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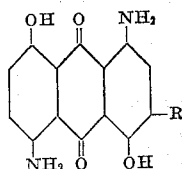
3,043,646

DYEING OF ARTIFICIAL FIBERS

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6 Claims. (Cl. 8—40)

It has been found that the anthraquinone dyestuffs of the formula



wherein R stands for an aryl radical which may contain substituents except halogen atoms standing in para-position to the O—X-group or nitro or amino groups and which contains in the nucleus combined with the anthraquinone radical at least one —O—X-group in which X represents a hydrogen atom or an alkyl, cycloalkyl or aryl radical which may be further substituted, used alone or in mixtures with each other are eminently suitable for the dyeing of cellulose ester, synthetic polyamide and polyester fibers from aqueous suspension.

In many cases the mixtures of two or more dyestuffs of the Formula I show better building-up properties than the dye-stuffs used alone.

The dyeing operation is conducted advantageously in presence of wetting, dispersing or emulsifying agents such as Marseilles soap, fatty alcohol sulfonates or sulfates, e.g. sodium lauryl sulfate, or the condensation products of fatty acids, e.g. oleic acid, with the alkali metal salts of amino- and methyl-amino-ethane-sulfonic acid, highly sulfonated castor oil, etc.

The dyeing temperatures and times depend upon the material to be dyed and are correlated with each other. Secondary cellulose acetate can be dyed at temperatures between 75° and 90° C., preferably at 80–85° C., for 45 minutes to 1½ hours, preferably for 1 hour. But it is also possible to work at 95°–100° C. e.g. in the case of blended fabrics containing viscose and acetate, and even at about 120° C. under pressure, with a corresponding reduction of the dyeing time.

Cellulose triacetate and the synthetic polyamide fibers and dyed at 90–100° C. for 45 minutes to 1½ hours, preferably for 1 hour at the boil, or at temperatures between 105° and 120° C. under pressure, whereby the dyeing time can be shortened.

Polyester fibers, when dyed for about 1 hour at 95°–100° C., require the presence of a carrier: 2-hydroxy-1,1'-diphenyl, the methyl ester of 2-hydroxybenzene-1-carboxylic acid, benzoic acid or an emulsion of chlorinated benzene, whereas at temperatures higher than 100° C., e.g. between 110° and 130° C. the addition of a carrier is superfluous.

In any event when the dyeing temperature exceeds 100° C. and in the case of secondary cellulose acetate already when the dyeing temperature amounts to 95°–100° C., the dyebath must be maintained neutral in order to prevent saponification of the fibers.

2

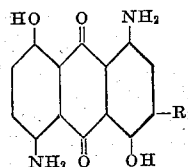
To enhance the degree of dispersion, the dry dyestuffs may be preliminarily ground with a suitable wetting or dispersing agent, such as sodium dinaphthylmethanedisulfonate, sodium ligninsulfonate or the dried residue of sulfite waste liquor. The dyestuffs may also be intimately mixed in the form of an aqueous paste with one of the aforesaid wetting or dispersing agents and, if desired, converted into the form of a dyestuff powder by suitable drying.

The dyeings obtained with these dyestuffs on secondary cellulose acetate possess excellent light fastness and good fastness to washing, perspiration and gas fumes. On cellulose triacetate and polyester fibers they give dyeings of very good fastness to light, heat setting and pleating, and good fastness to washing and perspiration. The dyestuffs reserve wool, cotton and viscose rayon.

The dyeings on synthetic polyamide fibers are fast to light, washing and perspiration.

In Formula I R preferably represents a mono-, di- or trihydroxyphenyl radical, a monohydroxy, monomethoxy- or monoethoxynaphthyl radical, a mono- or dimethoxy- or -ethoxy-phenyl radical or a monohydroxymonomethoxy- or -monoethoxy-phenyl radical.

Of the anthraquinone dyestuffs of Formula I, those of the formula



wherein R₁ stands for a hydroxyphenyl, hydroxynaphthyl, methoxyphenyl or dihydroxyphenyl radical, are already known. They are obtained e.g. by (1) addition of phenol at the boric acid ester of 1,5-dihydroxy-4,8-diaminoanthraquinone-2,6-disulfonic acid in concentrated sulfuric acid solution (GP 445,268), (2) boiling the addition product in acid aqueous solution or heating it in alkaline solution at 20–60° C. to split off one sulfonic acid group (GP 446,563), (3) reductive splitting off from the latter of the remaining sulfonic acid group (GP 456,235).

