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

Werner Kirst and Hasso Hertel, Offenbach am Main, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft, Germany; assignors to Hoechst Aktiengesellschaft, Frankfurt am Main, Germany, a corporation of Germany

No Drawing. Continuation of application Ser. No. 360,779, Apr. 17, 1964. This application Oct. 18, 1968, Ser. No. 768,964
Claims priority, application Germany, Apr. 24, 1963, F 39,573

Int. Cl. C09b 29/02

2 Claims

ABSTRACT OF THE DISCLOSURE

Production of water insoluble azo-dyestuffs on cellulose or protein textile materials by treating the textile material in an alkaline bath containing a coupling component, an antiaziotate and a wetting or dispersing agent to fix the coupling component and thereafter contacting the textile material with an acid at a temperature below 40°C to produce the dyestuff on the textile material.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation of application Ser. No. 360,779, filed Apr. 17, 1964, now abandoned.

It has been known that alylamides of 2,3-hydroxynaphthoic acid in the form of their alkali metal salts can be printed on cellulose fibers together with antiaziotates from aromatic amines, they are then dried, and the dyestuff can be developed by a hot acid-salt passage or by exposing the treated material to air. It has already been proposed to pad cellulose fabrics with mixtures from alkali metal salts of 2,3-hydroxynaphthoic acid alylamides and antiaziotates, to dry them and to cause the coupling by a treatment with acid-salt solutions. These known processes, according to which in most cases azo components having a low substantivity are used, comprise a treatment of the fabric by printing or impregnating, subsequent intermediate drying and developing by means of acid or by exposing the treated material to air. Thus, three working stages, among them a drying process, are necessary for producing a dyeing.

It has now been found that the production of water-insoluble azo-dyestuffs on textile material of cellulose fibers or protein fibers can be simplified essentially by treating the textile material in an alkaline bath which contains an azo component, an antiaziotate and a wetting or dispersing agent and, if desired, an inorganic salt, and by causing the production of the dyestuff by a treatment with acid agents below 40°C.

The process of the invention is carried out by treating the textile material in the form of yarn in banks, wound bodies, combed or loose material in an alkaline bath which contains an azo component having a high substantivity, an antiaziotate and a wetting or dispersing agent and, if desired, an inorganic salt, for example sodium chloride or sodium sulfate. The treatment is carried out in the course of at least 10 minutes so that the azo component can be fixed sufficiently and uniformly on the textile material. In order to avoid a decomposition of the antiaziotate, it is advantageous to operate at a room temperature or at a moderately elevated temperature, preferably below 35°C. After the azo component has been absorbed and leveled on the material, an organic acid, for example formic acid, acetic acid, tartaric acid, citric acid, lactic acid or glycolic acid or a mixture of said acids or even a mixture of an inorganic acid, for example hydrochloric acid or sulfuric acid with an organic acid is added to the bath in such a quantity that the total quantity of alkali metal ions in the bath is not in excess of 2 moles on the textile material and a pH value between about 4 and 7 is attained, the temperature being below 40°C. In this stage the dyestuff is produced on the textile material. The treated material is then washed in a neutral or acid bath, if desired in the presence of dispersing agents, and the drying is finished in the usual manner. Dyeings are obtained which possess an excellent fastness to rubbing. Piecegoods can be dyed by impregnating the goods on a padding machine with two or several rollers with a mixture of the azo component and an excess of antiaziotate, and rolling them up, and after a retention period of 30 minutes for example, the coupling is caused by passing the treated goods through an organic acid, a mixture of organic acids or a mixture of organic and inorganic acids at a temperature below 40°C. This process can also be performed by a passage through a compartment of a roller vat or by several passages on a jigger or on a winch vat, whereby additions of inorganic salts and dispersing agents sometimes show an excellent effect in the impregnating and developing stage. Corresponding to the additional affinity of the azo component, the concentration of the azo component in the initial bath must be lowered in comparison with that of the feeding bath, whereas the concentration of the antiaziotate in the initial bath is not lowered in comparison with that of the feeding bath, when operating according to the afore-mentioned working method. By said process energy is saved, since an intermediate drying before developing the dyestuff is not necessary.

