United States Patent Office 3,183,052 Patented May 11, 1965

3,183,052

PROCESS FOR THE CONTINUOUS PRODUCTION OF BROWN WATER-INSOLUBLE AZO-DYESTUFFS ON FABRICS OF VEGETABLE FIBERS

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No Drawing. Filed June 15, 1962, Ser. No. 202,683
Claims priority, application Germany, Oct. 18, 1961, F 35,161
4 Claims. (Cl. 8—46)

For the production of brown water-insoluble azo-dyestuffs by the methods of the ice color technique there are mainly used arylamides of heterocyclic o-hydroxycarboxylic acids in combination with diazonium compounds from primary amines of the benzene series. The arylamides of 3-hydroxy-diphenylene oxide-2-carboxylic acid and 2-hydroxy-carbazole-3-carboxylic acid which permit the production of very fast brown tints are of particular importance. Some products of this series, therefore, are used for some time on an industrial scale for the production of brown dyeings on vegetable fibers, for example 1-(3'-hydroxy-diphenylene oxide-2'-carboylamino)-2.5-dimethoxybenzene (Naphtol AS–BT) or 1-(2' - hydroxy - carbazole - 3' - carboylamino) - 4 - chlorobenzene (Naphtol AS–LB) (cf. K. Venkataraman, The Chemistry of Synthetic Dyes, 1952, volume I, pages 652/653).

The substantivity of these compounds for vegetable fibers is relatively high so that they are very suitable for dyeing rowings, yarns or fabrics at a long goods-to-liquor ratio. However, when piece goods are dyed at a short goods-to-liquor ratio, and especially when a material is continuously dyed on the foulard, these known compounds exhibit disadvantages which make them appropriate only to a limited extent for such a dyeing method. The method of dyeing continuously piece goods on the foulard which is widely applied in the industry, demands that especially the coupling components used must fulfill certain requirements as a prerequisite for their practical application. As one of these requirements, the material treated with the coupling component shall have a high stability during the drying operation following the impregnation, in order to dry the material at a temperature as high as possible thus shortening the drying process. Furthermore, the material treated with the coupling component shall have a good wetting property so that the development with the diazonium compound can be conducted rapidly and the speed of the goods can be kept as high as possible. Furthermore, the coupling energy of the coupling component used shall be high and finally, the developed dyeings shall rapidly attain the final tint, when they are subsequently soaped, requirements which must also be met with regard to a rapid passage of the goods.

The arylamides of 3-hydroxy-diphenylene oxide-2-carboxylic acid and 2-hydroxycarbazole-3-carboxylic acid, Naphtol AS–BT and Naphtol AS–LB, which are known for a long time and used in the industry, only partly fulfill these requirements for continuously producing the dyestuffs on the foulard. The impregnations prepared with these compounds do not possess the necessary stability to temperatures ranging from 150–180° C. as they are lately used in hot air driers. Furthermore, the coupling energy is often insufficient or the production of the final tint requires very much time so that an economical dyeing process is not possible. Finally, the dyeings produced on piece goods with the coupling components hitherto used include the drawback that in many

cases they do not possess a constant tint and are not stable to a processing with synthetic resin finish, for example a finish to give resistance to creasing or a fast embossed print, which processing is conducted at present to a large extent. All these detrimental properties affect considerably an application of these compounds for the continuous dyeing method.

Therefore, the industry is for a long time looking for a process which permits the production of brown water-insoluble azo-dye-stuffs in a continuous procedure by the methods of the ice color technique and excludes the aforementioned disadvantages.

Now we have found that brown, water-insoluble azo-dyestuffs can be produced in a continuous manner on fabrics of vegetable fibers by treating the fabric at a speed of 40 to 90 meters per minute, at a temperature between 65° and 95° C., with the alkaline solution of 1 - (3' - hydroxy - diphenylene oxide - 2' - carboylamino) - 2-ethoxybenzene and drying it at a temperature between 130° and 180° C., then developing the dyestuff at a temperature between 15° and 25° C. and at a pH-value between 4 and 6.5 with the diazonium compound from a primary aromatic amine, passing the material through air for 20–30 seconds, then treating it at a temperature between 20° and 60° C. with an aqueous alkali metal carbonate or bicarbonate solution of 0.5 to 2% strength, rinsing, soaping with a detergent for 30–60 seconds at a temperature between 70 and 90° C. and drying it.

