

UNITED STATES PATENT OFFICE

2,448,448

DYEING OF TEXTILE FIBERS CONTAINING NITROGEN

James Hutchison MacGregor, Bocking, Braintree, England, assignor to Courtaulds Limited, London, England, a British company

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2 Claims. (Cl. 8-22)

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This application is a continuation in part application of Serial No. 494,582, filed July 13, 1943, now abandoned.

This invention relates to the dyeing of textile fibres containing nitrogen, such as wool, silk, casein and nylon, with direct cotton dyestuffs from a neutral bath. While a few direct cotton dyestuffs give shades of excellent fastness to washing and milling on wool, the majority of these dyestuffs have extremely poor affinity for this fibre. It has been suggested to pretreat wool and other animal fibres with certain cationic soaps, such as cetyl pyridinium bromide, to increase the affinity of these fibres for direct cotton dyestuffs from neutral baths.

United States Patent No. 2,238,949 describes a process of treating animal fibres or other neutral or artificial fibrous or film-like materials consisting of or containing protein substances or their derivatives or containing basic amino- or imino-groups attached to residues which are not removed from the materials by rinsing with water with a substance, such for example as cyanamide and its dialkyl derivatives, which is adapted to react with an amino- or imino- group with formation of a substituted amidine, the treatment being conducted under sufficiently drastic conditions to result in a detectable chemical reaction. It is stated that such treatment effects a change in the chemical character and therefore with the affinity of the material for various agents such as for instance dyestuffs.

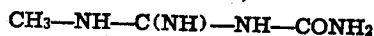
I have now found that I can obtain good dyeings on textile fibres containing nitrogen, such as wool, silk, casein and nylon, with direct cotton dyestuffs from a neutral bath by pretreating the said fibres with an aqueous solution of an amino compound as defined herein, in the presence of a small quantity of free acid.

The amino compounds used according to the present invention are cyanamide, dicyandiamide, melamine, dicyandiamidine, guanidine, biguanide, alkyl, hydroxyl-alkyl and aryl substituted dicyandiamidines, guanidines and biguanides and the salts of dicyandiamidine, guanidine, biguanide, alkyl, hydroxyalkyl and aryl substituted dicyandiamidines, guanidines and biguanides. The invention does not include the use of products obtained by the interaction of formaldehyde or compounds yielding formaldehyde or

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any of the amino compounds defined herein, and such products are not intended to be included in the hydroxyalkyl derivatives referred to above.

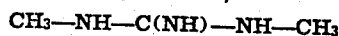
Examples of substituted dicyandiamidines are monomethyl dicyandiamidine,



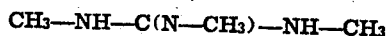
obtained by heating cyanourea and an alcoholic solution of methylamine in a sealed tube for 2 hours at 100° centigrade; dimethyl dicyandiamidine, $(\text{CH}_3)_2\text{—N—C(NH)—NH—CONH}_2$, prepared in the same way from cyanourea and dimethylamine; diphenyl dicyandiamidine,



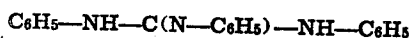
prepared in the same way from cyanourea and diphenylamine; and the tribeta-hydroxyethyl dicyandiamidine obtained by reacting the necessary quantity (3 mols) of ethylene oxide with dicyandiamidine. Examples of substituted guanidines are dimethyl guanidine,



and trimethyl guanidine,

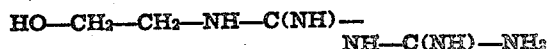


which are the NN'-dimethyl guanidine and NN'N'-trimethyl guanidine referred to by T. L. Davis and R. C. Elderfield in the "Journal of the American Chemical Society" (1932) volume 54, pages 1499-1503; mono-beta-hydroxyethyl guanidine, the hydrochloride of which is prepared by refluxing monoethanolamine and cyanamide in the presence of hydrochloric acid; di-beta-hydroxyethyl guanidine, obtained in a similar manner from diethanolamine and cyanamide; the tri-beta-hydroxyethyl guanidine obtained by the reaction of ethylene oxide (3 mols) on guanidine; monophenyl guanidine as described in the "Journal of the American Chemical Society" (1929) volume 51, page 476; di-ortho-tolyl guanidine, $\text{C}_7\text{H}_7\text{—NH—C(NH)—NH—C}_7\text{H}_7$, diphenyl guanidine, $\text{C}_6\text{H}_5\text{—NH—C(NH)—NH—C}_6\text{H}_5$, and triphenyl guanidine,

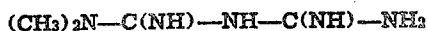


(see for example W. J. S. Naunton, "Journal of the Society of Chemical Industry," 1925, volume 44, pages 243T-247T, and British patent specifications Nos. 223,410 and 262,155). Examples of biguanide derivatives are monomethyl biguanide,

