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3,441,364

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

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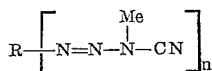
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2 Claims

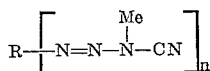
ABSTRACT OF THE DISCLOSURE

Process for the production of water-insoluble azo dyestuffs on textile material comprising treating the textile material in an alkaline bath containing a coupling component and a compound of the formula



wherein R is a radical of an aromatic or heterocyclic amine, Me is an alkali metal or alkaline earth metal and *n* is 1 or 2, a wetting or dispersing agent and, optionally, an inorganic salt, and producing the dyestuff by treatment with acid agents below 40° C.

It has been found that water-insoluble azo dyestuffs can be produced on textile material comprising cellulose or protein fibers by treating the textile material in an alkaline bath containing a coupling component and a diazoamino or tetrazoamino compound of the formula



in which R represents the radical of an aromatic or heterocyclic amine, Me represents an alkali metal or alkaline earth metal and *n* stands for one of the integers 1 and 2, a wetting or dispersing agent and, if desired, an inorganic salt, and producing the dyestuff by 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 hanks, wound bodies, combed or loose material in an alkaline bath which contains a coupling component having a high substantivity and a diazoamino or tetrazoamino compound of the above formula, a wetting or dispersing agent and, if desired, an inorganic salt, for example sodium chloride, sodium phosphate or sodium sulfate. The treatment is carried out for at least 10 minutes so that the coupling component can be sufficiently and uniformly fixed on the textile material. In general, the treatment is carried out at room temperature or at moderately elevated temperature, preferably below 35° C. After the coupling component has been substantially absorbed and levelled on the material, an organic acid is added to the bath, for example formic acid, acetic acid, tartaric acid, citric acid, lactic acid or glycolic acid or a mixture of said acids or a mixture of an inorganic acid, for example hydrochloric acid or sulfuric acid, with an organic acid, in an amount such that the total quantity of alkali in the bath and on the textile material is neutralized 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

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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 dyeing is finished in the usual manner. Dyeings which possess an excellent fastness to rubbing are obtained.

Piece goods can be dyed by impregnating the goods on a padding machine having two or more rollers with a mixture of the coupling component and an excess of diazoamino or tetrazoamino compound, rolling them together, and after 30 minutes for example, coupling is effected 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 passing the material through a compartment of a roller vat or by several passages on a jig or on a winch vat, in which process additions of inorganic salts and dispersing agents sometimes show an excellent effect in the impregnating and developing stage. In this method, because of the additional affinity of the coupling component, the concentration of the latter in the initial bath must be lowered in comparison with that of the feeding bath, whereas the concentration of the diazoamino or tetrazoamino compound in the initial bath is not lowered in comparison with that of the feeding bath. In the present process much energy is saved, since an intermediate drying before developing the dyestuff is not necessary.

As coupling components in the process of the present invention compounds can be used which are distinguished by a high substantivity for the textile material, i.e. coupling components which at a goods-to-liquor ratio of 1:20, a dyeing period of 30 minutes at 30° C., a concentration of 1 gram per liter of water without the addition of salts and an excess of 4.5 grams of sodium hydroxide per liter of bath, possess such a high substantivity that at least 9 grams are absorbed by 1 kilogram of cotton. Suitable compounds are, for example: 2,3-hydroxynaphthoyl-amino-benzenes such as 1-(2',3'-hydroxynaphthoyl-amino)-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 aryl amides such as 1-(6'-bromo-2',3'-hydroxynaphthoylamino)-2-methoxybenzene; condensation products of 2,3-hydroxynaphthoic acid and polynuclear isocyclic or heterocyclic amines such as 2-(2',3'-hydroxynaphthoylamino)-naphthalene, 2-(2',3'-hydroxynaphthoylamino)-carbazole, 2-(2',3'-hydroxynaphthoylamino)-3-methoxydiphenylene oxide, 6-(2',3'-hydroxynaphthoylamino)-benzimidazole, 6-(2',3'-hydroxynaphthoylamino)-indazole, 5-(2',3'-hydroxynaphthoylamino)-2-methylbenzothiazole; 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'-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, such as 1-(2'-hydroxyanthracene-3'-carboylamino)-2-methylbenzene; 2-hydroxycarbazole-3-carboxylic acid aryl amides, such as 1-(2'-hydroxycarbazole-3'-carboylamino)-4-chlorobenzene; 5-hydroxy - 1,2,1',2'-benzocarbazole-4-carboxylic acid arylamides, such as 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; furthermore terephthaloyl-bis-acetic acid arylamides, such as terephthaloyl - bis-(1-acetylamino-2,4-dimethoxy-5-chlorobenzene) or terephthaloyl-bis-(1-acetylamino-2-methoxy-4-chloro-5-methylbenzene).

