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UNITED STATES PATENT OFFICE

2,263,559

PROCESS OF PRODUCING FAST DYEINGS AND THE DYED FIBER OBTAINED THEREBY

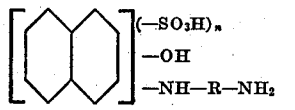
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14 Claims. (Cl. 8—46)

The present invention relates to the production of fast dyeings and to the dyed fiber obtained thereby.

I have found that dyeings of good properties of fastness on animal fibers, natural or artificial cellulose fibers, as well as on mixtures of animal fibers with cellulose fibers may be obtained by applying to the fiber a salt of a sulphonic acid of the following constitution:



wherein n represents the number 1 or 2 and R represents one of the following atomic groupings: —CO—aryl—NHCO—aryl—, —CONH—aryl—NHCO—aryl—, —CONH—aryl—NHCONH—aryl—, —CO—aryl—NHCONH—aryl—, —CO—aryl—NHCO—aryl—NHCO—aryl or longer chains wherein the members —NHCO—aryl— and —NHCONH—aryl— may be present in any number and any order, with the exception of such derivatives as do not contain in the naphthalene ring a free position capable of coupling with diazo compounds, then diazotizing the compound and causing it to combine with itself. The aryl radicals may contain substituents as, for instance, alkyl-, alkoxy-, trifluoromethyl- or nitro-groups.

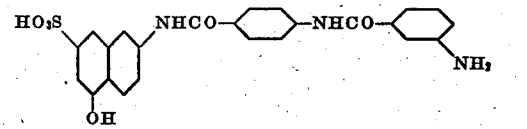
The self-coupling may be performed or completed, for instance, by adding to the diazo-bath an agent neutralizing the acid or having an alkaline action, after the diazotization is finished, or by passing the goods through a bath having an alkaline action.

The salts of the sulphonic acids of the constitution indicated above may be applied to the fiber in a neutral or feebly acid bath; thus damage of the animal fiber is avoided, whereas, for instance, the process of preparing insoluble azo-dyestuffs on the fiber by self-coupling amino-arylides of hydroxy-carboxylic acids as described in U. S. Patent No. 1,922,463, cannot be applied to animal fibers, since the amino-arylides of the hydroxy-carboxylic acids must be brought on the fiber in a strongly alkaline bath. For the same reason the self-coupling dyestuffs described by J. S. Turski in "Melliand's Textilberichte" (1937), vol. XVIII, part 1, page 75, cannot be used for animal fibers and mixtures thereof with cellulose fibers.

The new process is distinguished by a simple mode of application and by a high degree of certainty in the dyeing operation. The dyeings obtained have a good fastness to wet processing and very good fastness to rubbing; those obtained on mixtures of wool and staple fiber from regenerated celluloses are of especial value, if in the above-indicated formula n represents the number 1, since the fibers may be dyed uniformly.

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

1. 1 kilo of mixed yarn consisting of 30 parts of staple fiber from viscose and 70 parts of wool is treated for 1 hour at 85° C. in a solution containing per 24 litres of liquor 30 grams of the sodium salt of 3''-amino-4'-benzoyl-amino-2-benzoylamino - 5 - hydroxynaphthalene - 7 - sulphonic acid of the following constitution:



and 50 grams of ammonium sulphate. The whole is then cooled to about 70° C. by adding 60 grams of sodium sulphate dissolved in 6 litres of cold water and allowed to stand for 1 hour at this temperature. The goods are then centrifuged and treated for ½ hour in the cold in a fresh bath containing:

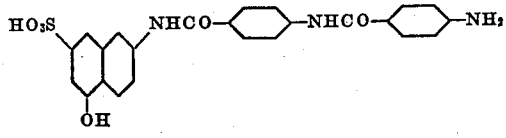
30 grams of sodium nitrite,
80 grams of formic acid of 85 per cent strength and
30 grams of sodium dibutylnaphthalenesulphonate in
30 litres of cold water,

then centrifuged and developed in

30 litres of cold water, containing
45 cc. of ammonia of 25 per cent strength and
15 cc. of a solution of 30 per cent strength of the product of the action of ethylene oxide upon octodecyl alcohol.

The material is then rinsed and dried. A beautiful red-orange shade of good fastness to washing and fulling and good fastness to rubbing is obtained.

2. By using in Example 1 instead of the sodium salt of 3''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxy-naphthalene-7-sulphonic acid, 30 grams of the sodium or ammonium salt of 4''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxy-naphthalene-7-sulphonic acid of the formula:



a brilliant scarlet dyeing is obtained.