The process of the present invention is carried out in such a manner that fabrics of vegetable fibers, for example of cotton or regenerated cellulose, are padded on a foulard, for example a two- or three-roller foulard having a color box of a volume as small as possible, at a speed of goods of about 50 to 90 meters per minute at about 85° to 95° C., with an alkaline solution of 1-(3'-hydroxy-diphenylene oxide-2'-carboylamino) - 2 - ethoxybenzene, preferably a solution rendered alkaline with sodium hydroxide, then squeezed off to a ratio of liquor of about 60 to 100% and dried at about 130° to 180° C., preferably on a hot air drier. The dyestuff is then developed at a temperature between 15° and 25° C. and a pH-value between 4 and 6.5 on a two- or three-roller foulard with a diazonium compound from a primary aromatic amine. As diazonium compounds there may be used diazonium chlorides, diazonium sulfates, diazonium borofluorides, diazonium chloride-zinc chloride double salts and diazonium naphthalene disulfonates from primary aromatic amines of the benzene, azobenzene and anthracene series, for example diazonium compounds from 1-amino-2-methyl-5-nitrobenzene, 1-amino-2,5-dichlorobenzene, 1-amino-2-chloro-5-methoxy-4-benzoylamino-benzene, 1-amino-3,5 - bis-trifluoromethylbenzene, 1 - amino - 4 - chloro - 2 - trifluoromethylbenzene, 1-amino - 2 - chloro - 5 - trifluoromethylbenzene, 1 - amino-2-chlorobenzene, 1-amino-4-nitrobenzene, 1-amino-2-methoxy-4-nitrobenzene, 1-amino-2-methyl-4-chlorobenzene, 1 - amino - 2 - methyl - 5 - chlorobenzene, 1 - amino-2-methyl-3-chlorobenzene, 1-amino-2-methoxy-benzene-5-sulfonic acid-n-butylamide, 1-amino-2-methoxybenzene-5-sulfonic acid diethylamide, 1-amino-2,4-dimethyl-5-benzoylaminobenzene, 2-amino-4-chloro-diphenyl ether, 2-amino-4,4'-dichlorodiphenyl ether or 1-aminoanthraquinone.

When the development with the diazonium compound is complete, the material is passed for about 20 to 30 seconds through air and then after-treated at 20° to 60° C. with an aqueous alkali metal carbonate or bicarbonate solution containing, per liter of water, about 5 to 20 grams of an alkali metal carbonate or bicarbonate, for example sodium carbonate or sodium bicarbonate, in order to complete the coupling. The material is then

rinsed hot and cold and soaped for 30 to 60 seconds, at a temperature between 70° and 90° C., on a full width washing machine with a washing or dispersing agent, for example soap or a fatty alcohol polyglycol ether, an alkylphenol polyglycol ether or an alkylnaphthol polyglycol ether and a small amount of sodium carbonate, whereby the tint is not or only slightly changed. The material is then rinsed and dried.

The process of this invention avoids the disadvantages hitherto involved with the use of the commercial coupling components. When 1-(3'-hydroxy-diphenylene oxide-2'-carboylamino)-2-ethoxybenzene is used as coupling component, impregnations can be prepared which are very stable during drying and possess a very good wetting capacity. Moreover, the dyeings attain very rapidly the final tint when they are soaped so that the process can be carried out at a very high speed of goods.

The brown, khaki and olive dyeings obtainable by this invention possess a very constant tint and very good properties of fastness; particularly even the light tints possess a good fastness to light. The dyeings are dischargeable to a white and are, therefore, very suitable in the textile printing for the production of discharge grounds. Furthermore, they are resistant to a further processing and, therefore, the material provided with these dyeings can be easily given a resistance to creasing.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

Example 1

A mercerized cotton fabric was padded at 90° C. on the foulard at a speed of goods of 45 meters per minute, with the solution described below and squeezed off to a ratio of liquor of 60%.

3.2 grams of 1-(3'-hydroxy-diphenylene oxide-2'-carboylamino)-2-ethoxybenzene, dissolved in 6.4 cc. of denatured ethyl alcohol, 9.5 cc. of water and 1.6 cc. of sodium hydroxide solution of 32.5% strength were stirred into a solution containing, per liter of water, 3 grams of a condensation product of fatty acids of high molecular weight and protein degradation products, and 10 cc. of sodium hydroxide solution of 32.5% strength. The material was then dried on a hot air drier at 165° to 175° C. and the dyestuff was developed at 20° C. with a diazo solution containing, per liter of water, the diazonium compound from 2.5 grams of 1-amino-3,5-bis-trifluoromethylbenzene and 2 grams of the reaction product from about 20 mols of ethylene oxide and 1 mol of octadecyl alcohol, and 7.5 cc. of acetic acid of 50% strength and having a pH-value of about 4. After an air passage for 30 seconds, the material was treated at 60° C. with a solution containing 10 grams of sodium bicarbonate per liter of water, rinsed, soaped for 30 seconds at 90° C. with a solution containing, per liter of water, 1 gram of a reaction product from 10 mols of ethylene oxide and 1 mol of isododecyl phenol and 3 grams of sodium carbonate, rinsed again and dried.

