

UNITED STATES PATENT OFFICE

2,593,930

PROCESS OF PRINTING FABRICS WITH
ARYL SULFONHYDRAZIDES

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5 Claims. (Cl. 8—71)

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This invention relates to the manufacture of insoluble azo dyestuffs and in particular on the fiber and to the process by which such insoluble azo dyestuffs are printed and developed on the fiber.

The problem of developing azo colors in situ on fabrics and the methods of producing printed designs on textiles have been the subject of considerable study. The earlier attempts to develop azo colors on the fabrics were made by padding an alkaline solution of 2-naphthol on to the cloth and then treating this with a diazotized amine. As many amines are unstable when warm, ice had to be added to the diazo solutions to prevent their decomposition, hence this type of color produced from the reaction of the diazotized amine and the padded coupling component became known as an ice color.

Since the use of ice was obviously undesirable, methods of improvement were sought. It was later discovered that certain compounds such as zinc chloride, naphthalene sulfonic acids, fluoroboric acid and other agents which would form salts of the diazonium chloride would produce stable products which would nevertheless couple with the naphthol coupling components. However, the strong coupling tendency of these diazonium salts precluded mixing them with couplers and it was still necessary to pad the cloth with the naphthol coupler. This class of stabilized diazo components is known as the Fast Color Salts. Other compounds found to be useful for the in situ printing of fabrics with azo colors are the nitrosamines which have gained only limited use due to the lack of brightness and instability of the colors.

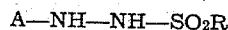
A major step in the development of this art was made by the discovery that diazonium compounds reacted with certain secondary amines to give diazo amino or triazene compounds which were quite stable, but could be hydrolyzed under acidic conditions to the diazo compound. These diazo amino or triazene compounds may be mixed with the coupling component and the mixture printed on the fabric. The color is then developed by exposing the printed fabric to an acid condition, such as moist formic or acetic acid fumes, whereupon hydrolysis of the diazo amino compound and coupling of the diazo compound with the coupling component occurred simultaneously. This method of azo dye printing in situ on the fabric has enjoyed extended use for a number of years, but

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has the disadvantage that the fumes necessary for the development of the color are very corrosive and hence undesirable. It is obvious, therefore, that any method of developing azo dyes on the fabric under neutral conditions or in the absence of corrosive acid fumes would be most desirable.

Accordingly this invention has for its object the provision of preparations which are stable under practical conditions pending and during their application to fabrics from which insoluble azo colors may be developed under neutral conditions, such as air, and air and steam, without the use of acid fumes.

It has been discovered, in the accomplishment of this object, that the 2-aryl sulfonhydrazides when applied in a print paste may be employed for the production of insoluble azo colors on fabrics by a process involving oxidation by air, and steam and air of the aryl sulfonhydrazides in the presence of the coupling component. These aryl sulfonhydrazides may be represented by the formula:



wherein A is an aryl radical such as phenyl, naphthyl, biphenyl and bis-biphenyl and R represents an alkyl or aryl radical. The aryl sulfonhydrazides may be applied to the fabric and the color developed by one of two methods.

1. The fabric is first impregnated with a solution of the coupling component such as a naphthol derivative capable of performing the coupling function. The sulfonhydrazide is then made into a paste and is printed on the thus impregnated fabric. The azo dye color is then developed by immersing the printed fabric into a solution containing mild oxidizing agents and coupling accelerants or by introducing it into an atmosphere of oxygen, or air, air and steam (vat aging), or air and steam under pressure in a vat aging chamber (cottage aging).

2. The sulfonhydrazide, the coupling component and a stabilizing agent may be made into a paste and printed on the textile fabric. The development of the azo dye print is then carried out by one of the methods recited above. In preparing the paste of the sulfonhydrazide and the coupling component sodium sulfite or sodium hydro-sulfite, for example, may be used as stabilizing agents.

