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3,502,425

PROCESS FOR THE PRODUCTION OF WATER-INSOLUBLE AZO-DYESTUFFS ON TEXTILE MATERIALS CONSISTING OF CELLULOSE FIBERS OR NATURAL SILK

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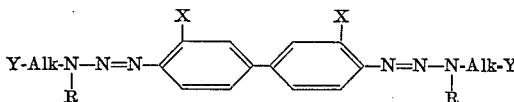
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2 Claims

ABSTRACT OF THE DISCLOSURE

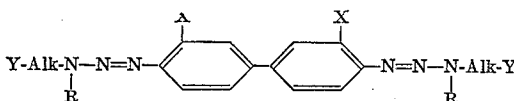
The production of water-insoluble azo-dyestuffs on textile materials of cellulose fibers or natural silk by treating the textile material in an alkaline bath containing (1) an aryl amide of the 5-hydroxy-1,2,1',2'-benzocarbazole-4-carboxylic acid, (2) a tetrazo-amino compound of the formula:



wherein X represents hydrogen, lower alkyl or lower alkoxy, R represents lower alkyl, Alk represents alkylene having 1 or 2 carbon atoms and Y represents the grouping —COOMe or —SO₂Me wherein Me stands for the monovalent radical of an alkali metal or alkaline earth metal, (3) a wetting or dispersing agent and, optionally, (4) inorganic or organic salts, and subsequently forming the dyestuff in the same bath, without intermediate drying by treatment with acid agents at a temperature below 40° C.

It is known that water-insoluble azo-dyestuffs can be produced on textile material consisting of vegetable fibers by printing the textile material with printing pastes which contain a tetrazo-amino compound of an aromatic diamine and an o-hydroxy-carboxylic acid aryl amide, drying the textile material and developing the dyestuff by a treatment with an acid at an elevated temperature. It has also been proposed to add mixtures of such tetrazoamino compounds and o-hydroxy-carboxylic acid amides onto cellulose fabrics, to dry the fabrics and to subsequently provoke coupling by a treatment with an acid. Thus, these processes require 3 stages for the production of a dyeing.

Now, we have found that water-insoluble azo-dyestuffs can be produced on textile material consisting of cellulose fibers or natural silk in a considerably simpler manner by treating the textile material in an alkaline bath which contains an aryl amide of the 5-hydroxy-1,2,1',2'-benzocarbazole-4-carboxylic acid and a tetrazo-amino compound of the general formula



in which X represents hydrogen, lower alkyl or lower alkoxy, R represents lower alkyl, Alk represents alkylene having 1 or 2 carbon atoms and Y represents the grouping —COOMe or SO₂Me in which Me stands for the monovalent radical of an alkali metal or alkaline earth metal, furthermore a wetting or dispersing agent and, if required or desired, inorganic or organic salts, and subsequently provoking the formation of the dyestuff by a

treatment with acid agents at a temperature below 40° C.

The process of the present invention is carried out in the following manner: the textile material in the form of hanks, wound bodies, combed or loose material is treated in an alkaline bath which contains the coupling component and a tetrazoamino compound of the indicated composition, a wetting or dispersing agent, and, if desired or required, inorganic or organic salts, for example, sodium chloride, a sodium phosphate, sodium sulfate or sodium acetate. The treatment is carried out for a period of at least 10 minutes in order to allow the coupling component to fix sufficiently and uniformly onto the textile material. In general, the process is carried out at room temperature or at a slightly elevated temperature, advantageously below 35° C. When the coupling component has fixed to a large extent and has levelled, an organic acid, for example, formic acid, acetic acid, tartaric acid, citric acid, lactic acid or glycolic acid or a mixture of these acids or a mixture of a mineral acid, for example, hydrochloric acid or sulfuric acid, with an organic acid is added to the bath in a quantity such that the total quantity of alkali in the bath and on the textile material is neutralised and a pH-value in the range of about 5.5 and 7 is reached. The addition of acid must be carried out very carefully, because if the indicated pH-range is exceeded or if the pH is below the indicated range, the strength of the dyestuff is reduced. Therefore, the process is preferably carried out in the presence of suitable buffers, for example, trisodium phosphate, which permit the adjustment to the optimum pH-value. When mixtures of mineral or organic acids are used, care must be taken that no local pH-variations occur.