$\text{CH}_3\text{NH}-\text{C}(\text{NH})-\text{NH}-\text{C}(\text{NH})-\text{NH}_2$, prepared by heating dicyandiamide and an aqueous (25 per cent) solution of methylamine with crystalline copper sulphate under pressure at 95° centigrade; mono- beta- hydroxyethyl biguanide,



prepared in the same way using dicyandiamide and ethanolamine; dimethyl biguanide,



prepared in the same way using dicyandiamide and dimethylamine; and the triphenyl biguanide prepared by heating dicyandiamide and aniline hydrochloride in the molar proportions (3 mols) to form the triphenyl compound. Examples of suitable salts are given below.

The acid may conveniently be a weak organic acid, such as, for example, acetic acid.

The process is particularly valuable in the dyeing of union fabrics, for example those containing cellulosic fibres, including animalized cellulosic fibres, and animal fibres, particularly wool, since such union fabrics can be dyed in fast solid shades with direct cotton dyestuffs in neutral baths.

In carrying out my invention I have found that the wool or other nitrogen-containing fibre can be advantageously treated with 50 volumes of a solution of a guanidine salt, such for instance as the citrate and adipate, or with a guanidine salt of an alkyl ester of an aliphatic dibasic acid, such as guanidine ethyl oxalate and guanidine octyl succinate, or with dicyandiamide, or with a dicyandiamidine salt, such as the sulphate thereof, or with a biguanide salt, such as mono-ethanol biguanide neutral sulphate, or with cyanamide itself, the treatment being carried out in the presence of a small amount of acetic acid, say 2 cubic centimetres of 80 per cent acetic acid in each litre of solution, at the boil for about 30 minutes, and then rinsed, whereupon the dyeing can be carried out in a neutral dyebath. Among the direct cotton dyestuffs which can be employed when carrying out my invention, I may mention:

Chlorazol Fast Orange GS—Journal of the Society of Dyers and Colourists, 1938, page 269.

Chlorantine Fast Green 5G LL—Journal of the Society of Dyers and Colourists, 1938, page 269.

Chlorazol Fast Scarlet 4BS—Colour Index No. 327.

Chlorantine Fast Blue 3G LL—Journal of the Society of Dyers and Colourists, 1938, page 273.

Chlorazol Fast Orange AGS—Journal of the Society of Dyers and Colourists, 1938, page 270.

Diphenyl Brilliant Blue FF—Colour Index No. 518.

Chlorazol Black BHS—Colour Index No. 401.

Diphenyl Fast Red 7BL—Journal of the Society of Dyers and Colourists, 1938, page 273.

The following examples will serve to illustrate this invention, which however is not limited to these examples. In each of the examples the dyeing is carried out in a dyebath with a liquor to fabric ratio of 40 to 1.

Example 1

Diocetyl succinate is prepared by treating, at a temperature below 20° centigrade, 2 mols of 2-ethyl-hexanol with 1 mol of succinyl chloride, and then heating at 100° centigrade for two hours. 684 parts of diocetyl succinate are boiled with 180 parts of guanidine carbonate in 2000

parts of ethanol for 2 hours under a reflux condenser, and after filtering, the ethanol is distilled off and the residue poured into water. The aqueous mixture is then extracted with ether to remove the 2-ethyl-hexanol and the aqueous layer evaporated to dryness when the guanidine octyl succinate is obtained as a white soapy solid, soluble in water. A length of an all woollen fabric is treated for 30 minutes at the boil in an aqueous solution containing 1 gram of guanidine octyl succinate and 2 cubic centimetres of 80 per cent acetic acid per litre of solution, the liquor to fabric ratio being 50-1. The fabric is then rinsed and immersed in a neutral dyebath at 60° centigrade containing 2 per cent of Diphenyl Brilliant Blue FF (Colour Index No. 518) calculated on the weight of the wool. The temperature of the dyebath is raised in 15 minutes to 95° to 100° centigrade and dyeing continued for one hour at this temperature, whereupon the wool is dyed a full shade of blue, and the bath is practically exhausted. The fastness to light and washing of the dyed fabric is better than that of a similar dyeing on untreated cellulosic material, while untreated wool is merely tinted.

Example 2

2/24's woollen yarn is treated for 30 minutes at the boil in an aqueous solution containing 1 gram of guanidine adipate and 2 cubic centimetres of 80 per cent acetic acid per litre, the liquor to yarn ratio being 50 to 1. The yarn is then rinsed and dyed in accordance with the procedure given in Example 1 in a neutral bath containing 2 per cent of Chlorantine Fast Blue 3G LL, calculated on the weight of the wool. A full shade of blue is obtained and the bath is practically exhausted. Untreated wool when dyed in the same bath is merely tinted.

