product, please consult the corresponding JLNB. Where fastness tests are reported, they represent average results in couplings with Bordeaux GP, Scarlet 2G, Scarlet R, Orange GC, Blue B, Red B, Red AL, Red RC, Garnet GBC diazos.

TABLE I

JLNB	Mono or di BON of	Purity by Nitrogen	Remarks
3727-120	p-Amino-phenoxy-acetamide		Product of no interest due to extremely poor chlorine fastness. Washing fastness of most combinations inferior to standard.
3778-50	Cresidine		Duplicates the dyeing properties of Naphthol AS-KR Supra. The Tech. Lab. completely evaluated this sample and found it to be of no interest with reference to addition to our line. See JLR-38-X, No. 39 for the identification of Naphthol AS-KR Supra.
3778-61	3-(4-Methyl-sulfone-benzoyl-amino)-aniline	97.4% by sulfur	This product was prepared by the condensation of 4-methyl-sulfone-benzoyl-chloride on the mono BON of meta-phenylene-diamine. The product was found to be inferior in chlorine and light fastness versus Naphthanil BM, the most promising combinations being the same as those found with Naphthanil BM.

It was suggested that several derivatives of salicylic acid be prepared and the anilide and dianisidide of these products be

evaluated as Naphthanil coupling components. A series of these products was prepared by L. Spiegler of the New Products Division and submitted to the Azo Division for evaluation. The general method employed for the preparation of these arylides is graphically represented as follows:

$$3ROH\text{-}COOH + 3RNH_2.HCl + PCl_3 \xrightarrow{\text{toluene}} \text{compounds} + H_3PO_3 + 6HCl.$$

The procedure employed is described in U.S. Patent 1,890,201 (1932) DuPont. After the condensation and removal of solvent by steam distillation, the products are isolated by filtration. The crude products are purified by repeated digestion with dilute sodium carbonate solution and with 2B alcohol. Yields shown are based on the salicylic acid derivatives employed.

The AOP values (apparent oxidation potential) were determined by the Analytical Division from aqueous solutions at a pH of approximately 10-11. The anilide of 2-hydroxy-4,5-dimethylbenzoic acid possesses approximately the same AOP (900) as Naphthanil AS (890). The product upon evaluation with representative Naphthanil Bases shows very poor soaping fastness with the exception of the Scarlet 2G and the Blue B combinations. These combinations, however, were found to be considerably inferior in light fastness versus combinations producible by components on the market. We have been unable to correlate the AOP values and dyeing properties of Naphthanil coupling components. No further work is planned in this connection. The following table summarizes the salicylic acid derivatives prepared and evaluated during this report:

TABLE II

JLNB	Name	Percentage Yield	Purity by Nitrogen Analysis	AOP	Remarks
3628-139	Anilide of 2-hydroxy-5-methylbenzoic acid	90	99	-	Weak brown shades of poor fastness properties with representative Diagen bases and std. Naphthanil Bases. See JLNB 3727-86 and 3778-24.

JLNB	Name	Percentage Yield	Purity by Nitrogen Analysis	AOP	Remarks
3628-143	Anilide of 2-hydroxy-3-methyl-benzoic acid	88	100	-	Very weak prints were obtained in combination with representative Diagen bases. See JLNB 3778-32.
3628-145	Dianisidide of 2-hydroxy-3-methyl-benzoic acid	81	93	-	Very dull and weak prints with representative Diagen bases. See JLNB 3778-32.
3628-147, 151	Anilide of 2-hydroxy-benzoyl-amino-benzoic acid	64	99	-	Weak brown shades were obtained with poor fastness properties with representative Diagen bases. See JLNB 3727-176.
3628-149	Dianisidide of 5-methyl-2-hydroxy-benzoic acid	23	81	-	Sample possesses very poor solubility in the printing paste. Weak brown shades are obtained which were of no interest.
3628-157	Dianisidide of 5-benzoyl-amino-2-hydroxy-benzoic acid	7.5	97	-	Weak brown shades which are of no interest are produced with representative Diagen bases. See JLNB 3727-176.
3628-159	Dianisidide of 5-nitro-2-hydroxy-benzoic acid	69	87	-	Solubility of this sample is extremely poor and could not be printed satisfactorily. Product is a very weak coupler and is of no interest for dyeing. See JLNB 3727-176.

JLNB	Name	Percentage Yield	Purity by Nitrogen Analysis	AOP	Remarks
3628-161	Benzidide of 2-hydroxy-5-methyl-benzoic acid	50	95	-	Weak brown shades are produced with representative Diagen bases. Product is of no interest for dyeing. See JLNB 3727-176.
3628-165	Tolidide of 5-methyl-2-hydroxy benzoic acid	35	94	-	Same as above.
3628-177	5-(4-Nitro-phenyl-azo)-2-hydroxy-benzoic acid	58	93	-	Poor coupling component. Prints obtained were weak and dull with very poor soaping fastness. Dyeings were of no interest because of weakness and poor fastness properties. See JLNB 3778-32.
3628-179	Benzidide of 5-(4-nitro-phenyl-azo)-2-hydroxy-benzoic acid	52	87	-	Product a very poor coupling component and prints and dyeings are weak browns of no interest. See JLNB 3778-32.
3628-191 3766-9	Anilide of 5-chlor-2-hydroxy-benzoic acid	82	98	-	Sample possesses very poor solubility for printing. Dyeings are of no interest due to weakness and poor fastness properties. See JLNB 3778-32.

JLNB	Name	Percentage Yield	Purity by Nitrogen Analysis	AOP	Remarks
3766-3	Benzidide of 5-chloro-hydroxy-benzoic acid	2	100	-	Very poor coupling component. Very weak tints obtained which are of no interest. Dyeings of no interest. JLNB 3778-32.
3766-111	Dianisidide of 2-hydroxy-4,5-dimethyl-benzoic acid	57	90	851	Product shows good coupling properties but weak brown shades of no interest are obtained.
3778-135 3766-113	Anilide of 2-hydroxy-4,5-dimethyl-benzoic acid	69	96	900	Product possesses approximately the same AOP as Naphthanil AS (890). Weak dyeings obtained which possess poor soaping fastness with the exception of Scarlet 2G, and Blue B Bases. These two products are of no interest vs. close approximations from standard combinations, in view of inferior fastness properties.
3766-125	Anilide of 5-methoxy-2-hydroxy-benzoic acid		98	780	Product possesses good coupling properties, but is of no interest due to poor soaping fastness in combination with standard bases. JLNB 3853-22.

JLNB	Name	Percentage Yield	Purity by Nitrogen Analysis	AOP	Remarks
3766-127	Dianisidide of 5-methoxy-2-hydroxy-benzoic acid	58	90	828	Product of no interest due to poor fastness properties in combination with std. bases. JLNB 3853-22.

In the above table under Remarks the phrase, "representative Diagen Bases" includes: Diagen A bases of 4-chloro-2-amino-toluene and 4-chloro-2-amino-anisole, Diagen MG Bases of cresidine and dianisidine and the diazoiminos of Scarlet R and Red B bases with 2-ethylamino-5-sulfo-benzoic acid.

It will be noted from the above table that no products show promise as Naphthanil coupling components being either poor couplers, weak tinctorially or giving dull shades of no interest with inferior fastness properties. No further work in this connection is planned.

In order to prepare the arylides of hydroxy benzoic acids above listed, it was necessary to prepare certain carboxylic acids which were not available at Jackson Laboratory. The following table summarizes these acids:

TABLE III

JLNB	Name	Yield	AOP
3628-141	2-Hydroxy-5-methyl-benzoic acid	80	1042
3628-155, 167	2-Hydroxy-5-chloro-benzoic acid	96	1040
3766-21	2-Hydroxy-4,5-dimethyl-benzoic acid	90	1100
3766-115	2-Hydroxy-5-methoxy-benzoic acid	60	840

Melting points were obtained on the above compounds and found in each case to check with that of the literature with in experimental error. The salicylic acid derivatives listed above were obtained by carbonation of the dry powdered sodium phenolate at 100-170°C. at 500 pounds CO_2 pressure. Yields above are based on the phenolic compounds employed.

AOP Values

The apparent oxidation potentials (AOP) in the two tables listed above were made of aqueous alkaline solutions of pH's between 10 and 11 by the Analytical Division. Comparisons are listed below of AOP values for a number of typical coupling components normally employed for the production of azo colors. Compounds are listed in approximate order of their ease in coupling. Those considered to be the best couplers are at the top of the list.

TABLE IV

Name	AOP (10 to 11) in water
Resorcinol	784
Phenyl methyl pyrazolone	714
β-naphthol	858
β-hydroxy-naphthoic acid	762
Naphthanil AS	890
4-Hydroxy-1,2-dimethyl-benzene	811
ortho-Cresol	833
para-Cresol	857
Phenol	877
para-Chlor-phenol	894
Salicylic acid	1043
ortho-Cresotinic acid	1056

It is noted from the above table that within the same series (benzene or naphthene) the AOP is somewhat of a measure of the coupling speed.

Miscellaneous Coupling Components

The following table summarizes miscellaneous coupling components evaluated during the period covered by this report:

TABLE V

JLNB	Name	Remarks
3778-20-A	N-methyl-triacetone-amine	Prepared by W. S. Struve, JLNB 3607-89-B. Product of no interest due to weak prints obtained.
3778-20-B	Triacetone amine hydrate	Prepared by W. S. Struve, JLNB 3607-88-B. Product of no interest in printing. Weak shades obtained with standard Diagen bases.
3778-86	Dianisidide of citrazinic acid mono-butyl-ether	(Purity 94% by nitrogen analysis). Combinations with standard diazos show poor soaping fastness. Of no interest.
3853-38	Anilide of citrazinic acid mono butyl ether	Purity - 96%. Combinations with standard diazos are of no interest due to poor soaping fastness.
3727-22	2,4,6-Tri-(4-hydroxy-1-naphthyl)-triazine	Prepared by L. J. Conrad, JLNB 3675-5. Product gives dull shades of inferior fastness properties versus Naphthanils in our line.

As noted in the above table, none of the above products are of interest.

The Preparation of Naphthanil AS Without the Use of Phosphorus Trichloride

The New Products Division has synthesized Naphthanil AS without the use of phosphorus trichloride. (See JLR-38-A, No. 93.) The most promising samples were evaluated versus Naphthanil AS in dyeing - these samples were prepared by the reaction of acetanilide and BON in the presence of ortho-dichlor-benzene, by the reaction of BON and acetanilide in the presence of xylidine, and by the reaction of BON, aniline in the presence of acetic acid. These products were found to be essentially equal

to Naphthanil AS in shade and fastness properties when coupled with Naphthanil Scarlet R Base. However, the products showed very poor solubility and required approximately three times the normal amount of alcohol for solution for the preparation of the pads. For this reason the products were considered of no interest. Attempts to improve the solubility of these products by the method employed for the standardization of Naphthanil AS failed.

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fmb
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