The temperatures should be below 40° C. At this temperature, the dyestuff is formed on the textile material. The material is washed in a neutral or acid bath, if desired or required in the presence of dispersing agents, washed again, and the dyeing thus produced is processed as usual. In this manner, level dyeings which are fast to rubbing are obtained.

As coupling components, there may be used in the process of the present invention arylamides of 5-hydroxy-1,2,1',2'-benzocarbazole-4-carboxylic acid which are distinguished by a high substantivity towards the textile material used. Suitable compounds for use in the process are, for example,

- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-4-methoxybenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-2-methyl-4-methoxybenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-4-chlorobenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-4-methylbenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-2-methoxybenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-3,4-dimethoxybenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-2-methoxy-5-chlorobenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-3-methyl-4-methoxybenzene,
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-2,5-dimethoxybenzene or
- 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonyl-amino)-2,4-dimethoxybenzene.

As tetrazo-amino compounds, there may be used the compounds obtained by coupling tetrazotized benzidine or the 3,3'-dialkyl- or 3,3'-dialkoxy derivatives thereof with alkali metal salts or alkaline earth metal salts of N-alkylamino-acetic acids, N-alkylamino-propionic acids or N-alkylamino-ethane sulfonic acids.

As wetting or dispersing agents, there may be used the compounds usually applied in the ice colour technique, for example, the condensation products of higher molecular fatty acids and protein degradation products, the condensation products of higher molecular fatty acids and aminoalkyl-sulfonic acids, the condensation products of formaldehyde and naphthalene-sulfonic acids, or purified sulfite cellulose waste layer.

The process of the invention can be applied to textile material consisting of natural or regenerated cellulose or natural silk.

Compared with the dyeing processes using ice colours, the process of the present invention is much simpler. In the known dyeing processes, the dyebath is usually drained after the impregnation with the coupling component, the goods are centrifuged, squeezed with suction or rinsed intermediately and the dyestuff is developed in a second bath with a diazonium compound. In contradistinction thereto, the process of the present invention combines impregnation and development in one bath and after the period of time necessary for fixing the coupling component, coupling is effected without any other intercalated operation, which considerably reduces the time required for the whole dyeing operation.

From German Patent 1,057,061 it is known that water-insoluble azo-dyestuffs can be produced on vegetable fibers by treating these fibers at long goods-to-liquor ratios in a bath containing a coupling component and a diazo-amino or tetrazo-amino compound without solubilising groups and by subsequently developing the dyestuff by a treatment in an acid bath.

Compared with this process, the process of the present invention using substantive coupling components and the above-indicated tetrazo-amino compounds is distinguished by the fact that the development of the dyestuffs can be carried out at low temperatures and that after the addition of the acid it is not necessary to increase the temperature. A further advantage of the process of the invention resides in the fact that the tetrazo-amino compounds are present in the alkaline bath in the form of dissolved alkali metal salts and, therefore, completely penetrate into the material to be dyed, which ensures complete coupling, whereas when water-insoluble diazo-amino compounds are used, these are deposited on the surface of the material to be dyed, resulting in a poor penetration of the dye and insufficient fastness to rubbing.

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

EXAMPLE

Cross-wound bobbins of cotton were pre-wetted with a highly effective wetting agent and then treated for 30 minutes at 30° C., at a goods-to-liquor ratio of 1:13, in a bath that had been prepared as follows:

36 g. of 1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonylamino)-4-methoxybenzene were dissolved in 80 cc. of denatured ethanol, 18 cc. of sodium hydroxide solution having 38° Bé., 72 cc. of water having 70° C. and 36 cc. of a formaldehyde solution having a strength of 30%, and the whole was introduced into a bath containing 140 g. of a tetrazo-amino compound having a strength of 33% and obtained from tetrazotized 4,4'-diamino-3,3'-dimethoxy-diphenyl and the sodium salt of N-methyltaurine, 47 cc. of a sodium hydroxide solution having 38° Bé., 55.2 g. of trisodium phosphate and 13. g. of a condensation product of oleic acid and methyltaurine in about 13,000 cc. of water having 30° C.