The anthraquinone dyestuffs used in the present process are produced in an analogous manner.

In the following examples the parts and percentages are by weight and the temperatures in degrees centigrade.

Example 1

A dyebath is prepared with 1 part of the dyestuff 1,5-dihydroxy-4,8-diamino-2-(4'-hydroxy)-phenylanthraquinone dispersed with Turkey red oil, 6 parts of a sulfonated fatty alcohol, and 3000 parts of water. 100 parts of cellulose triacetate are entered in the bath at room temperature and the temperature is raised to 100° in 1 hour and maintained at 100° for a further hour. After this time the dyeing process is completed. The goods are removed, rinsed and dried. They are dyed a blue shade of good fastness to washing, gas fumes, heat setting and pleating, and very good light fastness. The dyestuff gives a good reserve of wool. To improve

the dispersion the dyestuff can be previously ground with wetting, dispersing or emulsifying agents, or intimately mixed with a dispersing agent to form an aqueous paste which is then converted into a powder by drying under suitable conditions.

Example 2

1 part of 1.5-dihydroxy-4.8-diamino-2-(4'-methoxy)-phenylanthraquinone, 1 part of the sodium salt of dinaphthylmethanedisulfonic acid and 8 parts of water are ground together until a fine dispersion is formed. It is run into a dyebath consisting of 3000 parts of water and 6 parts of Marseilles soap. 100 parts of a cellulose acetate fabric are entered in the dyebath; the temperature is raised to 80° in 30 minutes and this temperature maintained for 1 hour. Then the fabric is removed from the dyebath, rinsed with water and dried. A bright blue dyeing is obtained which has excellent light fastness and good fastness to washing, perspiration and gas fumes.

Example 3

100 parts of "Dacron" polyethylene terephthalate fibers made by the condensation of dimethyl terephthalate and ethylene glycol (see "Handbook of Material Trade Names," by Zimmermann and Lavoine, 1953 edition, p. 159) are entered in a dyebath at 60° containing 3000 parts of water, 2 parts of the dyestuff used in Example 1, and 1.5 parts of 2-hydroxy-1.1'-diphenyl. The dyebath is brought to the boil in 20 minutes and boiled for 1 hour. The goods are then removed, rinsed with water and dried. The "Dacron" fabric is dyed an attractive blue shade which is fast to washing and has very good fastness to light, heat setting and pleating. Cotton present in the dyebath is reserved.

Example 4

A fine dyestuff dispersion is prepared with 1 part of 1.5-dihydroxy-4.8-diamino-2-(4'-ethoxy)-phenylanthraquinone, 1 part of sulfite cellulose waste liquor (in powder form) and 8 parts of water. This paste is added to a dyebath of 3000 parts of water and 3 parts of Igepon T in a high-temperature dyeing machine. 100 parts of "Terylene" polyester fiber are added, the machine closed, and the inner temperature increased to 120°. After 1 hour at this temperature dyeing is completed. The material is removed, rinsed and dried. It is dyed a blue shade which shows good washing and perspiration fastness and very good fastness to light, heat setting and pleating. Wool present in the dyebath is reserved. "Dacron," "Dralon" and "Tergal" polyester fibers can be dyed by the same method.

Example 5

1 part of 1.5-dihydroxy-4.8-diamino-2-(4'-methoxy)-phenylanthraquinone, 1 part of the sodium salt of dinaphthylmethanedisulfonic acid and 8 parts of water are ground together until a fine dispersion is obtained. It is run into a dyebath containing 4000 parts of water and 4 parts of a highly sulfonated castor oil. 100 parts of a "Nylon 66" fabric are entered in the bath and the temperature is increased to 100° in 45 minutes. Dyeing is continued for 1 hour at 95-100°. The nylon is then rinsed in warm and cold water and dried. It is dyed a bright blue shade which has very good fastness to washing and perspiration and good light fastness.

With other synthetic polyamide fibers such as "Perlon" (=Nylon 6), "Mirlon," "Grilon" or "Rilsan" dyeings of similar fastness properties are obtained.