As azo components in the process of the present invention compounds enter into consideration which are distinguished by a high substantivity for the textile material used, i.e. azo components which at a long goods-to-liquor ratio of 1:20, a duration of the dyeing of 30 minutes at 30°C, a concentration of 1 g per liter of water without the addition of salts and an excess of 4.5 gms of sodium hydroxide per liter of bath, possess such a high substantivity that at least 9 gms are absorbed by 1000 gms of cotton. Suitable compounds are for example:

1-2',3'-hydroxynaphthylaminio)-2,5-dimethoxy-4-chlorobenzene or
1-(2',3'-hydroxynaphthylaminio)-2-methoxy-4-chloro-5-methylbenzene;
6-bromo- or 6-methoxy-2,3-hydroxynaphthoic acid alylamides, such as
1-(6'-bromo-2',3'-hydroxynaphthylaminio)-2-methoxybenzene;
condensation products of 2,3-hydroxynaphthoic acid and polynuclear isocyclic or heterocyclic amines, such as
2-(2',3'-hydroxynaphthylaminio)-naphthalene,
2-(2',3'-hydroxynaphthylaminio)-carbazol,
3,516,780

2-(2',3'-hydroxynaphthoylamino)-4-methoxy-diphenylene-oxide, 6-(2',3'-hydroxynaphthoylamino)-benzimidazol, 2-(2',3'-hydroxyphenylamino)-indazol, 5-(2'-hydroxynaphthoylamino)-2-methyl-phenothiazol or 4-(2',3'-hydroxynaphthoylamino)-diphenyl and its substitution products, 4,4'-bis-(2',3'-hydroxynaphthoylamino)-diphenyl and its substitution products, such as 4,4'-bis-(2',3'-hydroxynaphthoylamino)-3,3'-dimethoxy-diphenyl, 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)-diphenyl-urea, 2-hydroxyanthracene-3-carboxylic acid arylamides, such as 1-(2'-hydroxyanthracene-3-carboxylic acid)-2-methyl-benzene; 2-hydroxy-carbazol-3-carboxylic acid arylamides, such as 1-(2'-hydroxy-carbazol-3-carboxylic acid)-4-chlorobenzene; 5-hydroxy-1,2',1'-benzocarbazol-4-carboxylic acid arylamides, such as 1-(5'-hydroxy-1',2',1'-benzocarbazol-4'-carboxylic acid)-4-methoxy-benzene or 1-(5'-hydroxy-1',2',1'-benzocarbazol-4'-carboxylic acid)-2-methyl-4-methoxybenzene; 3-hydroxydiphenylethene-2-carboxylic acid arylamides, such as 1-(3'-hydroxydiphenylethene-2'-carboxylic acid)-2,5-dimethylbenzene or 1-(3'-hydroxydiphenylethene-2'-carboxylic acid)-naphthalene; or terephthaloyl bis-acetic acid arylamides, such as terephthaloyl bis-(1-acetylbenzol-2,4-dimethoxy-5-chlorobenzene) or terephthaloyl bis-(1-acetylbenzol-2,4-dimethoxy-5-methylbenzene).

As antidizatomes particularly those from aromatic amines enter into consideration, for example from monoclanilines and dichloranilines, toluidines, chlorotoluidines, chloranilines, xylenines, phenetidines, naphthilines, nitrotoluidines, nitransindines, nitroxylinines, nitrophenetidines, ditoluidines, cyananilines, aminobenzensulfonic acid amides, benzidines, dianisidines or tolidine.

As wetting or dispersing agents the compounds used in ice-color technique enter into consideration, for example condensation products of high molecular weight fatty acids and protein degradation products, condensation products of high molecular weight fatty acids and aminoketones, condensation products of formaldehyde with naphthalene-sulfonic acid or purified sulfite cellulose waste liquor.

The process of the present invention can be carried out on textile material of natural or regenerated cellulose, cyano-ethylated cellulose, wool, natural silk or regenerated protein fibers.