A yellowish brown dyeing was obtained.

Example 2

Mercerized cotton sateen was padded at 95° C. on the foulard, at a speed of goods of 50 meters per minute, with the solution described below and squeezed off.

7.46 kilograms of 2-(3'-hydroxy-diphenylene oxide-2'-carboylamino)-2-ethoxybenzene were made into a paste with 1.81 kilograms of Monopole Brilliant Oil, mixed with 14.2 liters of sodium hydroxide solution of 38° Bé. and made up with hot water to 1000 liters.

The material was then dried at 165° to 180° C. on the hot flue and the dyestuff was developed at 20° C. with a diazo solution containing in 380 liters of water 13.6 kilograms of the diazonium compound from 1-amino-2-methyl-4-benzoylamino-5-chlorobenzene, 3.62 kilograms

of a reaction product from about 20 mols of ethylene oxide and 1 mol of octadecyl alcohol and 7.26 kilograms of acetic acid of 50% strength and having a pH-value of about 4.5. After an air passage for 30 seconds. the material was treated with a solution containing 4.5 kilograms of sodium carbonate in 378 liters of water, rinsed with water at 70° C., soaped for 50 seconds at 90° C. with a solution containing per liter of water 1 gram of a reaction product from 10 mols of ethylene oxide and 1 mol of isododecyl phenol, rinsed hot and dried.

A yellowish brown dyeing was obtained.

The following table indicates a number of further water-in-soluble azo-dyestuffs which were produced by this invention on fabrics of vegetable fibers by using the same coupling component and other diazo components, and also the tints of the dyeings.

Diazo component	Tint
1-amino-4-chloro-2-trifluoromethylbenzene	Yellowish orange brown.
1-amino-2-chloro-5-trifluoromethylbenzene	Yellowish krown.
1-amino-2-chlorobenzene	Do.
1-amino-4-nitrobenzene	Bluish brown.
1-amino-2-methoxy-4-nitrobenzene	Do.
1-amino-2-methyl-4-chlorobenzene	Yellowish brown.
1-amino-2-methyl-5-chlorobenzene	Do.
1-amino-2-methyl-3-chlorobenzene	Do.
1-amino-2-methoxybenzene-5-sulfonic acid-n-butylamide.	Bluish brown.
1-amino-2-methoxybenzene-5-sulfonic acid-diethylamide.	Do.
1-amino-2,4-dimethyl-5-benzoylaminobenzene	Yellowish brown.
2-amino-4-chlorodiphenyl ether	Do.
2-amino-4,4'-dichlorodiphenyl ether	Do.
1-aminoanthraquinone	Reddish brown.

We claim:

1. Process for the continuous production of brown, water-insoluble azo-dyestuffs on fabrics of vegetable fibers which comprises treating the fabric at a speed of goods of 40 to 90 meters per minute, at a temperature between 65° and 95° C., with an alkaline solution of 1-(3'-hydroxy-diphenylene oxide-2'-carboylamino)-2-ethoxybenzene and drying it at a temperature between 130° and 180° C., then developing the dyestuff in the fabric at a temperature between 15° and 25° C. and at a pH between 4 and 6.5 with a diazonium compound of a primary aromatic amine, passing the fabric through air for 20 to 30 seconds, then treating it at a temperature between 20° and 60° C. with an aqueous solution of 0.5 to 2% strength of an alkali selected from the group consisting of alkali-metal carbonates and alkali-metal bicarbonates, and subjecting it to rinsing, soaping with a detergent for 30 to 60 seconds at a temperature between 70° and 90° C. and drying.

2. A process as defined in claim 1 in which the alkali is sodium carbonate.

3. A process as defined in claim 1 in which the alkali is sodium bicarbonate.

4. A process as defined in claim 1 in which the detergent is a reaction product of ethylene oxide on isododecylphenol.

References Cited by the Examiner

UNITED STATES PATENTS

2,032,463	3/36	Bergdolt et al.	8—46
2,845,326	7/58	Streck	8—46
3,029,122	4/62	Posselt et al.	8—46

OTHER REFERENCES

Venkataraman: The Chemistry of Synthetic Dyes, vol. 1, pp. 652, 653, 658, and 668–672.

Colour Index, vol. 2, 2nd ed., 1956, The Soc. of Dyers and Colourists, pp. 2569–2570.

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