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PROCESS FOR THE PRODUCTION OF WATER-INSOLUBLE AZO DYESTUFFS ON TEXTILE MATERIAL OF CELLULOSE OR PROTEIN FIBERS

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ABSTRACT OF THE DISCLOSURE

Process for the production of water-insoluble azo dyestuffs on textile material of cellulose or protein fibers by impregnation with a substantive azo component and developing with a diazonium compound of an aromatic amine, wherein the developing stage is carried out by adding the diazonium compound as well as alkali binding agents to the impregnation bath in the presence of a wetting or dispersing agent.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation of application Ser. No. 728,899, filed May 14, 1968, now abandoned.

The present invention relates to a process for the production of water-insoluble azo dyestuffs on textile material of cellulose or protein fibers.

When producing water-insoluble azo dyestuffs on textile material of cellulose or protein fibers according to the ice-color technique there are used, for dyeing the material from a long goods-to-liquor ratio, azo components having a high substantivity which are absorbed, in the course of the so-called impregnation, from the highly alkaline impregnation bath by the material to be dyed, and then coupled in a second, weakly acid bath, the so-called developing bath, with the diazonium compounds from aromatic amines. Before being introduced with the impregnated material into the developing bath, the residual azo component which has not been absorbed by the material to be dyed is substantially removed to prevent as far as possible the formation of dyestuff outside the fiber. The dyestuff which is formed outside the fiber in the developing bath partly deposits mechanically on the fiber so that dyeings are obtained having a poor fastness to rubbing.

Various methods are used to remove the excess azo component which has not been absorbed by the fiber:

(1) discharging the impregnation baths and allowing the fabric to drain off,
(2) intermediate rinsing of the impregnated fabric with an alkaline, salt-containing solution,
(3) squeezing out the impregnated fabric,
(4) centrifuging the impregnated fabric, or

(5) drying the impregnated fabric, wherein the residual adhering azo component is absorbed by the fiber.

The more completely the adhering impregnation liquor is removed, the better is the fastness to rubbing obtained (cf. H. Herzog in "Textilveredelung" 1, page 52 (1966)).

The production of water-insoluble azo dyestuffs on the fiber according to the ice color technique which has been described in detail in "Manual for the Dyeing with Naphtol AS Products," published by Farbwerke Hoechst A.G. (Hoe. 2275), on pp. 28 through 80, comprises four stages:

(I) impregnation with the azo component in a bath alkaline with soda,
(II) removal of the residual azo component which has not been absorbed by the fiber,
(III) developing with the diazonium compound, and
(IV) after-treatment.

To render the dyeing process more economic, there has existed for a long time a demand for reducing the number of working stages.

Now we have found that the production of water-insoluble azo dyestuffs on textile material of cellulose or protein fibers by impregnating the textile material with a substantive azo component and developing with a diazonium compound of an aromatic amine can be simplified essentially by carrying out the developing stage by adding the diazonium compound as well as alkali binding agents to the impregnation bath in the presence of a wetting or dispersing agent.

The process of the invention is carried out by treating the textile material in the form of yarn in hanks, wound bodies, combed or loose material, woven or knitted fabrics in an alkaline bath containing an azo component having a high substantivity, an excess amount of alkali, a wetting or dispersing agent or a mixture of dispersing agents and, if resired, an inorganic salt, for example sodium chloride, sodium sulfate or trisodium phosphate. The treatment is carried out for at least 10 to 20 minutes so that the azo component can be sufficiently and uniformly fixed on the textile material. Generally, this operation is carried out at room temperature or at a slightly elevated temperature, suitably at a temperature below 35° C. If a material is to be treated that can be dyed through with difficulty only, it is possible to start with a temperature near boiling temperature of the bath and to allow the temperature to descend to approximately 20° to 30° C.