After about 15 minutes, 260 g. of sodium chloride were added and the treatment was continued for 15 minutes. Then, 138 cc. of a 50% acetic acid were added portionwise and the treatment of the goods was continued for 30 minutes at a pH-value in the range of 6 to 6.5. The goods were then rinsed with a solution containing, per liter of water, 0.5 g. of a condensation product of oleic acid and methyltaurine, treated for 15 minutes at 60° C. with

a solution containing, per liter of water, 3 g. of a mixture consisting of 63% of perchlorethylene, 17% of a reaction product of about 10 mols of ethylene oxide with 1 mol of nonylphenol, and 20% of isopropyl alcohol, and 0.5 g. of the sodium salt of nitrilotriacetic acid, rinsed, treated at the boiling temperatures for 15 minutes with a solution containing, per liter of water, 1 g. of a condensation product of oleic acid and methyltaurine, 0.5 g. of the sodium salt of nitrilotriacetic acid and 0.5 g. of soda ash, rinsed and dried.

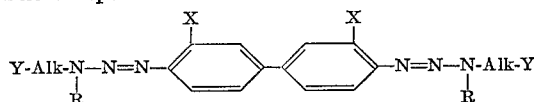
A bluish black dyeing having good properties of fastness was obtained.

The following table lists a number of further components which may be used according to the present invention and the tints of the azo-dyestuffs produced on cellulose fibers.

	Tetrazoamino-compound from tetrazotized	Coupling component	Tint
20	4,4'-diaminodiphenyl and the sodium salt of N-methyltaurine.	1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonylamino)-4-methoxybenzene.	Black.
	4,4'-diaminodiphenyl and the sodium salt of sarcosine.do.....	Do.
	4,4'-diamino-3,3'-dimethoxy-diphenyl and the sodium salt of N-methyltaurine.do.....	Do.
25	4,4'-diamino-3,3'-dimethoxy-diphenyl and the sodium salt of N-methyltaurine.	1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonylamino)-2-methyl-4-methoxybenzene.	Blue-black.
	4,4'-diamino-3,3'-dimethoxy-diphenyl and the sodium salt of sarcosine.	1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carbonylamino)-2,4-dimethoxybenzene.	Black.
30	4,4'-diamino-3,3'-dimethoxy-diphenyl and the sodium salt of N-methyltaurine.do.....	Do.
	4,4'-diamino-3,3'-dimethoxy-diphenyl and the potassium salt of N-methyltaurine.do.....	Do.
35	4,4'-diamino-3,3'-dimethoxy-diphenyl and the potassium salt of N-methyltaurine.do.....	Do.

We claim:

1. A process for the production of water-insoluble azo-dyestuffs on textile material of cellulose or silk, which comprises treating said textile material in an alkaline bath which contains (1) an arylamide of the 5-hydroxy-1,2,1',2'-benzocarbazole-4-carboxylic acid, (2) a tetrazo-amino compound of the formula



wherein X is hydrogen, lower alkyl or lower alkoxy, R is lower alkyl, Alk is lower alkylene having 1 or 2 carbon atoms and Y is the grouping —COOMe or —SO₃Me wherein Me stands for the monovalent radical of an alkali metal or alkaline earth metal, and (3) a dispersing agent, and then treating the goods in the same bath, without an intermediate drying step at a temperature below 40° C. by adding to said bath a carboxylic acid, a mixture of carboxylic acids or a mixture of a mineral acid and a carboxylic acid until a pH-value in the range of about 5.5 to about 7 is reached.

2. The process as claimed in claim 1 wherein the initial treatment of the textile material in the alkaline bath is carried out in the presence of sodium chloride, sodium phosphate, sodium sulfate or sodium acetate.

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