In comparison with the usual dyeing process by means of ice colors, the process of the present invention represents an essential simplification. According to the known dyeing process the dyebath is discharged after the impregnation with the azo component, the fabric is centrifuged, filtered with suction or subjected to an intermediate rinsing, and the dyestuff is developed in a second bath with a diazonium compound. On the contrary, the process of the present invention includes the impregnation and development stage in one bath, and after a period which is necessary for fixing the azo component the coupling takes place without any interposed operation, so that the duration of such a dyeing process is essentially reduced. The same excess quantities of antidizatose, calculated on the fixed azo component, can be used, as is the case if the dyestuff is developed with diazonium salts in a second bath. Thus, the present invention represents a valuable advance in the art. The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

Example 1

A cross-wound bobbin with 500 grams of cotton yarn is wetted out on a cheese dyeing machine and treated in a bath containing in 6.5 liters of water of 20° C., 3.2 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lacetic casein, 1.6 grams of a condensation product of a-ethylhexyl carbamic acid ester and a-ethylhexyl thiocyanic acid ester, 6 grams of sodium ethylene-diaminotetraacetate of 50% strength, 48 cc. of sodium hydroxide solution of 38° Bé. and 14 grams of an alkaline composition of 42.2% strength of the antidiazotate of 1-amino-2-methyl-4-chlorobenzene. 9 grams of 2-(2',3'-hydroxynaphthoylamino)-3'-methoxy-diphenylene-oxide, dissolved in 18 cc. of denaturated ethyl alcohol, 4.5 cc. of sodium hydroxide solution of 38° Bé. and 9 cc. of water are slowly added to the afore-mentioned bath, the yarn is then treated for 10–15 minutes, 130 grams of sodium chloride are slowly added, and the treatment is continued for a further 20 minutes at 60° C. The solution obtained at the above temperature is then absorbed and levelled. 6 grams of a reaction product of 80% strength of about 20 mols of ethylene oxide and 1 mol of octadecyl alcohol are then added, and 87 cc. of acetic acid of 50% strength are caused to run into the bath. After about 20 minutes the bath is discharged, the treated yarn is then rinsed with 6 grams of a condensation product of an aminoalkyl sulfonic acid and a high molecular weight fatty acid in 6 liters of water, treated first at 60° C. and subsequently in a fresh bath at 95° C. with 12 grams of a reaction product of 30% strength of about 10 mols of ethylene oxide and 1 mol of nonyl phenol, and 12 cc. of sodium nitritotetraacetate of 25% strength per liter of water for 20 minutes each, rinsed again in the heat and in the cold, and dried. A red dyeing which is fast to rubbing.

If in the afore-mentioned example instead of 9 grams of 2-(2',3'-hydroxynaphthoylamino)-3'-methoxy-diphenylene-oxide, 10.75 grams of 1-(2',3'-hydroxyphenylamino)-2,5-dimethoxy-4-chlorobenzene, dissolved in 21 cc. of denaturated ethyl alcohol, 5.3 cc. of sodium hydroxide solution of 38° Bé., 11 cc. of water and 16.2 cc. of a formaldehyde solution of 35% strength are used, there is likewise obtained a red dyeing which is fast to rubbing. If instead of the antidiazotate of 1-amino-2-methyl-4-chlorobenzene, 13.2 grams of an alkaline composition of 44.8% strength of the antidiazotate of 1-amino-2-methyl-5-chlorobenzene is used, there is likewise obtained red dyeings which are fast to washing.

Example 2

1000 grams of cotton yarn are treated at a goods-to-liquor ratio of 1:20 at 30° C. in a bath which contains in 20 liters of water 9.6 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lactic casein, 4.8 grams of a condensation product of a-ethylhexyl-chlorocarbonic acid ester and a-ethylhexylthiouria, 200 cc. of sodium hydroxide solution of 38° Bé., 54 grams of an alkaline composition of 42.2% strength of the antidiazotate of 1-amino-2-methyl-4-chlorobenzene, 40 grams of 1-(5'-hydroxyl-1',2',1'-benzocarbazol-4'-carboxylamino)-4-methoxybenzene, dissolved in 80 cc. of denaturated ethyl alcohol, 10 cc. of sodium hydroxide solution of 38° Bé., 40 cc. of water of 79° C. and 40 cc. of a formaldehyde solution of 33% strength and 200 grams of sodium chloride. After 25 minutes 20 grams of a reaction product of 30% strength of about 20 mols of ethylene oxide and 1 mol of octadecyl alcohol, dissolved in water, and 300 cc. of acetic acid of 50% strength are added to the bath, the bath is treated for a further 20 minutes, the bath is discharged, the yarn is rinsed, soaped for 20 minutes each at 60° C. and 95° C. with 12 grams of a reaction product of 30%
strength of about 10 mols of ethylene oxide and 1 mol of nonyl phenol and 0.5 gram of sodium nitrotriacetate per liter of water, rinsed again and dried. There is obtained a dark violet dyeing possessing a very good fastness to rubbing.

If in the alkaline dye bath instead of the aforementioned condensation product 20 grams of a condensation product of oleic acid chloride and N-methyl-taurin are used as dispersing agent, a dyeing is obtained which possesses the same good fastness properties.

Example 3

1000 grams of cotton yarn are treated at a goods-to-liquor ratio of 1:20 at 20° C. in a bath which contains in 20 liters of water 9.6 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lactic casein, 4.8 grams of a condensation product of α-ethylhexyl-chlorocarboxylic acid ester and α-ethylhexyl-taurin, 140 cc. of sodium hydroxide solution of 38° Bé, 600 grams of sodium chloride, 27.8 grams of an alkaline composition of 60.8% strength of the antizidato 1-amino - 2- methylbenzene-5-sulfonic acid dimethylamide and 24 grams of 1-(2',3'-hydroxyphosphonylaminol-2,5-dimethoxy-4-chlorobenzene, dissolved in 48 cc. of denatured ethyl alcohol, 12 cc. of sodium hydroxide solution of 38° Bé, 24 cc. of water and 36 cc. of a formaldehyde solution of 33% strength. After 30 minutes 20 grams of a reaction product of 30% strength of about 20 mols of ethylene oxide and 1 mol of octadeyl alcohol, dissolved in water, and 300 cc. of acetic acid of 30% strength are added, the treatment is continued for a further 20 minutes, the yarn is then rinsed and soaped for 20 minutes each at 60° C. and 95° C. with 12 grams of a reaction product of 30% strength of about 10 mols of ethylene oxide and 1 mol of nonyl phenol and 0.5 gram of sodium nitrotriacetate per liter of water, rinsed again and dried. There is obtained a vivid red dyeing which is fast to rubbing.

If in the aforesaid example instead of 24 grams of 1-(2',3'-hydroxyphosphonylaminol-2,5-dimethoxy-4-chlorobenzene, 23 grams of 1-(2',3'-hydroxyphosphonylaminol-2,5-dimethoxy-4-chlorobenzene, dissolved in 46 cc. of denatured ethyl alcohol, 11.5 cc. of sodium hydroxide solution of 38° Bé, 23 cc. of water and 23 cc. of a formaldehyde solution of 33% strength are used, a vivid scarlet dyeing is obtained.

Example 4

1000 grams of cotton yarn are treated at 20° C. in the following bath: 20 liters of cold water are mixed with 20 grams of sodium ethylene-diaminotetraacetate of 50% strength, 9.6 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lactic casein, 4.8 grams of a condensation product of α-ethylhexyl-chlorocarboxylic acid ester and α-ethylhexyl-taurin, 120 cc. of sodium hydroxide solution of 38° Bé, 400 grams of sodium chloride, 44.5 g. of an alkaline composition of 44.8% strength of the antizidato 1-amino-2-methoxy-5-chlorobenzene, and 30 grams of terephthaloyl-bis-(1-acetamidino-2,4-dimethoxy - 5 - chlorobenzene), dissolved in 60 cc. of denatured ethyl alcohol, 15 cc. of sodium hydroxide solution of 38° Bé, and 60 cc. of water. After about 30 minutes 20 cc. of the reaction product of about 20 mols of ethylene oxide and 1 mol of octadeyl alcohol, and 150 cc. of hydrochloric acid of 20° Bé, and 100 cc. of acetic acid of 50% strength are added, the treatment is continued for a further 20 minutes. The yarn is then rinsed and soaped at 80° C. and 95° C. and dried. It is then rinsed again and dried, rinsed again and dried. There is obtained a full yellow dyeing, which is fast to rubbing.

Example 5

1000 grams of cotton yarn are treated at 20° C. in the following bath: 20 liters of cold water are mixed with 9.6 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lactic casein, 4.8 grams of a condensation product of α-ethylhexyl-chlorocarboxylic acid ester and α-ethylhexyl-taurin, 160 cc. of sodium hydroxide solution of 38° Bé, 600 grams of sodium chloride, 34 grams of an alkaline composition of 54% strength of the antizidato 1-amino-2-methoxy-4-chlorobenzene and 20 grams of 1-(2'-hydroxy-carbazol-3'-carboxamido)-4-chlorobenzene, dissolved in 40 cc. of denatured ethyl alcohol, 20 cc. of sodium hydroxide solution 38° Bé and 160 cc. of water. After 25 minutes 20 grams of a reaction product of 30% strength of about 20 mols of ethylene oxide and 1 mol of octadeyl alcohol and 300 cc. of acetic acid of 50% strength are added, the treatment is continued for a further 20 minutes, the yarn is then rinsed, soaped for 20 minutes each at 60° C. and 95° C. with 2 grams of a reaction product of 30% strength of about 10 mols of ethylene oxide and 1 mol of nonyl phenol and 0.5 gram of sodium nitrotriacetate per liter of water, rinsed again and dried. There is obtained a brown dyeing which is fast to rubbing.

Example 6

100 kilograms of a cotton fabric are impregnated on the padding machine at an immersion period of 0.65 hours and 60% squeezing efficiency with a feed containing 30% C. which contains in the initial bath 8 grams of 2-(2',3'-hydroxyphosphonylaminol-naphthalene, 1.3 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lactic casein, 0.6 gram of a condensation product of α-ethylhexyl-chlorocarboxylic acid ester and α-ethylhexyl-taurin, 14 cc. of sodium hydroxide solution of 38° Bé, 44.2 grams of an alkaline composition of 45.7% strength of the antizidato 1-amino-2-methoxy-4-nitrobenzene per liter of water and which contains in the feeding bath 16.5 grams of 2-(2',3'-hydroxyphosphonylaminol-naphthalene, 3 grams of a condensation product of palm-kernel fatty acid chloride and partially decomposed lactic casein, 0.6 gram of a condensation product of α-ethylhexyl-chlorocarboxylic acid ester and α-ethylhexyl-taurin, 14 cc. of sodium hydroxide solution of 38° Bé and 44.2 grams of an alkaline composition of 45.7% strength of the antizidato 1-amino-2-methoxy-4-nitrobenzene per liter of water. The fabric is rolled up, and the roll is slowly turned with the exclusion of air for about 30-60 minutes. The fabric is then developed in 6 passages on the jigg with 500 liters of water, containing 2.5 liters of acetic acid of 50% strength, 0.5 liter of a reaction product of 30% strength of about 20 mols of ethylene oxide and 1 mol of octadeyl alcohol and 10 kilograms of sodium chloride. The fabric is then rinsed, soaped at 60° C. and 95° C. in the usual manner, rinsed again and dried. There is obtained a clear dyeing possessing a good fastness to rubbing.

We claim:

1. A process for the production of water-insoluble azo-dyes on textiles materials of cellulose or protein fibers comprising treating the textile material at a long goods-to-liquor ratio in an alkaline bath containing (1) a coupling component highly substantive for the material to be dyed and selected from the group consisting of the amides of aromatic ortho-hydroxy carbocyclic acids, arylamides of heterocyclic ortho-hydroxy carbylic acids and arylamides of acyl acetic acids, (2) an antizidato from a primary aromatic amine and (3) an anionic dispersing agent, for a time sufficient to absorb and level the coupling component on the fiber material and thereafter, without intermediate drying, adding to the alkaline bath an acid agent selected from the group consisting of an organic acid and a mixture of an organic acid with an inorganic acid at a temperature below 40° C., said acid agent being in an amount sufficient to neutralize the
7

total quantity of alkaline material and to obtain a pH of from 4 to 7 on the textile material.

2. The process as claimed in claim 1 wherein the treating of the textile material in the alkaline bath is carried out in the presence of an inorganic salt selected from the group consisting of sodium chloride and sodium sulfate.

References Cited

UNITED STATES PATENTS

1,882,560 10/1932 Gleitenberg et al. 8—45
1,882,561 10/1932 Haller et al. 8—45
2,088,506 7/1937 Chambers 8—45
2,926,986 3/1960 Petitcolas 8—45

8

OTHER REFERENCES


DONALD LEVY, Primary Examiner
J. P. BRAMMER, Assistant Examiner

U.S. Cl. X.R.

8—46, 49