As azo components in the process of the present invention compounds may be used which are distinguished by a high substantivity for the textile material used, i.e. azo components which, at a goods-to-liquor ratio of 1:20, an impregnating period of 30 minutes at 30° C., a concentration of 1 gram per liter of water without the addition of a salt and an excess of 4.5 grams of sodium hydroxide per liter of bath, possess such high substantivity that at least 9 grams are absorbed by 1 kilogram of the material to be dyed. Suitable compounds are, for example, 2,3 - hydroxynaphthoylaminobenzenes, e.g. 1 - (2′,3′ - hydroxynaphthoylamino)-2,5-dimethoxy - 4 - chlorobenzene or 1-(2′,3′-hydroxynaphthoylamino)-2-methoxy-4-chloro-

5-methylbenzene, 6-bromo- or 6-methoxy-2,3-hydroxynaphthoic acid arylamides, e.g. 1-(6′-bromo-2′,3′-hydroxynaphthoylamino)-2-methoxybenzene, 6-methoxy-2,3-hydroxynaphthoic acid anilide or 1-(6′-methoxy-2′,3′-hydroxynaphthoylamino)-2,4-dimethoxy-5-chlorobenzene, condensation products of 2,3-hydroxynaphthoic acid and poly-nuclear isocyclic or heterocyclic amines, e.g. 2-(2′,3′-hydroxynaphthoylamino)-naphthalene, 2-(2′,3′-hydroxynaphthoylamino)-carbazole, 2-(2′,3′-hydroxynaphthoylamino)-3-methoxydiphenyleneoxide, 6-(2′,3′-hydroxynaphthoylamino)-benzimidazole, 6-(2′,3′-hydroxynaphthoylamino)-indazole, 5-(2′,3′-hydroxynaphthoylamino)-2-methylbenzthiazole or 4-(2′,3′-hydroxynaphthoylamino)-diphenyl and its substitution products, 4,4′-bis-(2″,3″-hydroxynaphthoylamino)-diphenyl and its substitution products, e.g. 4,4′-bis-(2″,3″-hydroxynaphthoylamino)-3,3′-dimethoxydiphenyl, 1,4-bis-(2″,3″-hydroxynaphthoylamino)-benzene and its substitution products, 4,4′-bis-(2″,3″-hydroxynaphthoylamino)-stilbene, 4,4′-bis-(2″,3″-hydroxynaphthoylamino)-azobenzene and its substitution products, 4,4′-bis-(2″,3″-hydroxynaphthoylamino)-diphenylurea, 2-hydroxyanthracene-3-carboxylic acid arylamides, e.g. 1-(2′-hydroxyanthracene-3′-carboylamino)-2-methylbenzene, 2-hydroxycarbazole-3-carboxylic acid arylamides, e.g. 1-(2′-hydroxycarbazole-3′-carboylamino)-4-chlorobenzene, 5-hydroxy-1,2,1′,2′-benzocarbazole-4-carboxylic acid arylamides, e.g. 1-(5′-hydroxy-1′,2′,1″,2″-benzocarbazole-4′-carboylamino)-4-methoxybenzene or 1-(5′-hydroxy-1′,2′,1″,2″-benzocarbazole-4′-carboylamino)-2-methyl-4-methoxybenzene; or terephthaloyl-bis-acetic acid arylamides, e.g. terephthaloyl-bis-(1-acetylamino-2,4-dimethoxy-5-chlorobenzene) or terephthaloyl-bis-(1-acetylamino-2-methoxy-4-chloro-5-methylbenzene).

When using textile material by which the substantive azo components are more completely absorbed than by cotton, for example textile material of viscose staple fibers or mercerized cotton, there may be used as azo components also 1-(2′,3′-hydroxynaphthoylamino)-naphthalene, 1-(2′,3′-hydroxynaphthoylamino)-2-methyl-4-chlorobenzene, 1-(2′,3′-hydroxynaphthoylamino)-2,4-dimethoxy-5-chlorobenzene or 1-(2′,3′-hydroxynaphthoylamino)-2-methoxy-5-chlorobenzene.

As wetting or dispersing agents the compounds commonly used in the ice-color technique enter into consideration, for example condensation products of high molecular weight fatty acids and protein decomposition products, condensation products of high molecular weight fatty acids and aminoalkyl-sulfonic acids, condensation products of formaldehyde with naphthalene-sulfonic acids or purified sulfite cellulose waste liquor, or mixtures of these compounds. Moreover, they may still be added further highly effective wetting agents, for example alkylaryl sulfonates.