Example 3

2/24's woollen yarn is treated for 30 minutes in 50 volumes of a boiling 0.5 per cent aqueous solution of mono-beta-hydroxyethyl biguanide neutral sulphate (prepared as described in Example 11 of U. S. patent specification No. 2,223,935), containing 3 cubic centimetres of 80 per cent acetic acid per litre. The yarn is then rinsed and dyed in accordance with the procedure given in Example 1 in a neutral dyebath containing 2 per cent of Chlorazol Fast Scarlet 4BS, calculated on the weight of the wool. A full shade of scarlet is obtained, and the bath is practically exhausted.

Example 4

2/24's woollen yarn is treated for 30 minutes at the boil in 50 volumes of a 0.5 per cent aqueous solution of dicyandiamidine sulphate, containing 2 cubic centimetres of 80 per cent acetic acid in each litre. The yarn is then rinsed and dyed in accordance with the procedure given in Example 1 in a neutral dyebath containing 2 per cent of Chlorazol Fast Scarlet 4BS, calculated on the weight of the wool. A full shade of scarlet is obtained, and the bath is practically exhausted.

Example 5

A length of dress fabric composed of a spun viscose staple fibre warp and a Botany worsted weft is treated for 30 minutes with 50 volumes of a boiling 0.5 per cent aqueous solution of guanidine octyl succinate containing 2 cubic centimetres of 80 per cent acetic acid per litre. The fabric is then rinsed lightly and dyed with 8 per cent Chlorazol Black BHS and 35 per cent of

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common salt, based on the weight of the fabric. The salt is added gradually over a period of 20 minutes, while the bath is maintained at a temperature of 60° centigrade. The temperature is then raised to from 95° to 100° centigrade and the dyeing is continued at this temperature for one hour. Both the spun viscose and the wool are dyed to the same depth and a solid navy shade is obtained, which is very fast to washing.

Example 6

A length of an all woollen fabric is treated for 30 minutes at the boil in 50 volumes of an aqueous solution containing 1 gram of guanidine cetyl succinate (prepared as described in Example 5 of my co-pending British patent specification No. 558,892) and 2 cubic centimetres of 80 per cent acetic acid per litre. The fabric is then rinsed and dyed in accordance with the procedure given in Example 1 in a neutral bath containing 2 per cent of Diphenyl Fast Red 7BL, calculated on the weight of the wool. The wool is dyed a full shade of red and the bath is almost entirely exhausted. The fastness to light and to washing of the so dyed wool is distinctly better than that of a similar dyeing with Diphenyl Fast Red 7BL on untreated viscose fabric.

Example 7

A length of an all woollen fabric is treated for 30 minutes at the boil in 50 volumes of an aqueous solution containing 10 cubic centimetres of a 50 per cent cyanamide solution and 2 cubic centimetres of 80 per cent acetic acid per litre. The fabric is then rinsed and dyed in accordance with the procedure given in Example 1 in a neutral bath containing 2 per cent of Diphenyl Fast Red 7BL, based on the weight of the wool. The wool is dyed a full shade of red and the bath is almost entirely exhausted, while the fastness to washing of the dyeing is better than that of a similar dyeing of Diphenyl Fast Red 7BL on untreated viscose fabric.

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What I claim is:

1. A process of dyeing nitrogenous textile fibres which comprises treating the said fibres with an aqueous solution containing a small quantity of free acid and a compound selected from the group consisting of cyanamide, dicyandiamide, melamine, dicyandiamidine, guanidine, biguanide, alkyl, hydroxyalkyl and aryl substituted dicyandiamidines, guanidines and biguanides, and salts of dicyandiamidine, guanidine, biguanide and the alkyl, hydroxyalkyl and aryl substituted dicyandiamidines, guanidines and biguanides, and dyeing the thus-treated fibres with a direct cotton dyestuff from a neutral bath.

2. A process of dyeing union fabrics containing nitrogenous and cellulosic fibres which comprises treating the said fabric with an aqueous solution containing a small quantity of free acid and a compound selected from the group consisting of cyanamide, dicyandiamide, melamine, dicyandiamidine, guanidine, biguanide, alkyl, hydroxyalkyl and aryl substituted dicyandiamidines, guanidines and biguanides, and salts of dicyandiamidine, guanidine, biguanide and the alkyl, hydroxyalkyl and aryl substituted dicyandiamidines, guanidines and biguanides, and dyeing the thus-treated fabric with a direct cotton dyestuff from a neutral bath.

JAMES HUTCHISON MacGREGOR.

REFERENCES CITED

The following references are of record in the file of this patent:

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2,238,949	Schlack	Apr. 22, 1941
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