3. 1 kilo of yarn from viscose artificial silk is treated for 1 hour at 70° C. in a solution containing in 30 litres of water 30 grams of the ammonium salt of 3''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonic acid, and 60 grams of sodium sulphate. The yarn is squeezed or centrifuged, then treated for ½ hour in a fresh bath containing

30 grams of sodium nitrite,
30 grams of sodium dibutylnaphthalenesulphonate and
80 cc. of hydrochloric acid of 20° Bé. in
30 litres of cold water,

squeezed and treated for ½ hour in

30 litres of cold water containing
45 cc. of ammonia of 25 per cent strength and
15 cc. of a solution of 30 per cent strength of the product obtained by causing ethylene oxide to act upon octodecyl alcohol.

The material is then rinsed and dried. A beautiful red-orange dyeing is obtained.

4. 1 kilo of wool is treated for 1 hour at 85° C. to 90° C. in a solution containing in 30 litres of liquor 30 grams of sodium 4''-amino-3'-benzoylamino-2-benzoylamino-5-hydroxy-naphthalene-7-sulphonate, 80 grams of ammonium sulphate and 20 grams of sodium sulphate. The wool is squeezed and diazotized for half-an-hour with a solution containing

30 grams of sodium nitrite,
30 grams of sodium dibutylnaphthalenesulphonate and
80 cc. of formic acid of 85 per cent strength in
30 litres of cold water.

300 grams of sodium acetate, previously dissolved, are added to this bath; the material is further treated for about ½ hour in the solution, rinsed, if necessary with addition of a small quantity of ammonia or sodium carbonate, rinsed again and dried. A scarlet red shade is obtained.

5. Red-orange dyeings are obtained on natural silk by treating 1 kilo thereof under conditions similar to those described in Example 4, with 30 grams of sodium 3''-amino-3'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonate instead of sodium 4''-amino-3'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonate used in Example 4.

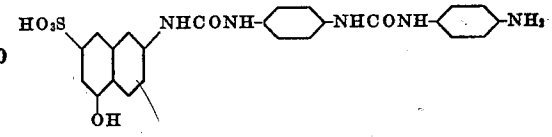
6. A fabric of staple fiber from viscose is printed with a printing paste containing

15 grams of sodium 3''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonate in
175 cc. of an aqueous solution,
500 grams of wheat starch tragacanth thickening and
25 grams of sodium nitrite, dissolved in
280 cc. of water.

The fabric is dried, steamed for about 10 minutes in a room containing an acid vapor obtained for instance by evaporating a mixture of 25 parts of acetic acid of 50 per cent strength and 5 parts of formic acid of 85 per cent strength; it is then passed through a bath containing per litre of water 10 grams of sodium carbonate, rinsed, soaped, rinsed again and dried. Red-orange printing effects are obtained.

Instead of steaming the material in acid vapor the printed fabric may be passed through a dilute acid solution, then exposed to air and treated in a dilute sodium carbonate solution for developing the dyeing. Alternatively, the fabric may be padded with a mixture of sodium 3''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonate and sodium nitrite, then printed with a non-volatile acid and passed through a bath having an alkaline action, whereby at the places printed with acid red-orange printing effects are obtained.

7. 1 kilo of wool is treated for 1 hour at 85° C. in a solution containing per 24 litres of liquor 30 grams of the sodium salt of the sulphonic acid of the following constitution:



and 30 grams of ammonium sulphate. 600 grams of sodium sulphate dissolved in 6 litres of water are added and the whole is further treated for 1 hour at the temperature of 65° C. to 70° C. so obtained. The wool is then squeezed and diazotized for ½ hour in a bath containing

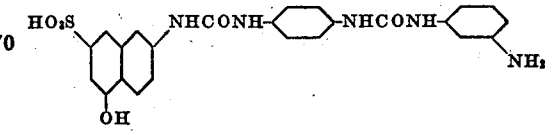
30 grams of sodium nitrite,
30 grams of sodium dibutylnaphthalenesulphonate and
80 cc. of formic acid of 85 per cent strength in
30 litres of cold water,

squeezed and treated for about half-an-hour in the cold with

80 cc. of ammonia of 25 per cent strength in
30 litres of water.