As diazoamino or tetrazoamino compounds there can be used particularly those from aromatic mono- or diamines, for example from mono- or dichloroanilines, toluidines, chlorotoluidines, chloroanisidines, xyloidines, phenetidines, nitranilines, nitrotoluidines, nitroanisidines, nitroxylidines, nitrophenetidines, cyanotoluidines, cyanoanisidines, aminobenzene-sulfonic acid amides, aminophenylalkylsulfones, aminobenzene - carboxylic acid amides, aminodiphenyl ethers, monoacylated phenylene diamines, aminoazobenzenes, benzidine, dianisidine or toluidine, as well as from heterocyclic amines, for example aminocarbazoles. They can be prepared, for example according to the process disclosed in German Patent 614,198.

As wetting or dispersing agents the compounds commonly used in the ice-colour 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 aminoalkyl-sulfonic acids, condensation products of formaldehyde with naphthalene-sulfonic acids 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, regenerated protein fibers or on mixtures of natural or regenerated cellulose with copolymers of acrylonitrile, vinylidene chloride and N-vinylpyrrolidone.

In comparison with the usual ice-colour dyeing process, the process of the present invention provides an essential simplification. According to the known dyeing process the dyebath is discharged after impregnation with the coupling 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. In contrast thereto, the process of the present invention includes the impregnation and developing stage in one bath, and after a period necessary for fixing the coupling component coupling takes place without any intervening operation so that the duration of such a dyeing process is essentially reduced.

It is known from German Patent 624,765 that diazoamino compounds from diazotized aromatic amines and cyanamide can be used for producing azo dyestuffs on the fiber by mixing the said diazoamino compounds with coupling components, printing the mixtures obtained on the fibers and developing the dyestuff by an acid treatment. However, the said patent does not suggest that mixtures of this type can be used for dyeing the fibers in all stages of manufacture, even in the form of wound bodies, without intermediate drying of the material.

German Patent 1,057,061 teaches a process for producing water-insoluble azo dyestuffs on vegetable fibers by treating the said fibers at a long goods-to-liquor ratio in a bath containing a coupling component and a diazo- or tetrazoamino compound without solubilizing groups and developing the azo dyestuff by treatment in an acid bath.

As compared with the known process the process according to the invention, which is carried out with the use of substantive coupling components and diazoamino- or tetrazoamino compounds from diazotized aromatic mono- or diamines and cyanamide, is distinguished in that the dyestuffs can be developed at low temperatures and an elevation of the temperature after the addition of acid is not necessary. A further advantage of the present process resides in the fact that the diazoamino or tetrazoamino compounds with cyanamide are present as stabilizers in the alkaline bath in the form of dissolved alkali metal salts whereby a complete penetration of the material to be dyed is achieved resulting in a quantitative coupling, whereas with the use of water-insoluble diazoamino compounds the latter are superficially deposited on the material to be dyed, which may result in an incomplete penetration of the dyestuff. A re-coupling of the diazonium

compound with the cyanamide cannot take place because on splitting neutral salts and urea are formed in addition to the diazonium compound. In this manner the dyestuff components used are fully utilized.

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

EXAMPLE 1

A cross-wound bobbin of 500 grams of cotton yarn was treated in a dyeing machine having a content of about 6 liters for 30 minutes with a solution of 20° C. (circulation towards the outside) containing in about 5.8 liters of water 8.1 grams of the diazonium compound of diazotized 1-amino-2,5-dichlorobenzene and sodium cyanamide and 3 grams of the sodium salt of ethylene diamine-tetracetic acid with de-aeration of the core of the bobbin. 24 grams of a dispersing agent containing 16% of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α -ethylhexylchlorocarbonic acid ester and sodium α -ethylhexyltaurate, and 42 cc. of sodium hydroxide solution of 38° Bé. where successively added, whereby the last inclusions of air in the bobbin disappeared. With a circulation of the bath towards the inside a solution of 7.5 grams of 1-(5'-hydroxy-1',2'-1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene in a mixture of 30 cc. of denatured ethyl alcohol, 4.25 cc. of sodium hydroxide solution of 38° Bé., 15 cc. of water of 70° C. and 7.5 cc. of formaldehyde solution of 30% strength was introduced and after a change of the bath direction the material was further treated for about 30 minutes at 20° C., the direction of the bath being changed on a rhythm of 2 minutes/4 minutes. 120 grams of sodium chloride were then added and the treatment was continued for a further 20 minutes, 6 cc. of a reaction product of about 20 mols of ethylene oxide and cresyl camphane, 51.3 cc. of hydrochloric acid of 20° Bé. and 48 cc. of acetic acid of 50% strength were then added whereby a pH of 4.4 to 4.6 was adjusted and coupling occurred.