After the azo component has substantially been absorbed and levelled on the material, from the alkaline bath containing a wetting or dispersing agent, the diazonium compound and the alkali binding agent, in the form of an aqueous solution concentrated in a higher or lesser degree, are added to the impregnation bath, and the treatment is continued. As diazonium compounds particularly those from aromatic mono- and diamines enter into consideration, for example those from monochloranilines and dichloranilines, toluidines, chlorotoluidines, chloranisidines, phenetidines, nitranilines, nitrotoluidines, nitroanisidines, nitroxylidines, nitrophenetidines, cyanotoluidines, cyanoanisidines, aminobenzene-sulfonic acid amides, aminophenyl-alkyl-sulfones, aminobenzene carboxylic acid amides, aminodiphenyl ethers, monoacylated phenylenediamines, amino-azobenzenes, benzidine, dianisidine and toluidine as well as from heterocyclic amines, e.g. aminocarbazoles.

As alkali binding agents which are added to the impregnation bath together with the diazonium compound and which serve to neutralize the excess amount of alkali, there may be used inorganic acids, for example hydrochloric acid, sulfuric acid or phosphoric acid, organic acids, for example acettic acid or formic acid, or acid alkali metal salts, for example mono-sodium phosphate and acid sodium sulfate. The aqueous solution containing the diazonium compound and the alkali binding agent, may additionally contain further dispersing agents. These dispersing agents promote the fine division of the dyestuff pigment which is formed when stirring the diazo solution into the impregnation bath. There may be used with special advantage condensation products of high molecular weight fatty acids and aminoalkyl sulfonic acids, condensation products of formaldehyde with naphthalene-sulfonic acids and purified sulfite cellulose waste liquor.

The amount to be used of the diazonium compound capable of coupling depends on the amount applied of the azo component. The diazonium compound is advantageously applied in an amount which exceeds the stoichiometric proportion, i.e. approx. 30 to 200 percent, calculated on the azo component.

The alkali binding agents which are simultaneously added together with the diazonium compound are used in such an amount that in the bath a pH-value of approximately 3 to 8, preferably approximately 4.5 to 6.5 is attained.

After the dyestuff has been formed on the textile material, the dyeing liquor is allowed to act upon the material for a further 10 to 30 minutes to assure complete coupling and penetration of the material to be dyed. The material is then rinsed, washed with effective dispersing agents, and the dyeing is finished in the usual manner. Full dyeings are obtained which possess an unexpectedly good fastness to rubbing.

The process of the present invention can be applied to textile material of natural or regenerated cellulose, cyanoethylated cellulose, wool, natural silk or regenerated protein fibers. As compared with the usual methods for dyeing textile materials made of cellulose or protein fibers at a long goods-to-liquor ratio according to the ice-color technique, the process of the present invention is distinguished in that working stage II (removal of the residual azo component not absorbed on the fiber) is omitted and for working stage III (developing with the diazonium compound) the preparation of a fresh developing bath is no longer necessary.

When working according to the process of the present invention, the dyeing period and expenditure of work are substantially reduced. Therefore, the present process constitutes a considerable advance in the art.

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

EXAMPLE 1

1 kilogram of cotton hank was treated in a bath of 25° C. containing, in 20 liters of soft water, 40 grams of purified sulfite cellulose waste liquor, 10 grams of the sodium salt of ethylenediamine-tetracetic acid and 149 cc. of sodium hydroxide solution of 32.5% strength as well as 26 grams of 1-(2′,3′-hydroxynaphthoylamino)-2,5-dimethoxy-4-chlorobenzene, dissolved in 39 cc. of denatured alcohol, 11 cc. of sodium hydroxide solution of 32.5% strength, 52 cc. of water of 40° C. and 20 cc. of formaldehyde of 33% strength. After 30 minutes, the solution of a diazonium salt prepared from 20.6 grams of 1-amino-2-methyl-5-chlorobenzene and 10 grams of a condensation product of oleic acid and methyl-taurine in 300 cc. of acetic acid of 50% strength was introduced into the impregnation bath, whereby a pH of 5–6 was attained in the bath and the dyestuff was formed on the textile material. Then the treatment of the material was continued at 25° C. for a further 20 minutes, and after having rinsed with water, the dyeing was treated for 15 minutes in a fresh bath of 60° C. with 1 gram/liter of a reaction product of approximately 10 moles of ethylene oxide per 1 mol of nonylphenol, 1 gram/liter of the sodium salt of ethyl-

enediamine-tetracetic acid and 1 gram/liter of calcined sodium carbonate. Subsequently, the goods were boiled for 15 minutes with a liquor containing 1 gram/liter of a condensation product of oleic acid and methyl-taurine and 1 gram/liter of sodium carbonate, rinsed and dried.