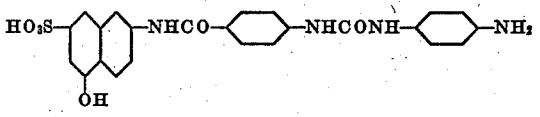
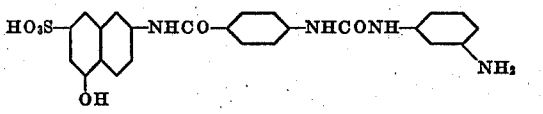
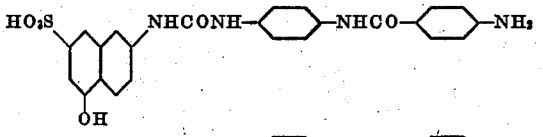
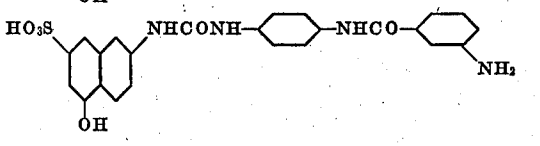
A Bordeaux shade of very good properties of fastness is obtained.

8. By using in Example 7 instead of the compound mentioned therein 30 grams of the sodium salt of a sulphonic acid of the following constitution



a copper red shade is obtained.

The following table illustrates a number of other dyeings obtainable according to the present invention by self-coupling on the fiber:

Parent component	Shade
	Red.
	Red.
	Scarlet.
	Red orange.

9. 1 kilo of mixed yarn consisting of 30 parts of staple fiber from viscose and 70 parts of wool is treated for 1 hour at 85° C. in a solution containing per 24 litres of liquor 30 grams of sodium 3'' - amino - 4'' - methoxybenzoyl - 4' - aminobenzoyl - 2 - amino - 5 - hydroxynaphthalene-7-sulphonate. 600 grams of sodium sulphate dissolved in 6 litres of water are added and the whole is further treated for 1 hour at about 70° C. The material is centrifuged and treated in the cold for half-an-hour in a bath containing in 30 litres of water

30 grams of sodium nitrite,
30 grams of sodium dibutylnaphthalenesulphonate and
80 cc. of hydrochloric acid of 20° Bé.,
centrifuged and treated for about half-an-hour in the cold with
80 cc. of ammonia of 25 per cent strength in
30 litres of water.

The yarn is then rinsed. A vivid red shade is obtained which by treating with 3 per cent of copper sulphate and 2 per cent of acetic acid of 50 per cent strength or 3 per cent of copper sulphate and 7 per cent of ammonia of 25 per cent strength at 90° C. may be converted into a Bordeaux red shade.

10. 1 kilo of wool yarn is treated for 1 hour at 85° C. to 90° C. in a solution containing per 30 litres of liquor 30 grams of sodium 3''-amino-4''-methoxybenzoyl - 3' - aminobenzoyl - 2 - amino - 5 - hydroxynaphthalene - 7 - sulphonate and 80 grams of ammonium sulphate. The material is rinsed and treated in the cold for half-an-hour in a bath containing per 30 litres of water

30 grams of sodium nitrite,
30 grams of sodium dibutylnaphthalenesulphonate and
80 cc. of hydrochloric acid of 20° Bé.

The material is centrifuged and treated for about half-an-hour in the cold with

80 cc. of ammonia of 25 per cent strength in
30 litres of water.

It is then rinsed. A vivid red shade is obtained which by treatment with copper salts may be converted into a Bordeaux red shade.

11. 30 grams of the sodium salt of 4''-aminobenzoyl - 4' - aminobenzoyl - 2 - amino - 8 - hydroxynaphthalene-6-sulphonic acid are dissolved in water, 30 grams of ammonium sulphate are added and the whole is made up to 24 litres of liquor. 1 kilo of mixed yarn consisting of 30 parts of staple fiber from viscose and 70 parts of wool is treated for 1 hour at 85° C. in this bath. A solution of 600 grams of sodium sulphate in 6 litres of cold water is then added. The material is further treated at the temperature of about 70° C. so obtained for about 1 hour. It is then centrifuged, treated for ½ hour in a bath containing per 30 litres of cold water 30 grams of sodium nitrite, 30 grams of sodium dibutylnaphthalene sulphonate and 80 cc. of formic acid of 85 per cent strength or hydrochloric acid of 20° Bé., centrifuged and developed for about ½ hour in a bath containing 80 cc. of ammonia of 25 per cent strength in 30 litres of cold water. The material is rinsed first cold and then hot; a vivid red dyeing of very good properties of fastness is obtained.

12. 30 grams of the sodium salt of 4''-methoxy-3'' - aminobenzoyl - 4' - aminobenzoyl-2-amino-8-hydroxynaphthalene-6-sulphonic acid are dissolved in 22 litres of water. In this bath 1 kilo of mixed fabric consisting of 30 parts of staple fiber from cuprammonium cellulose and 70 parts of wool is treated for one hour at 85° C. A solution of 800 grams of sodium sulphate in 8 litres of cold water is then added. The material is further treated for one hour at the temperature of about 65° C. so obtained. It is then centrifuged and treated in the cold for half an hour in a bath containing 30 grams of sodium nitrite, 30 grams of sodium dibutylnaphthalenesulphonate, 80 cc. of formic acid of 85 per cent strength or hydrochloric acid of 20° Bé. in 30 litres of cold water, centrifuged and treated for ½ hour in a solution of 80 cc. of ammonia of 25 per cent strength in 30 litres of cold water. The material is rinsed cold and then rinsed hot; a vivid red dyeing of good properties of fastness is obtained.

By after-treating this dyeing for ½ hour at 90° C. with 30 grams of copper sulphate and 10 cc. of glacial acetic acid in 30 litres of water or with

30 grams of copper sulphate and 70 cc. of ammonia of 25 per cent strength in 30 litres of water, a Bordeaux dyeing is obtained.

13. 30 grams of the sodium salt of 4''-methoxy-3''-aminobenzoyl-3'-aminobenzoyl-2-amino-8-hydroxynaphthalene-6-sulphonic acid are dissolved in 20 litres of water. In this bath 1 kilo of a mixed fabric consisting of 30 parts of staple fiber from cuprammonium cellulose and 70 parts of wool is further treated for 1 hour at 85° C. Thereupon, a solution of 1 kilo of sodium sulphate in 10 litres of cold water is added and the material is treated for one hour at the lower temperature so obtained. It is then centrifuged and further treated as indicated in Example 13. After diazotization and development on the fiber a vivid very bluish red is obtained. By after-treatment with a copper salt on the fiber Bordeaux-red dyeings are obtained.

14. 1 kilo of natural silk is treated for 1 hour at 85° C. in a bath containing 30 grams of the sodium salt of 3''-aminobenzoyl-4'-aminobenzoyl-2-amino-8-hydroxynaphthalene-6-sulphonic acid and 100 grams of sodium sulphate in 30 litres of water. It is then centrifuged and diazotized for ½ hour in the cold with a solution of 30 grams of sodium nitrite and 80 cc. of hydrochloric acid of 20° Bé. in 30 litres of water, centrifuged and treated for ½ hour in the cold with a solution of 60 grams of sodium carbonate in 30 litres of water, rinsed and dried; a scarlet-red dyeing of very good properties of fastness is obtained.

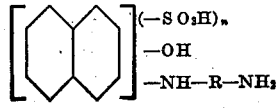
15. 1 kilo of wool is treated at 90° C. for 1 hour in a bath containing 30 grams of the sodium salt of 4''-aminobenzoyl-4'-aminobenzoyl-1-amino-8-hydroxynaphthalene-3.6-disulphonic acid and 80 grams of ammonium sulphate in 30 litres of water, centrifuged, treated for ½ hour in a cold solution containing per 30 litres of water 30 grams of sodium nitrite and 80 cc. of hydrochloric acid, rinsed and developed at ordinary temperature for about 30 minutes with a solution containing 60 grams of sodium carbonate in 30 litres of water. The material is then rinsed first cold and then hot. A ruby-red dyeing is obtained.

The following table illustrates a number of other dyeings obtainable according to the present invention by self-coupling on the fiber:

	Parent component	Shade
1	Sodium 4''-aminobenzoyl-4'-aminobenzoyl-1-amino-5-hydroxynaphthalene-7-sulphonate.	Vivid scarlet red.
2	Sodium 4''-aminobenzoyl-4'-aminobenzoyl-1-amino-6-hydroxynaphthalene-3-sulphonate.	Vivid yellowish scarlet.
3	Sodium 4''-aminobenzoyl-4'-aminobenzoyl-1-amino-8-hydroxynaphthalene-4-sulphonate.	Garnet.
4	Sodium 4''-aminobenzoyl-4'-aminobenzoyl-2-amino-3-hydroxynaphthalene-6-sulphonate.	Scarlet red.
5	Sodium 4'''-aminobenzoyl-4''-aminobenzoyl-4'-aminobenzoyl-2-amino-8-hydroxynaphthalene-3.6-disulphonate.	Red.
6	Sodium 4'''-aminobenzoyl-4''-aminobenzoyl-3'-aminobenzoyl-2-amino-5-hydroxynaphthalene-7-sulphonate.	Scarlet red.

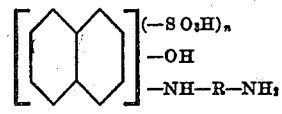
I claim:

1. The process which comprises applying to the fiber an alkali metal salt of a sulphonic acid of the following constitution:



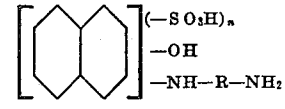
wherein n represents one of the numbers 1 and 2 and R represents a member of the group consisting of -CO-aryl-NHCO-aryl-, -CONH-aryl-NHCO-aryl-, -CONH-aryl-NHCONH-aryl-, -CO-aryl-NHCONH-aryl- and -CO-aryl-NHCO-aryl-NHCO-aryl-, with the exception of such derivatives as do not contain in the naphthalene ring a free position capable of coupling with diazo-compounds, then diazotizing the compound on the fiber and causing it to combine with itself.

2. The process which comprises applying to the fiber an alkali metal salt of a sulphonic acid of the following constitution:



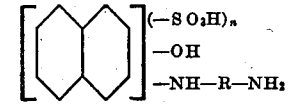
wherein n represents one of the numbers 1 and 2 and R represents a member of the group consisting of -CO-aryl-NHCO-aryl-, -CONH-aryl-NHCO-aryl-, -CONH-aryl-NHCONH-aryl-, -CO-aryl-NHCONH-aryl- and -CO-aryl-NHCO-aryl-NHCO-aryl-, with the exception of such derivatives as do not contain in the naphthalene ring a free position capable of coupling with diazo-compounds, then diazotizing the compound on the fiber and causing it to combine with itself by adding to the diazo-bath an agent neutralizing the acid.

3. The process which comprises applying to the fiber an alkali metal salt of a sulphonic acid of the following constitution:



wherein n represents one of the numbers 1 and 2 and R represents a member of the group consisting of -CO-aryl-NHCO-aryl-, -CONH-aryl-NHCO-aryl-, -CONH-aryl-NHCONH-aryl-, -CO-aryl-NHCONH-aryl- and -CO-aryl-NHCO-aryl-NHCO-aryl-, with the exception of such derivatives as do not contain in the naphthalene ring a free position capable of coupling with diazo-compounds, then diazotizing the compound on the fiber and causing it to combine with itself by passing the fiber through a bath having an alkaline action.

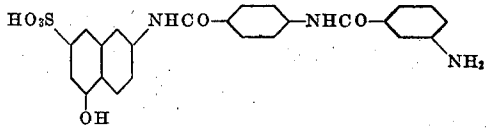
4. The process which comprises applying to the fiber an alkali metal salt of a sulphonic acid of the following constitution:



wherein n represents one of the numbers 1 and 2 and R represents a member of the group consisting of —CO—R_1—NHCO—R_1—, —CONH—R_1—NHCO—R_1—, —CONH—R_1—NHCONH—R_1—, —CO—R_1—NHCONH—R_1— and —CO—R_1—NHCO—R_1—NHCO—R_1—, R_1 being a radical of the benzene series, with the exception of such derivatives as do not contain in the naphthalene ring a free position capable of coupling with diazo-compounds, then diazotizing the com-

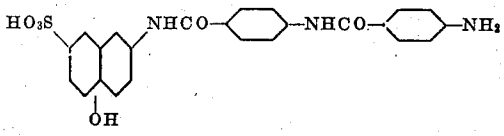
pound on the fiber and causing it to combine with itself.

5. The process which comprises applying to the fiber an alkali metal salt of 3''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonic acid of the following constitution:



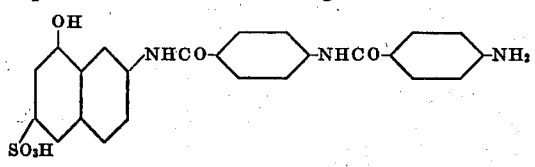
then diazotizing the compound on the fiber and causing it to combine with itself.

6. The process which comprises applying to the fiber an alkali metal salt of 4''-amino-4'-benzoylamino-2-benzoylamino-5-hydroxynaphthalene-7-sulphonic acid of the following constitution:



then diazotizing the compound on the fiber and causing it to combine with itself.

7. The process which comprises applying to the fiber an alkali metal salt of 4''-aminobenzoyl-4'-aminobenzoyl-2-amino-8-hydroxynaphthalene-6-sulphonic acid of the following constitution:



then diazotizing the compound on the fiber and causing it to combine with itself.

8. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 1.

9. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 2.

10. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 3.

11. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 4.

12. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 5.

13. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 6.

14. Fiber dyed with an azo compound obtainable on the fiber by the process claimed in claim 7.

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