The bath was discharged after about 30 minutes, the yarn was thoroughly rinsed and soaped for 15 minutes at 60° C. with 16.5 grams of a mixture of 63% of perchloroethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 20% of isopropyl alcohol and 13 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water. The bath was discharged, the yarn was rinsed and soaped for 15 minutes at the boil with 13 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 13 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water, the yarn was rinsed again and dried. A dark violet dyeing was obtained which was very fast to rubbing.

If in the above example instead of 8.1 grams of the diazoamino compound of diazotized 1-amino-2,5-dichlorobenzene and sodium cyanamide, 8.7 grams of the diazoamino compound of diazotized 1-amino-2,5-dichlorobenzene and potassium cyanamide were used, a dark violet dyeing fast to rubbing was likewise obtained.

As compared with a normal dyeing process with impregnation with a coupling component, intermediate rinsing and developing with a diazotized amine considerable time is saved.

EXAMPLE 2

In the manner described in Example 1, a cross-wound bobbin of 500 grams of cotton yarn was de-aerated at 20° C. in a dyeing machine having a capacity of 6 liters with a solution of 9.6 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-5-chlorobenzene and sodium cyanamide and 6 grams of sodium ethylene diamine tetraacetate in 6 liters of water. 24 grams of a dispersing agent containing 16% of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α -ethylhexyl-chloro-

carbonic ester and sodium α -ethylhexyltaurate and 42 cc. of sodium hydroxide solution of 38° Bé. were introduced and subsequently a solution of 9 grams of 2-(2',3'-hydroxynaphthoylamino)-3-methoxy-diphenylene oxide in a mixture of 20 cc. of denatured ethyl alcohol, 45 cc. of sodium hydroxide solution of 38° Bé. and 9 cc. of hot water was added. The yarn was further treated for 30 minutes with change of the bath direction, 120 grams of sodium chloride were added and treatment was continued for 20 minutes at 20° C. 6 cc. of a reaction product of about 20 mols of ethylene oxide with cresyl camphane, 51.3 cc. of hydrochloric acid of 20° Bé. and 36 cc. of acetic acid of 50% strength were added, whereby the pH was reduced to about 4.5 and coupling occurred. After a further 20 minutes the yarn was aftertreated as described in Example 1, rinsed and dried. A dark red dyeing was obtained which was fast to rubbing.

If the above example instead of 9.6 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-5-chlorobenzene and sodium cyanamide, 9.6 grams of the diazoamino compound of diazotized 1-amino-2-methyl-4-chlorobenzene and sodium cyanamide were used, a yellowish red dyeing fast to rubbing was obtained.

EXAMPLE 3

Cotton yarn was treated at 20° C. at a goods-to-liquor ratio of 1:20 in an aqueous solution containing per liter of water 1.1 grams of 2-(2',3'-hydroxynaphthoylamino)-3-methoxy-diphenylene oxide, 3 grams of a dispersing agent containing 16% of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α -ethylhexylchlorocarbonic acid ester and sodium α -ethylhexyltaurate, 5 cc. of sodium hydroxide solution of 38° Bé., 20 grams of sodium chloride and 1.62 grams of the diazo-amino compound of diazotized 1-amino-2-methoxybenzene-5-sulfonic acid butyl amide and sodium cyanamide. After 30 minutes 5.5 cc. of hydrochloric acid of 20° Bé. and 3 cc. of acetic acid of 50% strength were added per liter of bath and the yarn was further treated for 30 minutes at a pH of about 5.5. It was then rinsed and soaped as usual at 60° C. and at boiling temperature with 2 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 0.4 gram of sodium nitrilotriacetate per liter of water, rinsed again and dried. A full red dyeing was obtained.

If in the above example instead of 1.62 grams of the diazoamino compound of diazotized 1-amino-2-methoxybenzene-5-sulfonic acid n-butyl amide and sodium cyanamide, 1.4 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-5-ethylsulfonyl benzene and sodium cyanamide were used and the dyeing was developed at a pH of about 5, a full red dyeing was likewise obtained.

With the use of 1.7 grams of the diazoamino compound of diazotized 1-amino-2-methoxybenzene-5-sulfonic acid n-butyl amide and potassium cyanamide instead of 1.62 grams of the diazoamino compound of diazotized 1-amino-2-methoxybenzene-5-sulfonic acid n-butyl amide and sodium cyanamide a full red dyeing was likewise obtained.

EXAMPLE 4

Cotton yarn was treated at 20° C. at a goods-to-liquor ratio of 1:20 in an aqueous solution containing per liter of water 1.1 grams of 2-(2',3'-hydroxynaphthoylamino)-3-methoxy-diphenylene oxide, 3 grams of a dispersing agent containing 16% of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α -ethylhexylchlorocarbonic acid ester and sodium α -ethylhexyltaurate, 5 cc. of sodium hydroxide solution of 38° Bé., 20 grams of sodium chloride and 1.16 grams of the diazoamino compound of diazotized 1-amino-2-methyl-5-chlorobenzene and sodium cyanamide. After about 30 minutes 5.5 cc. of hydrochloric acid of 20° Bé. and 5 cc. of acetic acid of

50% strength were added per liter of bath and the yarn was treated for a further 30 minutes at a pH of 4-4.5. It was then rinsed, soaped at 60° C. and at boiling temperature, each time for 15 minutes with 2 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 0.4 gram of sodium nitrilotriacetate per liter of water, rinsed again and dried. A full red dyeing was obtained.

If in the above example instead of the diazoamino compound of diazotized 1-amino-2-methyl-5-chlorobenzene and sodium cyanamide, 1.04 grams of the diazoamino compound of diazotized 1-amino-2-methyl-3-chlorobenzene and sodium cyanamide was used a reddish-brown dyeing was obtained.

EXAMPLE 5

A cross-wound bobbin of 500 grams of cotton yarn was treated for de-aeration in a goods-to-liquor ratio of 1:12 at 20° C. with the aqueous solution of 5 grams of the diazoamino compound of diazotized 1-amino-2-methoxybenzene-5-carboxylic acid amide and sodium cyanamide, 3 grams of sodium ethylene diamine acetate, 24 grams of a dispersing agent containing 16% of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α -ethylhexylchlorocarbonic acid ester and sodium α -ethylhexyltaurate, and 120 grams of sodium chloride with circulation of the bath towards the outside. 42 cc. of sodium hydroxide solution of 38° Bé., and after having changed the direction of the bath, 13.5 grams of 1-(2',3'-hydroxynaphthoylamino) - 2,5 - dimethoxy-4-chlorobenzene dissolved in 27 cc. of denatured ethyl alcohol, 5.4 cc. of sodium hydroxide solution of 38° Bé., 13.5 cc. of warm water and 13.5 cc. of formaldehyde solution of 30% strength were added. After about 20 minutes 120 grams of sodium chloride and then 6 cc. of a reaction product of about 20 mols of ethylene oxide with cresyl camphane were gradually added. After a further 15 minutes the bath was acidified by adding 52.8 cc. of hydrochloric acid of 20° Bé. and 24 cc. of acetic acid of 50% strength and the yarn was treated for 30 minutes at 20° C. and a pH of about 5.4. The yarn was rinsed and soaped for 15 minutes at 60° C. with 16.5 grams of a mixture of 63% of perchloroethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 20% of isopropyl alcohol and 3 grams of sodium nitrilotriacetate in 6 liters of water, rinsed and soaped for 15 minutes at the boil with 12 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol, 1.5 grams of sodium nitrilotriacetate and 6 grams of sodium carbonate in 6 liters of water, rinsed and dried. A bright red dyeing having a good fastness to rubbing was obtained.

EXAMPLE 6

A cross-wound bobbin of 500 grams of cotton yarn was treated at a goods-to-liquor ratio of 1:12 at 20° C. with the aqueous solution of 13.6 grams of the diazoamino compound of diazotized 1-amino-2-methyl-3-chlorobenzene and sodium cyanamide, 3 grams of the sodium salt of ethylene diamine tetraacetic acid, 60 grams of sodium chloride and 24 grams of a dispersing agent containing 16% of a condensation product of partially decomposed casein and palm-kernel fatty acid and 8% of a condensation product of α -ethylhexylchlorocarbonic acid ester and sodium α -ethylhexyltaurate. After about 30 minutes with a circulation of the bath towards the outside 42 cc. of sodium hydroxide solution of 38° Bé. were added. After a few minutes a solution of 12 grams of 2-(2',3'-hydroxynaphthoylamino)-naphthalene in 24 cc. of denatured ethyl alcohol, 4.8 cc. of sodium hydroxide solution of 38° Bé. 12 cc. of hot water and 12 cc. of formaldehyde solution of 30% strength was introduced. With change of the direction of the bath treatment was continued for 20 minutes at 20° C., 60 grams of sodium

chloride were added and the yarn was treated for a further 15 minutes. 6 cc. of a reaction product of about 20 mols of ethylene oxide with cresyl camphane, 51 cc. of hydrochloric acid of 20° Bé. and 36 cc. of acetic acid of 50% strength were allowed to flow in. At a pH of about 5 the yarn was further treated for 30 minutes at about 20° C., rinsed, soaped for 15 minutes at 60° C. with 16.5 grams of a mixture of 63% of perchloroethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 20% of isopropyl alcohol and 3 grams of sodium nitrilotriacetate in 6 liters of water, and then for 20 minutes at boiling temperature with 12 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 1.5 grams of sodium nitrilotriacetate in 6 liters of water, rinsed again and dried. A scarlet dyeing of very good fastness to rubbing was obtained.

If instead of 13.6 grams of the diazoamino compound of diazotized 1-amino-2-methyl-3-chlorobenzene and sodium cyanamide, 14.7 grams of the diazamin compound of diazotized 1-amino-2-methyl-3-chlorobenzene and potassium cyanamide was used, a yellow dyeing fast to rubbing was obtained.

EXAMPLE 7

A cross-wound bobbin of 500 grams of cotton yarn was treated in a dyeing machine having a capacity of about 6 liters, for 15 minutes with circulation of the bath towards the outside with a solution of 20° C. containing 9.8 grams of the diazoamino compound of diazotized 1-amino-2,5-dichlorobenzene and sodium cyanamide and 6 grams of sodium ethylene diamine tetraacetate. 24 grams of a dispersing agent containing 16% 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 -ethylhexyltaurate, and 42 cc. of sodium hydroxide solution of 38° C. were then added successively. When the bobbin had been completely de-aerated, the bath was circulated in alternating direction, 9.6 grams of terephthaloyl-bis-(1-acetyl-amino - 2,4 - dimethoxy - 5 - chlorobenzene) dissolved in 48 cc. of denatured ethyl alcohol, 10.8 cc. of sodium hydroxide solution of 38° Bé. and 96 cc. of water were added in portions and after some time 60 grams of sodium chloride were added to the mixture. Subsequently, 6 cc. of a reaction product of about 20 mols of ethylene oxide with cresyl camphane and a mixture of 56 cc. of hydrochloric acid of 20° Bé and 48 cc. of acetic acid of 50% strength were added. After coupling for about 20 minutes at pH 4.2 the bath was discharged, the yarn was rinsed thoroughly, soaped for 15 minutes at 60° C. with a solution of 16.5 grams of a mixture of 63% of perchloroethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 20% of isopropyl alcohol and 12 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water, rinsed and soaped with 12 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol, 12 grams of calcined sodium carbonate and 4 grams of hydrosulfite in 6 liters of water, at the beginning at 50°-60° C. and then for 10 minutes at boiling temperature. The yarn was then rinsed hot and cold, and dried. A yellow dyeing fast to rubbing was obtained.

EXAMPLE 8

A cross-wound bobbin of 500 grams of cotton yarn was treated in a dyeing machine having a capacity of 6 liters, with circulation towards the outside, with a solution of 20° C. containing 8.4 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-5-nitrobenzene and sodium cyanamide and 6 grams of sodium ethylene diamine tetraacetate. After about 15 minutes 24 grams of a dispersing agent containing 16% 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 -ethylhexyltaurate, and after complete de-aeration of the bobbin, 42 cc. of sodium hydroxide with alternating direction of the bath, a solution of 7.5 grams of 4,4'-bis-(2'' - hydroxycarbazole - 3'' - carbonylamino)-3,3'-dimethoxydiphenyl in a mixture of 45 cc. of ethylene glycol, 4 cc. of sodium hydroxide solution of 38° Bé. and 14 cc. of water was added and after about 15 minutes 60 grams of sodium chloride were introduced and the bath was circulated for a further 15 minutes. 6 grams of a reaction product of about 20 mols of ethylene oxide with cresyl camphane and subsequently a mixture of 50 cc. of hydrochloric acid of 20° Bé. and 48 cc. of acetic acid of 50% strength were added and coupling was brought about for about 20 minutes at pH 4.2. The yarn was rinsed, treated with 16.5 grams of a mixture of 63% of perchloroethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 20% of isopropyl alcohol and 12 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water for 15 minutes at 60° C., rinsed and treated for 15 minutes at boiling temperature with 12 grams of a reaction product of about 10 mols of ethylene oxide with 1 mole of nonyl phenol and 12 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water, rinsed again and dried. A brownish-yellow dyeing of a very good fastness to rubbing was obtained.

EXAMPLE 9

A cross-wound bobbin of 500 grams of cotton yarn was treated in a dyeing machine having a capacity of 6 liters, with circulation of the bath towards the outside, at 20° C., with a bath containing 10.8 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-5-nitrobenzene and sodium cyanamide, 60 grams of sodium chloride and 6 grams of sodium ethylene diamine tetraacetate. After 15 minutes there were added for further de-aeration of the bobbin, 24 grams of a dispersing agent containing 16% 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 -ethylhexyltaurate and the bath was circulated for a further 15 minutes in the cold. After addition of 42 cc. of sodium hydroxide solution of 38° Bé., the direction of the bath was changed and a solution of 9.6 grams of 2-(2',3'-hydroxynaphthoylamino)-naphthalene in 19.2 cc. of denatured ethyl alcohol, 4 cc. of sodium hydroxide solution of 38° Bé., 9.6 cc. of warm water of 50° C. and 9.6 cc. of formaldehyde of 30% strength were added, the yarn was treated for a further 15 minutes with rhythmic change of the direction of flow of the bath, 60 grams of sodium chloride were added and after about 15 minutes a solution of 6 grams of a condensation product of oleic acid and methyltaurin was added and coupling was brought about by adding a mixture of 50 cc. of hydrochloric acid of 20° Bé. and 48 cc. of acetic acid of 50% strength at a pH of 4.2-4.4. In the course of about 30 minutes the temperature rose to about 30° C. The bath was discharged, the yarn was rinsed and treated for about 15 minutes at 60° C. with 16.5 grams of a mixture of 63% of perchloroethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol and 20% of isopropyl alcohol, and 12 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water, rinsed in the hot and treated for about 15 minutes at boiling temperature with 12 grams of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonyl phenol, 6 grams of calcined sodium carbonate and 12 grams of a solution of 25% strength of sodium nitrilotriacetate in 6 liters of water, thoroughly rinsed in the hot and cold and dried. A red dyeing of good fastness to rubbing was obtained.

EXAMPLE 10

Cotton sponge cloth (about 100 kilograms) was thoroughly wetted in a winch vat having a capacity of about 1600 liters with a wetting agent with the addition of sodium carbonate, and rinsed. The winch vat was then charged with a solution containing in 100 liters of water 3.6 kilograms of the diazoamino compound of diazotized 1-amino-2-methoxy-4-nitrobenzene and sodium cyanamide, 0.85 kilogram of a condensation product of oleic acid and methyltaurine and 2.8 kilograms of sodium sulfate. 6 liters of sodium hydroxide solution of 50% strength, 15.8 kilograms of sodium sulfate, 3.25 kilograms of 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene, dissolved in 13 liters of denatured ethyl alcohol, 1.63 liters of sodium hydroxide solution of 50% strength, 6.5 liters of water of 60° C. and 3.25 liters of formaldehyde solution of 30% strength were added. The fabric was treated for about 1 hour at 30° C., in the course of 5 minutes 17.8 liters of acetic acid of 60% strength were added and treatment was continued for 40 minutes at pH 5.7. The bath was discharged, the fabric was thoroughly rinsed and soaped at 60° C. and at boiling temperature each time for 20 minutes with 4.8 kilograms of Castile soap, 0.8 kilogram of sodium nitrilotriacetate and 0.8 kilogram of a condensation product of oleic acid and methyltaurine in 1600 liters of water, rinsed and dried. An even black dyeing fast to rubbing was obtained.