In the following table are listed further dyestuffs of Formula I which are highly suitable for dyeing cellulose acetate, cellulose triacetate, and synthetic polyamide polyester fibers. They are characterized in the table by the hydrocarbon radical RH forming the basis of the radical R, the dyeing material, and the shade of the dyeing.

Example No.	R-H	Dyeing Material	Shade of the Dyeing
5			
6	phenoxybenzene	Dacron	blue
7	1-hydroxy-2-chlorobenzene	do	reddish blue
8	1-hydroxy-2-methylbenzene	acetate	sky-blue
9	1-hydroxy-3-methylbenzene	Dacron	blue
10	1-hydroxy-4-methylbenzene	do	Do.
11	1-hydroxy-4-ethylbenzene	acetate	Do.
12	1-hydroxynaphthalene	do	Do.
13	2-hydroxynaphthalene	Dacron	Do.
14	1-hydroxy-2-amylnbenzene	acetate	sky-blue
15	1-hydroxy-4-amylnbenzene	cellulose-tri-acetate	Do.
16	1-hydroxy-4-octylbenzene	do	Do.
17	1-hydroxy-4-cyclohexylbenzene	do	reddish blue
18	1-hydroxy-2-phenylbenzene	acetate	Do.
19	1-hydroxy-4-phenylbenzene	Dacron	blue
20	1-hydroxy-2,6-di-isopropylbenzene	do	Do.
21	1-hydroxy-2-tert-butyl-5-methylbenzene	do	Do.
22	1-hydroxy-2,6-dimethylbenzene	do	Do.
23	1,2-dimethoxybenzene	do	Do.
24	1,4-dimethoxybenzene	acetate	Do.
25	1-hydroxy-2-methoxybenzene	do	Do.
26	1-hydroxy-4-methoxybenzene	acetate	sky-blue
27	(2'-hydroxy)-ethoxybenzene	cellulose-tri-acetate	Do.
28	1,2-dihydroxybenzene	Dacron	blue-violet
29	1,3-dihydroxybenzene	acetate	blue
30	1,4-dihydroxybenzene	Dacron	Do.
31	1-methoxy-4-methylbenzene	acetate	reddish blue
32	4'-amino-phenoxybenzene	do	blue
33	1-methoxy-4-propenylbenzene	do	Do.
34	1-hydroxy-2-methoxy-4-allylbenzene	Dacron	Do.
35	[2'-(2'-hydroxy)-ethoxy]ethoxybenzene	do	sky-blue
36	1,3,5-trihydroxybenzene	do	reddish blue
37	1-hydroxy-2-benzoyl-5-methoxybenzene	acetate	blue
38	2,2-bis(4'-hydroxyphenyl)-propane	Dacron	sky-blue
39	2-bromomethoxybenzene	do	blue
40	2-chloromethoxybenzene	do	Do.
41	3'-methoxypropoxybenzene	do	sky-blue
42	2'-ethoxyethoxybenzene	Nylon 66	blue
43	1-hydroxy-4-ethoxybenzene	acetate	sky-blue

Example 44

100 parts of "Dacron" polyester fiber are entered in a dyebath at 60° containing 3000 parts of water, 1 part of the dyestuff used in Example 1, 1 part of the dyestuff of Example 2 and 1.5 parts of 2-hydroxy-1.1'-diphenyl. The dyebath is brought to the boil in 20 minutes and boiled for 1 hour. The goods are then removed, rinsed with water and dried. The "Dacron" fabric is dyed an attractive blue shade which is fast to washing and has very good fastness to light, heat setting and pleating. Cotton or wool present in the dyebath is reserved.

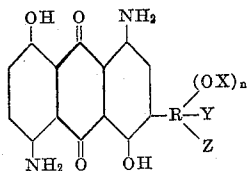
Other dyestuff mixtures suitable for the dyeing of acetate, triacetate and polyester fibers are e.g. the following: 1.5-dihydroxy-4.8-diamino-2-(4'-methoxy)-phenylanthraquinone and 1.5-dihydroxy-4.8-diamino-2-(2'-hydroxy-5'-amyl)-phenylanthraquinone, 1.5-dihydroxy-4.8-diamino-2-(4'-methoxy)-phenylanthraquinone and 1.5-dihydroxy-4.8-diamino-2-(4'-ethoxy)-phenylanthraquinone, 1.5-dihydroxy-4.8-diamino-2-(4'-ethoxy)-phenylanthraquinone and 1.5-dihydroxy-4.8-diamino-2-(4'-hydroxy)-phenylanthraquinone, etc. When used in equal concentration these mixtures yield stronger dyeings than the dyestuff 1.5-dihydroxy-4.8-diamino-2-(4'-methoxy)-phenylanthraquinone alone. In the case of weak dyeings the exhaust (i.e. the patterns used in the second dyeing process) remain white.