The after-treatment can also be carried out with the addition of 3 grams/liter of a mixture of 63% of perchloroethylene, 17% of a reaction product of 10 moles of ethylene oxide per 1 mol of nonyl phenol and 20% of isopropanol.

A full red dyeing was obtained having good properties of fastness.

In the above example, there may be used instead of 1-(2',3'-hydroxynaphthoylamino) - 2,5-dimethoxy-4-chlorobenzene also 2-(2',3'-hydroxynaphthoylamino)-naphthalene, 1-(2',3'-hydroxynaphthoylamino) - 2 - methoxy-4-chloro - 5 - methyl-benzene or 1-(6'-methoxy-2',3'-hydroxynaphthoylamino) - 2,4-dimethoxy-5-chlorobenzene, and instead of the diazonium compound of 1-amino-2-methyl-5-chlorobenzene the diazonium compounds of 1-amino-3-chlorobenzene, 1-amino-2,5-dichlorobenzene, 1-amino-2-methoxy-5-chlorobenzene, 1-amino-2-ethoxybenzene, 1-amino-4-nitrobenzene, 1-amino-2-methoxy-4-nitrobenzene, 1-amino-2-methoxybenzene-5-sulfonic acid diethylamide, 1-amino-2-methylbenzene-5-sulfonic acid dimethylamide, 1-amino-2-(4'-chlorophenoxy)-5-chlorobenzene or o-amino-azotoluene, in which cases there were likewise obtained full red to claret dyeings having good properties of fastness.

As compared with the customary dyeing process involving impregnation with the azo component, intermediate rinsing and developing with a diazonium compound in a separate developping bath, considerable time is saved.

EXAMPLE 2

A cross-wound bobbin of 500 grams of cotton yarn was treated in a dyeing machine having a capacity of approximately 6 liters and in which the direction of circulation of the bath was being changed, with a solution of 20° C. containing, in 6 liters of water, 12 grams of purified sulfite cellulose waste liquor, 3 grams of a condensation product of oleic acid and methyl-taurine and 42 cc. of sodium hydroxide solution of 32.5% strength, as well as 12 grams of 2 - (2',3'-hydroxynaphthoylamino)-3-methoxy-diphenyleneoxide, dissolved in 24 cc. of denatured alcohol and 6 cc. of sodium hydroxide solution of 32.5% strength. After approximately 15 minutes, a solution of 60 grams of sodium chloride was added and the treatment of the yarn was continued for a further 15 minutes. Then the aqueous solution of a diazonium salt prepared from 9.5 grams of 1-amino-2-methyl-4-nitrobenzene was added to the impregnation bath together with 192 grams of mono-sodium phosphate$\cdot 2H_2O$, whereby a pH of approximately 6 was attained in the bath and the dyestuff was formed on the yarn. For completion of the dyeing the bath was allowed to circulate for a further 20 minutes at 20° C., the liquor was discharged and then the dyed yarn was rinsed and treated as described in Example 1. Subsesuently, the yarn was rinsed again and dried. A claret dyeing was obtained having good properties of fastness.

In the above example, there may be used as an alkali binding agent, instead of 192 grams of mono-sodium phosphate, a mixture of 26 cc. of hydrochloric acid of 32% strength and 45 cc. of acetic acid of 50% strength.