EXAMPLE 11

1 kilogram of natural silk was treated at 25° C. at a goods-to-liquor ratio of 1:20 with an aqueous solution containing per liter of water 1.5 grams of 2-(2',3'-hydroxy-naphthoylamino)-naphthalene, 2.1 grams of the diazoamino compound of diazotized 1-amino-2-methyl-3-chlorobenzene and sodium cyanamide, 0.5 gram of a condensation product of oleic acid and N-methyltaurine, 2 grams of a dispersing agent containing 16% 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 -ethylhexyltaurate, 1.6 grams of sodium hydroxide and 23 grams of sodium chloride. After about 1 hour 8.1 cc. of acetic acid of 50% strength were added in portions and the silk was treated at a pH of about 5-5.5 for 30 minutes. It was then thoroughly rinsed for 15 minutes at 60° C. with 1 gram of a condensation product of oleic acid and methyltaurine per liter of water, soaped at the boil for about 15 minutes with 5 grams of soap and 0.5 gram of sodium nitrilotriacetate per liter of water, rinsed and dried. A bright scarlet dyeing was obtained. Wool could be dyed in the same manner. In this case the after-treatment was carried out with 1 gram of a condensation product of oleic acid and methyltaurine and 0.5 gram of sodium nitrilotriacetate per liter of water at 60° C. to avoid a damage of the wool fiber.

EXAMPLE 12

A cross-wound bobbin of 500 grams of cotton yarn was thoroughly wetted in a dyeing machine and treated at about 30° C. with a bath prepared in the following manner:

(a) 18 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-4-nitrobenzene and sodium cyanamide were dissolved in about 500 cc. of water of 50° C.;

(b) 15.5 grams of 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene were dissolved in 66 cc. of denatured ethyl alcohol, 8.25 cc. of sodium hydroxide solution of 38° Be., 16.5 cc. of formaldehyde solution of 33% strength and 13 cc. of water.

Solutions (a) and (b) were introduced successively into a bath of about 27° C. containing in about 5400 cc. of water 29.5 cc. of sodium hydroxide solution of 38° Be., 50.4 grams of trisodium phosphate and 6.5

grams of a condensation product of oleic acid and methyltaurine. After about 45 minutes 100 cc. of acetic acid of 50% strength were added over a period of about 3 minutes, whereby a pH of about 5.8 was adjusted. The yarn was treated for a further 30 minutes, rinsed thoroughly and soaped, each time for 15 minutes, at 60° C. and 95° C. with 12 grams of a condensation product of oleic acid and methyltaurine and 3 grams of sodium nitrilotriacetate per liter of water, rinsed and dried. A deep black dyeing having a very good fastness to rubbing was obtained.

EXAMPLE 13

1 kilogram of cotton hank was treated at 30° C. in a bath prepared as follows:

(a) 24 grams of 1-(6'-methoxy-2',3'-hydroxynaphthoylamino)-2,5-dimethoxy-4-chlorobenzene were dissolved in 48 cc. of denatured ethyl alcohol, 12 cc. of sodium hydroxide solution of 38° Bé. and 48 cc. of water of 60°-70° C.;

(b) 36 grams of diazoamino compound of diazotized 1-amino-2-methyl-4-nitrobenzene and sodium cyanamide were dissolved in 900 cc. of water of 70° C.

Solutions (a) and (b) were introduced into a bath containing in 19 liters of water 20 grams of a condensation product of oleic acid and methyltaurine, 148 cc. of sodium hydroxide solution of the 38° Bé., 600 grams of sodium chloride and 10 grams of sodium ethylene diamine tetraacetate. After 45 minutes 97 cc. of acetic acid of 50% strength and 138 cc. of hydrochloric acid of 20° Bé. were added over a period of 3-5 minutes and the material was treated for about 30 minutes at a pH of about 4.8. It was then thoroughly rinsed, first at 30°-40° C. and then in the cold, and treated, each time for 15 minutes, at 60° C. and at boiling temperature in baths containing in 20 liters of water 40 grams of a condensation product of oleic acid and methyltaurine, 5 grams of sodium nitrilotriacetate and 20 grams of sodium carbonate, rinsed and dried. A red-violet dyeing was obtained having very good properties of fastness.

If instead of 36 grams of the diazoamino compound of diazotized 1-amino-2-methyl-4-nitrobenzene and sodium cyanamide, 38.5 grams of the diazoamino compound of 1-amino-2-methyl-4-nitrobenzene and potassium cyanamide were used a red-violet dyeing of very good fastness properties was likewise obtained.

EXAMPLE 14

1 kilogram of a mixed fiber yarn of 50 parts of cotton and 50 parts of a copolymer of acrylonitrile, vinylidene chloride and N-vinyl-2-pyrrolidone was treated at 30° C. in a goods-to-liquor ratio of 1:20 with an aqueous solution containing per liter of water 1.6 grams of 2-(2',3'-hydroxynaphthoylamino)-naphthalene, 2.2 grams of the diazoamino compound of diazotized 1-amino-2-methyl-5-chlorobenzene and sodium cyanamide, 0.5 gram of a condensation product of oleic acid and N-methyltaurine, 1.6 grams of sodium hydroxide and 33 grams of sodium chloride. The yarn was treated for 1 hour and over a period of 3-5 minutes 7 cc. of acetic acid of 50% strength were added. The yarn was treated for 30 minutes at a pH of about 5.5, thoroughly rinsed hot and cold and soaped for 30 minutes at the boil with 2 grams of a condensation product of oleic acid and methyltaurine and 0.5 gram of sodium nitrilotriacetate per liter of water, rinsed hot and cold and dried. A red dyeing having a very good covering capacity for both fibers was obtained.

EXAMPLE 15

1 kilogram of viscose staple fiber was treated at 30° C. at a goods-to-liquor ratio of 1:20 in a bath prepared as follows:

(a) 1.25 grams of 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene were dissolved in 5 cc. of denatured ethyl alcohol, 0.63 cc. of

sodium hydroxide solution of 38° Bé., 2.5 cc. of water of 60° C. and 1.25 cc. of formaldehyde solution of 30% strength;

(b) 1.8 grams of the diazoamino compound of diazotized 1-amino-2-methoxy-4-nitrobenzene and sodium cyanamide were dissolved in 80 cc. of water of 50° C.

Solutions (a) and (b) were introduced with stirring into a solution of 1 gram of a condensation product of oleic acid and methyltaurine, 3 cc. of sodium hydroxide solution of 38° Bé. and 20 grams of sodium chloride in 920 cc. of water of 30° C. The material was treated for 30 minutes, 8 cc. of acetic acid of 50% strength were slowly added and treatment was continued at a pH of about 5.5 for a further 30 minutes. The material was rinsed at a moderate temperature and in the cold and soaped, each time for 15 minutes at 60° C. and at boiling temperature, with 1 gram of a condensation product of oleic acid and methyltaurine and 0.5 gram of sodium nitrilotriacetate per liter of water, rinsed and dried. A fast black dyeing was obtained.

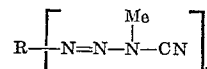
In the following table are recited a number of further diazoamino compounds to be used according to the invention as well as the tints of the azo dyestuffs produced on cellulose fibers using as coupling component 1.1 grams of 2-(2',3'-hydroxy-naphthoylamino)-3-methoxydiphenylene oxide.

TABLE

Diazoamino compound of sodium cyanamide and diazotized	Gram/liter	Goods-to-liquor ratio	pH value during coupling	Tint
1-amino-2-phenoxy-5-chlorobenzene.	1.49	1:20	4.5	Red.
1-amino-2-chlorobenzene.	1.02	1:20	4.5	Brownish red.
1-amino-2-trifluoromethyl-4-chlorobenzene.	1.35	1:20	3.5	Do.
1-amino-2-nitrobenzene.	1.08	1:20	4	Reddish-brown.
1-amino-2-methoxybenzene-5-sulfonic acid diethylamide.	1.68	1:20	5	Red.
1-amino-2-methylbenzene-5-sulfonic acid dimethylamide.	1.65	1:20	5-6	Red.
1-amino-2-(4'-chloro)-phenoxy-5-chlorobenzene.	1.70	1:20	4.5	Red.
1-amino-2-methyl-5-nitrobenzene.	1.15	1:20	4-5	Bluish red.
1-amino-3-nitrobenzene.	1.08	1:20	4	Brownish red.
1-amino-2-methoxy-5-nitrobenzene.	1.23	1:20	4-5	Claret.

We claim:

1. A process for the production of water-insoluble azo dyestuffs on textile material comprising fibers selected from the group consisting of cellulose fibers, protein fibers and fiber mixtures of cellulose and a copolymer of acrylonitrile, vinylidene chloride and N-vinyl pyrrolidone, which comprises treating the textile material in an alkaline bath which contains a coupling component highly substantive for the material to be dyed selected from the group consisting of arylamides of aromatic ortho-hydroxy carboxylic acids, arylamides of heterocyclic ortho-hydroxy carboxylic acids and arylamides of acylacetic acids and which furthermore contains a compound of the formula



in which R represents a radical of the group consisting of aromatic and heterocyclic amines, Me represents a member selected from the group consisting of an alkali metal atom and an alkaline earth metal atom and n stands for one of the integers 1 and 2, and a dispersing agent, and then treating the goods without intermediate drying with acid agents selected from the group consisting of inorganic acids, organic acids and mixtures thereof in the same bath at a temperature below 40° C.

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.

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