Having thus disclosed the invention what I claim is:

1. A dyeing process comprising applying to an artificial fiber material selected from the group consisting of secondary cellulose acetate, cellulose triacetate, and polyethylene terephthalate fibers, from an aqueous dispersion,

5

a member selected from the group consisting of a single anthraquinone dyestuff and a mixture of anthraquinone dyestuffs of the formula



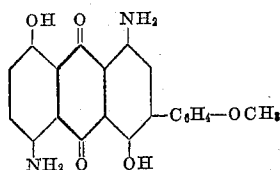
wherein R represents a member selected from the group consisting of radicals of the benzene, diphenyl and naphthalene series,

X represents a member selected from the group consisting of hydrogen, lower alkyl, lower hydroxy-alkyl, lower alkoxyalkyl, lower hydroxy-alkoxyalkyl, lower halogeno-alkyl, phenyl and aminophenyl,

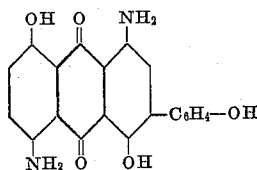
Y represents a member selected from the group consisting of hydrogen, alkyl with 1 to 8 carbon atoms, alkoxy with 1 to 2 carbon atoms, alkenyl with 3 carbon atoms, cyclohexyl and chlorine provided that the latter stands in a other than the para-position to the —OX-group,

Z represents a member selected from the group consisting of hydrogen, lower alkyl and lower alkoxy, n represents one of the integers 1, 2 and 3. and

2. A dyeing process comprising applying to an artificial fiber material selected from the group consisting of secondary cellulose acetate, cellulose triacetate, and polyethylene terephthalate fibers, from an aqueous dispersion, the anthraquinone dyestuff of the formula



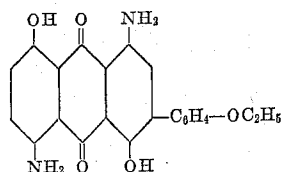
3. A dyeing process comprising applying to an artificial fiber material selected from the group consisting of secondary cellulose acetate, cellulose triacetate, and polyethylene terephthalate fibers, from an aqueous dispersion, the anthraquinone dyestuff of the formula



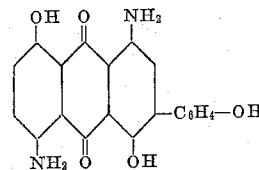
4. A dyeing process comprising applying to an artificial fiber material selected from the group consisting of secondary cellulose acetate, cellulose triacetate, and poly-

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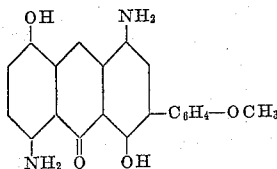
ethylene terephthalate fibers, from an aqueous dispersion, the anthraquinone dyestuff of the formula



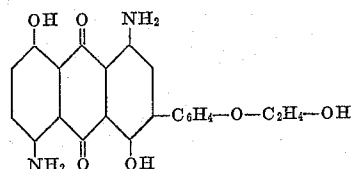
5. A dyeing process comprising applying to an artificial fiber material selected from the group consisting of secondary cellulose acetate, cellulose triacetate, and polyethylene terephthalate fibers, from an aqueous dispersion, a mixture of the two dyestuffs of the formulae



and



6. A dyeing process comprising applying to an artificial fiber material selected from the group consisting of secondary cellulose acetate, cellulose triacetate, and polyethylene terephthalate fibers, from an aqueous dispersion, the anthraquinone dyestuff of the formula



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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,043,646

July 10, 1962

Paul Buecheler

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 27, before "n", in italics, insert -- and --; line 28, strike out "and".

Signed and sealed this 16th day of June 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents