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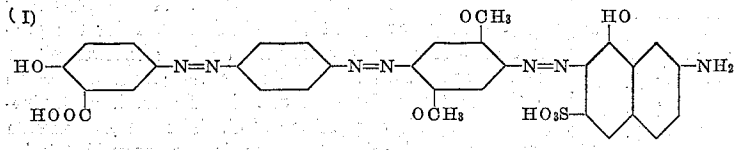
PROCESS FOR THE PRODUCTION OF BLACK DYEINGS ON CELLULOSE FABRICS

Bernhard Kramer, Cologne-Braunsfeld, and Gerd Henes, Opladen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

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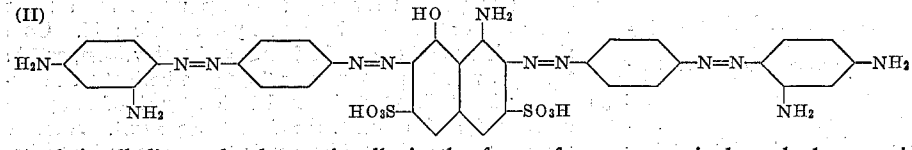
It has been found that fast deep black dyeings are obtained on cellulose fabrics when a mixture of azo dyestuffs of the composition

(I)



and

(II)



or their alkali metal salts, optionally in the form of a mixture with other toning dyestuffs, is diazotised on the fibre and combined with coupling components free from sulphonic acid groups.

The dyestuffs to be employed according to the process are known polyazo dyestuffs by the use of which black dyeings may be produced on cellulose fabrics, and in particular on textile materials of native or regenerated cellulose. Although the dyestuffs are satisfactory in respect of their fastness properties, they produce weak (empty) dyeings on staple rayon. On the other hand, diazotisation black dyestuffs are known for cellulose but their dyeings do not exhibit the necessary fastness properties. By the use of the mixture to be employed in accordance with the process, it becomes possible to achieve deep bloomy black shades on cotton as well as on cellulose fibre without any reduction in the fastness level of the individual dyestuffs.

The diazotisation on the fibre of the mixtures to be employed according to the process is carried out by the method known for diazotisation dyestuffs. In order to produce intensive full black shades, between 5 and 10% of the dyestuff mixture is applied in practice on cotton and on cellulose fibre. Dyeings on skeins, cross wound bobbins and piece goods lead to results of the same quality.

The process is carried out in detail in that the goods are padded with the mixture of the specified dyestuffs, optionally with the addition of other toning dyestuffs, for instance on a Foularding machine at an elevated temperature, preferably a temperature of 50 to 75° C., and that they are subsequently steamed, rinsed, and squeezed out. The fabric is then treated in a bath containing the required amount of sodium nitrite. A further bath treatment follows, where hydrochloride acid is applied at an elevated temperature so as to cause diazotisation. It is subsequently rinsed in the cold and finally developed at an elevated temperature in a bath containing a solution of the coupling component. When the developed dyeing has been rinsed again, it can be washed or after-treated with soap. The wet fastness properties can be improved in known manner by the addition

of suitable assistants, for instance of cation-active after-treatment agents, during the diazotisation or the coupling operation, or subsequent to coupling.

In accordance with the choice of the coupling component selected for development, different colour shades of black are obtained. Thus, if development is for instance carried out with the aid of an alkaline solution of 2,4-toluylene diamine, a full brownish black colour is obtained, whereas development with an alkaline solution of β-naphthol produces a more bluish black colour. Other suitable coupling components which may be applied in the form of their alkali metal salts or of their salts with hydracids are, for instance, m-phenylene diamine, α - naphthol, 1 - phenyl-3-methyl-5-pyrazolone, resorcinol, m-hydroxy-aminobenzene, 2,3-hydroxynaphthoic acid, N - ethyl - β - naphthylamine, 4 - chloro - 1,3-diaminobenzene, phenol, N-ethyl-α-naphthylamine and 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester.

The mixture proportions of the dyestuffs (I) and (II), optionally in conjunction with other toning dyestuffs, may vary within wide limits, for instance in the range 1:5 to 5:1, the preferred range being 1:2 to 2:1.

The developed black dyeings are not subsequently coppered. It is surprising that the dyeings nevertheless exhibit the same good fastness properties as dyeings with mixtures of the dyestuffs (I) and (II) which had been treated with copper discharging agents, although on comparison with the latter they exhibit the advantage of giving a considerably deeper coloration on rayon staple. The mixture may contain a proportion of about 1 to 35% of the usual dyestuffs employed as toning or accompanying dyestuffs in black mixtures, such as p,p'-diaminodiphenylurea→salicyclic acid; 4-amino-1-methylbenzene-2-sulphonic acid→3 - amino - 1 - glycolylamino - benzene, treated with phosgene; C-acid→α-naphthylamine→Cleve acid-1,7→I-acid; C-acid→α-naphthylamine→Cleve acid-1,7→I-acid; salicyclic acid←benzidine→(o-chloraniline-5-sulphonic acid→resorcinol), dyestuff coppered; copper complex of 2-amino-5-sulphobenzoic acid→1-(4'-aminophenyl) - 3 - methyl - 5 - pyrazolone→1-amino-2-ethoxynaphthalene-6-sulphonic acid→phenyl-I-acid, salicyclic ←p-nitraniline, reduced→aminohydroquinone - dimethyl ether$\xrightarrow{alk}$γ-acid condensation product of 1-amino-4-(4'-amino-phenylamino)-anthraquinone - 2 - sulphonic acid with the urethane from 4-amino-4'-hydroxy-3'carboxy-1,1'-azobenzene; and nitroanthranilic acid→phenyl-I-acid, reduced, treated with phosgene and coppered.

The results attained with the mixture to be employed according to the invention not only produce an advantage in dyeing in relation to the nearest comparable dyestuffs, but in addition they are unexpected since it may be seen from Colour Index, 2nd edition, volume II, page 2332 (Benzo Fast Black G=C.I. Direct Black 19) and page 2358 (Benzo Fast Copper Black GL=C.I. Direct Black 95) that both the individual dyestuffs are said to be unsuitable for diazotisation on the fibre and subse-

quent development.

The following examples, wherein the term "parts" denotes parts by weight, are given for the purpose of illustrating the invention.

Example 1

A 5 to 7% dyeing is prepared on cotton or staple rayon in accordance with the usual method of dyeing with the addition of 10 to 40% of Duisburg sodium sulphate, using a mixture of:

(a) 40 parts of dyestuff (I) (concentration 50:100) and
(b) 30 parts of dyestuff (II) (concentration 35:100), or with a mixture of
(c) 45 parts of dyestuff (I) (concentration 40:100) and
(d) 35 parts of dyestuff (II) (concentration 25:100) and
(e) 25 parts of the azo dyestuff 1-amino-4-nitrobenzene-2 - carboxylic acid→2-phenylamino-5-hydroxy-naphthalene-7-sulphonic acid, reduced at the nitro groups and treated with phosgene and coppered (concentration 80:100) and
(f) 15 parts of the azo dyestuff which is obtained by treatment of approximately equimolar amounts of 4-amino - 4'-hydroxy-3'-carboxy-1,1'-azobenzene and 1-amino - 4-(4' - aminophenylamino)-anthraquinone-2-sulphonic acid with phosgene (concentration 70:100),

dyeing being carried out at about 80 to 95° C. during 1 to1.5 hours.

The resultant dyeings are thoroughly rinsed and treated for 20 minutes in a fresh cold aqueous bath containing 0.75 to 1.5 g./l. of sodium nitrite and 2.5 to 4 ml. of hydrochloric acid (20° Bé.) or, if iron vessels are employed, 1.5 to 2.5 ml. of sulphuric acid (66° Bé.) so that they are diazotised. It is thereafter thoroughly rinsed again and the dyeing is at once developed in a fresh aqueous bath containing a solution of 0.8 to 1.5 g./l. of β-naphthol or 0.5 to 1 g./l. of 2,4-toluylene diamine. The treatment in the developing liquid requires about 20 to 30 minutes and is carried out at room temperature. A full black with excellent fastness properties is obtained.

The mixtures with other accompanying or toning dyestuffs mentioned in the description may also be employed with the same good results in place of the dyestuff mixtures applied in this example. The proportions in the mixture may vary, depending on the character of the desired shade of black.

Other developing agents, such as the salts mentioned in the description, may also be employed in place of the developing agents β-naphthol and 2,4-toluylene-diamine employed in this example.

Dyestuff mixtures are generally adjusted to the desired concentration with the aid of assistants such as sodium carbonate, dextrine, trisodium phosphate, sodium sulphate and the like. The two dyestuff mixtures mentioned under (a) to (f) may for instance be diluted with 10 parts of sodium carbonate and 7 parts of dextrine and 16 parts of trisodium phosphate.

Example 2

A fabric of cotton or staple rayon is foularded by the usual method at a residual moisture content of 80% and a temperature of 60–70° C., 20 g. of a dyestuff is employed which in this case consists of the following individual components:

30 parts of dyestuff (I) (concentration 20:100),
15 parts of dyestuff (f) from Example 1,
33 parts of dyestuff II (concentration 30:100), and
22 parts of dyestuff (e) from Example 1.

The dyestuff mixture is diluted with 9.5 parts of sodium carbonate, 7 parts of dextrine and 16 parts of trisodium phosphate.

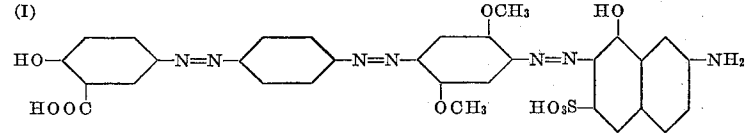
The fabric is sequentially steamed at 103° C., and thereafter the goods are passed through a rinsing box filled with water, squeezed out and treated in two further vessels each of which contains 20 g./l. of sodium nitrite and is kept at a temperature of 50° C. A subsequent air passage lasting for about 15 seconds serves for the purpose of improving the penetration of the sodium nitrite into the fibre. After the air passage, the goods are passed into the next vessel which contains 50 cc./l. of hydrochloric acid and is warmed to 40° C. The above described intermediate foularding operation is necessary if it is intended to prevent too much sodium nitrite from being carried over into the bath of hydrochloric acid. Cold rinsing is carried out in the fourth and fifth vessels, and in the sixth vessel the goods pass through a bath at a temperature of 40° C. which is filled with 10 g./l. of toluylene diamine (pH 8 to 8.5), the developing agent. Another air passage for about 15 seconds follows in order to improve the coupling of the dyestuff. It is then rinsed in the seventh and eighth vessel, or soaped with 1 to 2 g./l. of the sodium salt of a paraffin-sulphonic acid at 40–60° C. The sodium nitrite, hydrochloric acid and developer baths have to be replenished by continuous further additions.

In the description and the examples the arrows → or ← are to indicate the coupling direction of the diazo compound of the diazotizable amine upon the given coupling component; "alk" means that coupling takes place under alkaline conditions and thus occupies the o-position relative to the —OH group of the coupling component. The double arrow indicates coupling of 1 mol of the tetrazo compound with two mols of the coupling component. I-acid is 2-amino-5-hydroxynaphthalene-7-sulfonic acid, γ-acid is 2-amino-8-hydroxynaphthalene-6-sulfonic acid, phenyl-I-acid is 2-phenylamino-5-hydroxynaphthalene-7-sulfonic acid, Cleve acid-1,7 is 1-amino-naphthalene-7-sulfonic acid, and C-acid is 2-amino-naphthalene-4,8-disulfonic acid.

We claim:

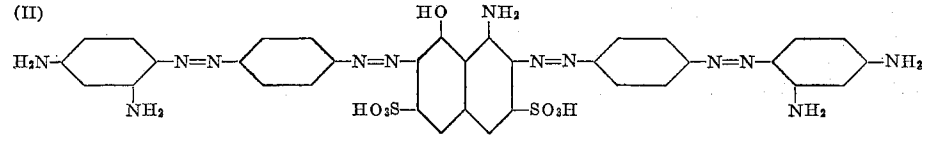
1. Process for the production of black dyeings on cellulose fabrics, which comprises applying a mixture of azo dyestuffs which in the free acid state are of the formula

(I)



and

(II)



diazotizing them on the fibre and combining with coupling components free of sulfonic acid groups.

2. Process according to claim **1** wherein the dyestuffs are applied onto the cellulosic fabrics in admixture with other toning dyes.

3. Process according to claim **1**, characterised in that a proportion of about 1:2 to 2:1 of said dyestuffs is present in the mixture.

4. Cellulose fabrics dyed in accordance with the process of claim **1**.

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NORMAN G. TORCHIN, *Primary Examiner.*

T. J. HERBERT, *Assistant Examiner.*