The oxidizing agents, i. e. oxygen, air, air and steam, are particularly useful for the develop-

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ment of azo dyes wherein the coupling component is impregnated into the fabric and this is over-printed by a paste containing the sulfonylhydrazide. A typical paste of the sulfonylhydrazide which is adapted for printing on cotton and acetate would contain

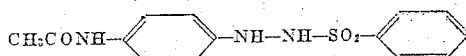
0.25 g. of the sulfonylhydrazide.
4 cc. dimethyl formamide.
4 cc. of water.
22 g. starch tragacanth.

The immersion time in the developing or oxidizing solution is approximately twenty minutes.

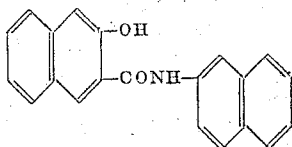
The invention is more fully and specifically illustrated by the following examples:

Example 1

A solution of .25 g. β -(4-acetamidophenyl)-benzenesulfonylhydrazide



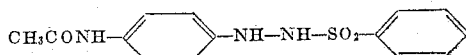
in 4 cc. dimethylformamide was poured into a mixture of 4 cc. water and 22 g. starch tragacanth. The resulting paste was screen printed on textile fabrics which had been impregnated with the sodium salt of naphthyl amide derivative of 2,3-hydroxy naphthoic acid.



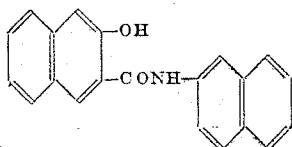
The red azo dye print was developed by introducing the fabric into a chamber containing steam and oxygen for a period of ten to twenty minutes.

Example 2

A solution of 0.2 g. β -(4-acetamidophenyl)-benzenesulfonylhydrazide



in 4 cc. dimethyl formamide was thoroughly mixed into a paste with 0.15 g. of the naphthyl amide derivative of 2,3-hydroxy naphthoic acid

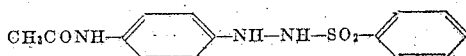


0.7 g. aqueous sodium hydroxide (40° Bé.), 2 cc. water, 0.5 cc. of 10% sodium sulfite and 22.0 g. starch tragacanth. The paste was printed on acetate and cotton fabrics and was developed in the same manner as in Example 1.

The β -(4-acetamido phenyl)-benzene sulfonylhydrazide used in these examples and other typical sulfonylhydrazides which may be substituted therefor are made in accordance with the following procedures:

Example 3

β - (4 - acetamidophenyl) - benzenesulfonylhydrazide



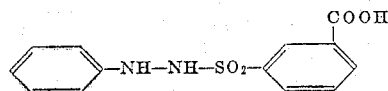
A solution of 15.2 g. (0.05 mole) of 4-acetamidobenzene diazo-(phenyl)-sulfone in 100 cc. dimethyl formamide, 5.8 cc. glacial acetic acid and 5 cc. water was slowly treated with zinc dust until

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the color of the solution had changed from a deep orange to a faint yellow. The temperature was not allowed to rise above 40° C. The zinc salts were removed by filtration and the filtrate was poured into a cold solution of 10 cc. concentrated hydrochloric acid in 1000 cc. water. The sulfonylhydrazide, which precipitated, was removed by filtration, washed well with water and air dried. Yield=11.4 g. (74%).

Example 4

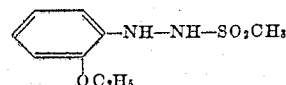
β - (Phenyl) -3-carboxybenzenesulfonylhydrazide



To a solution of 43.0 g. (0.4 mole) phenylhydrazine in 250 cc. ether was slowly added (ice bath) with stirring, 44.3 g. (0.2 mole) 3-chlorosulfonyl benzoic acid in 250 cc. of ether. After the mixture had remained at room temperature for 1 hour, 250 cc. of low boiling petroleum ether was added, and the solid material was removed by filtration and washed with petroleum ether. The product was digested with 1 liter dilute hydrochloric acid to remove the phenylhydrazine hydrochloride, and the residue was recrystallized from dilute ethanol. Yield=44.0 g. (75%); M. P. 178 C. with decomposition.

Example 5

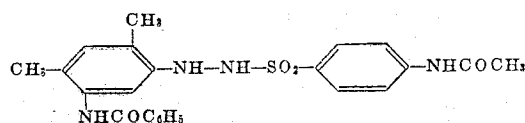
β - (2 - ethoxyphenyl) - methanesulfonylhydrazide



A mixture of 37.0 g. (0.2 mole) of 2-ethoxyphenylhydrazine hydrochloride, 22.9 g. (0.2 mole) methane sulfonyl chloride and 33.6 g. (0.4 mole) sodium bicarbonate in 400 cc. ethyl ether was stirred for 1 hour at room temperature and finally refluxed for 2 hours on a steam bath. The cooled mixture was treated with 400 cc. low boiling petroleum ether, and the precipitated material was removed by filtration and was washed with petroleum ether. The solid was digested twice at room temperature with dilute hydrochloric acid (5 cc. hydrochloric acid in 250 cc. water), and was finally washed with water and air dried. Yield=40 g. (87%) M. P. 105 C.

Example 6

β - (2,4-dimethyl-5-benzamidophenyl) -4-acetamidobenzenesulfonylhydrazide

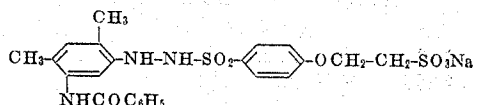


A solution of 3.0 g. (0.00665 mole) of 2,4-dimethyl-5-benzamidodiazot(4 - acetamidophenyl)-sulfone in 25 cc. of dimethyl formamide and 2 cc. glacial acetic acid was treated with zinc dust until the color of the solution had changed from a deep orange to a faint yellow. The zinc salts were removed by filtration, and the filtrate was poured into 100 cc. water. The sulfonylhydrazide was removed by filtration, washed, first with water, finally with 50% ethanol and was dried in a vacuum desiccator over phosphorus pentoxide. Yield=2.8 g. (93%) M. P. 165 with decomposition.

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Example 7

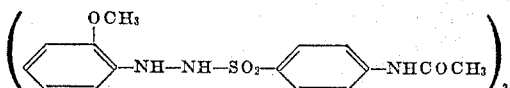
β -(2,4 - dimethyl-5-benzamidophenyl) - 4-(β' -sulfoethoxy) - benzenesulfonylhydrazide (sodium salt)



A solution of 2.1 g. (0.0039 mole) of 2,4-dimethyl - 5 - benzamidobenzene diazo[4 - (β' -sulfoethoxy)-phenyl]-sulfone in 20 cc. of dimethylformamide and 1 cc. glacial acetic acid was treated with sufficient zinc dust to cause the color of the solution to change from an orange to a faint yellow. The zinc salts were removed by filtration, and the filtrate was diluted with 75 cc. acetone and 100 cc. of low boiling ether. The sulfonylhydrazide was removed by filtration and was air dried. Yield=1.7 g. (81%).

Example 8

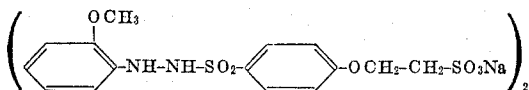
β,β' - Di(4-acetamidobenzenesulfonyl) 3,3' - dimethoxy-4,4'-biphenylene dihydrazine



A solution of 5.0 g. (0.0075 mole) of 3,3'-dimethoxy - 4,4'-biphenyl-bis-diazo[4 - acetamidophenyl]disulfone in 35 cc. dimethyl formamide and 2 cc. glacial acetic acid was reduced in the usual manner with zinc dust. The zinc salts were removed by filtration and the filtrate was poured into 100 cc. water. The sulfonylhydrazide was removed by filtration, washed well with water and dried in a vacuum desiccator over phosphorus pentoxide. Yield=4.1 g. (82%).

Example 9

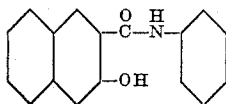
β,β' - Di[4 - (β' -sulfoethoxy)benzenesulfonyl]-3,3'-dimethoxy-4,4'-biphenylenedihydrazine (disodium salt)



A solution of 2.1 g. (0.0025 mole) of 3,3'-dimethoxy-4,4'-biphenylene-bis-diazo[4 - (β' -sulfoethoxy)-phenyl]-disulfone in 2 cc. water, 1 cc. acetic acid and 25 cc. of dimethyl formamide was treated with zinc dust at room temperature until the color of the solution changed from a deep red to a faint orange. The zinc compounds were removed by filtration, and the filtrate was poured into 150 cc. of cold acetone. The bis-sulfonylhydrazide, which separated, was removed by filtration and washed with acetone. Yield=1.3 g. (62%).

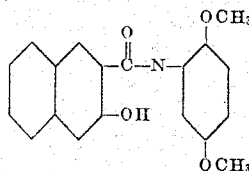
Any coupling component which can be impregnated into the fiber which it is desired to print or which can be incorporated into the printing paste with the sulfonylhydrazide to produce the desired color may be employed in place of the naphthylamide of 2,3-hydroxy naphthoic acid used in Examples 1 and 2. The following are typical of such coupling components:

1. The anilide of 2,3-hydroxy naphthoic acid having the formula—

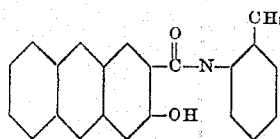


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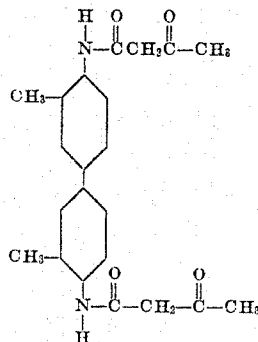
2. 2,5-dimethoxy anilide of 2,3-hydroxy naphthoic acid having the formula—



3. The o-toluidide of 2-hydroxy anthracene-3-carboxylic acid



4. Diacetoacet-o-toluidide having the formula—



Various modifications of our invention will occur to persons skilled in the art and, therefore, we do not intend to be limited in the patent granted except as required by the prior art and the appended claims.

This application is a continuation-in-part of our application Serial Number 66,566, filed December 21, 1948, now abandoned.

We claim:

1. A process of printing and dyeing textile fabrics by developing azo dyes on the fabric which comprises padding the textile fabric with a composition containing a coupling component, printing over with a 2-aryl sulfonylhydrazide dissolved in a print paste, and introducing the padded textile fabric into an atmosphere selected from the class consisting of air and steam and air.

2. A process of printing and dyeing textile fabrics by developing azo dyes on the fabric, which comprises padding the textile fabric with a composition containing an arylamide of 2,3-hydroxynaphthoic acid, printing over with a 2-aryl sulfonylhydrazide dissolved in a print paste, and introducing the padded textile fabric into an atmosphere selected from the class consisting of air and steam and air.

3. A process of printing and dyeing textile fabrics by developing azo dyes on the fabric, which comprises padding the textile fabric with a composition containing an arylamide of 2,3-hydroxynaphthoic acid, printing over with a 2-aryl sulfonylhydrazide dissolved in a print paste, and introducing the padded textile fabric into air.

4. A process of printing and dyeing textile fabrics by developing azo dyes on the fabric which comprises padding the textile fabric with a composition containing an arylamide of 2,3-hydroxy naphthoic acid, printing over with a 2-aryl sulfonylhydrazide dissolved in a print paste and introducing the padded textile fabric into an atmosphere of steam and oxygen.

5. A process of printing and dyeing textile fabrics by developing azo dyes on the fabric, which comprises padding the textile fabric with a composition containing an arylamide of 2,3-hydroxynaphthoic acid, printing over with a 2-aryl sulfonhydrazide dissolved in a print paste, and introducing the padded textile fabric into an atmosphere of oxygen.

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REFERENCES CITED

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