EXAMPLE 3

1 kilogram of natural silk was treated, at a goods-to-liquor ratio of 1:20, in a bath of 25° C. containing, in 20 liters of soft water, 10 grams of a condensation product of oleic acid and methyl-taurine, 40 grams of a dispersing agent containing 16 percent of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α-ethylhexyl-chlorocarbonic acid ester and sodium α-ethylhexyl-taurate, and 45% cc. of sodium hydroxide solution of 32.5% strength as well as 30 grams of 1-(2',3'-hydroxynaphthoylamino)-2-methyl-4-chlorobenzene dissolved in 45 cc. of denatured alcohol, 15 cc. of sodium hydroxide solution of 32.5% strength, 60 cc. water of 40° C. and 30 cc. of formaldehyde of 33% strength. After 15 minutes, a solution of 400 grams of sodium chloride was introduced into the bath and treatment of the silk was continued for a further 15 minutes. Then an aqueous solution of a diazonium salt prepared from 20 grams of 1-amino-2-methyl-4-chlorobenzene and 240 grams mono-sodium phosphate$\cdot 2H_2O$ was introduced into the impregnation bath, whereby a pH of almost 6 was attained in the bath and the dyestuff was formed on the silk. For completion of the dyeing the bath was allowed to circulate for a further 40 minutes, the liquor was discharged and then the silk was rinsed and washed for 15 minutes with a liquor of 60° C. containing 1 gram/liter of a condensation product of oleic acid and methyl-taurine. Subsequently, the dyed silk was again rinsed and dried. A full red dyeing was obtained having good properties of fastness.

Wool instead of natural silk could be dyed in the same manner.

EXAMPLE 4

1 kilogram of viscose staple fiber was treated, at a goods-to-liquor ratio of 1:20, in a bath of 25° C. containing, in 20 liters of soft water, 10 grams of a condensation product of oleic acid and methyl-taurine, 40 grams of purified sulfite cellulose waste liquor and 74 cc. of sodium hydroxide solution of 32.5% strength as well as 12 grams of 1-(2',3'-hydroxy-naphthoylamino)-naphthalene, dissolved in 18 cc. of denatured alcohol, 6 cc. of sodium hydroxide solution of 32.5% strength, 18 cc. of water and 12 cc. of formaldehyde of 33% strength. After 15 minutes, a solution of 400 grams sodium chloride was added to the bath and the treatment of the viscose staple fiber was continued for a further 15 minutes. Then the solution of a diazonium salt prepared from 12.8 grams of 1-amino-2-methoxy-4-nitrobenzene in 24 cc. of formic acid of 85% strength and 75 cc. of acetic acid of 50% strength was introduced into the bath, whereby a pH of approximately 5 was attained in the bath and the dyestuff was formed on the fiber. For completion of the dyeing the goods were treated in the bath having a temperature of 20° to 30° C. for a further 20 minutes, then the dye liquor was discharged and the dyeing was finished as described in Example 1. A red dyeing was obtained having good properties of fastness.

In the above example, there may also be used instead of 1-(2',3'-hydroxynaphthoylamino) - naphthalene with the same good result 1-(2',3'-hydroxynaphthoylamino)-2-methoxy-5-chlorobenzene, 1-(2',3' - hydroxynaphthoylamino)-2-methyl-4-chlorobenzene, 6-methoxy - 2,3 - hydroxynaphthoic acid anilide or 1-(2',3'-hydroxynaphthoylamino)-2,4-dimethoxy-5-chlorobenzene.

We claim:

1. In the process for the production of water-insoluble azo dyestuffs on cellulose and protein textile materials wherein the textile material is first impregnated with an azo component selected from the group consisting of arylamides of aromatic orthohydroxy carboxylic acids, arylamides of heterocyclic ortho-hydroxy carboxylic acids, arylamides of acylacetic acids and arylamides of terephthaloyl - bis - acetic acid and thereafter the dyestuff is developed on the textile material with a diazonium compound of an aromatic or heterocyclic mono- or diamine, the improvement which consists of impregnating the textile material with an alkaline impregnation bath, said bath containing the azo component and a wetting or dispersing agent so that the azo component is substantially absorbed and levelled on the textile material and then developing the dyestuff on the textile material, without intermediate drying of the textile material, in the same bath which still contains the wetting or dispers-

ing agent, by adding to the bath the diazonium compound and an alkali binding agent.

2. The process as claimed in claim **1**, wherein the alkali binding agent is an inorganic or organic acid, an acid alkali metal salt or mixtures thereof.

3. The process as claimed in claim **1**, wherein the alkali binding agents are added in such an amount that a pH of 3 to 8 is obtained in the bath.

4. The process as claimed in claim **3** wherein the pH obtained is 4.5 to 6.5.

5. The process as claimed in claim **1** wherein in addition to the diazonium compound and alkali binding agent, a wetting or dispersing agent is added to the bath to develop the dyestuff.

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