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PROCESS FOR THE COLORATION OF NYLON TYPE 11 FIBRES

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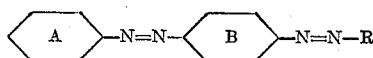
4 Claims. (Cl. 8-55)

The present invention is concerned with the colouration of fibres based on condensation products of ω -amino-undecanoic acid such as "Rilsan."

It is known that "nylon," obtained from the condensation of hexamethylenediamine with adipic acid, contains five methylene groups to one amido group, whereas "Rilsan," resulting from the polymerisation of ω -amino-undecanoic acid possesses 10 of them. Because this latter fibre has a longer polymethylene chain its paraffinic character is more marked, and it follows that it swells very little in water. For this reason and because of the low percentage of amido groups, its chemical inertia is greater and its tinctorial affinity less than those of "nylon," although the two fibres show certain analogies in their general properties. Thus the very great difficulties met with in obtaining the depth of colour usually required on "Rilsan" fibres with the acid dyestuffs actually known are partly explained, the lack of uniformity in dyeing being common to all the polyamide fibres.

Although the exhaustion of the dye baths can be improved by lowering the pH, by means of mineral acid which causes the activation of a larger number of groups of the fibre capable of combining with the anionic dyestuff, the complete elimination during drying of the mineral acid which is injurious to the fibre is very often difficult. The sought-for result would be obtained if, parallel to the exhaustion of the baths by lowering the pH, the diffusion of the dyestuffs towards the interior of the fibre could be realised. The use of carriers for this purpose is often rejected by the users who consider it prejudicial to the good preservation of the properties of this fibre. As for the use of high temperatures for prolonged periods, this requires apparatus which is resistant to attack by the dyeing adjuvants, and all dyers do not possess such apparatus. Only the increase in the plastosolubility of the molecule enables the diffusion of the dyestuff in the fibre to be increased to a certain extent and consequently the retention of a greater amount of dyestuff by the use of all the functions of the fibre which react with the anionic dyestuff.

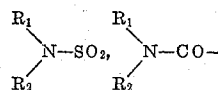
The object of the present invention is to avoid these disadvantages by the colouration of fibres based on condensation products of ω -aminoundecanoic acid of diazo dyestuffs of the following general formula:



in which R denotes a monosulphonated 1-aryl-5-pyrazolone having a methyl, carbonamido or carbonalkoxy group in the 3 position, and in which the aryl nucleus may also be substituted by halogen atoms or by non-solubilising groups such as alkyl or alkoxy groups, or a naphtholmonosulphonic acid, or an acylamino-naphtholmonosulphonic acid, the acyl group being, for example, an alkyl-CO-alkyl-O-CO-, alkyl-SO₂- or alkyl-O-CH₂-CH₂O-CO group. The benzene rings A and B may be substituted by non-solubilising groups such as for example halogen atoms or alkyl, hydro-aryl, alkyl-

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CO-, alkyl-O-CO-, alkyl-O, hydro-aryl-O-CO, aryl-CO-, alkyl-CO-NH, H₂N-SO₂,



alkyl-SO₂-, aryl-SO₂-O-, aryl-SO₂-CH₂, alkyl-O-CO-CH₂-O, or alkyl-O-CO-CH₂-S- groups, R₁ representing an alkyl group and R₂ a hydrogen atom or an alkyl, hydroxyalkyl or hydroaryl group, and R₁ and R₂ being able to form a heterocyclic ring with -N-.

These dyestuffs enable deep shades to be obtained by dyeing in a weakly acid bath i.e. a bath having a pH between 3 and 4. They possess good general fastness to wet tests and the fastness to light of some of them is excellent. The principle of the preparation of the dyestuffs of general Formula I is already known, but some of them, described below, are new.

The invention will be more clearly understood by reference to the following examples which are purely illustrative. The parts and percentages are by weight unless the contrary is indicated.

Example 1

19.7 parts of amino-azobenzene are made into a paste in 210 parts of water and 46 parts of 30% hydrochloric acid. The next morning ice is added to lower the temperature of the mixture to 7° C., and a solution of 6.6 parts of sodium nitrite in its own weight of water is introduced over a period of 5 minutes. The mixture is stirred for 4 hours without exceeding the temperature of 10° C. The yellow diazo derivative is in solution.

When coupling takes place, the excess nitrous acid is destroyed by the addition of sulphamic acid, and the solution is introduced over 30 minutes into a bath prepared by dissolving 32 parts of 1-(2'-chloro-5'-sulpho)-phenyl-3-methyl-5-pyrazolone in 300 parts of water by means of 9 parts of sodium carbonate to which are added 38 parts of sodium carbonate. The mixture is agitated for a further hour to finish the coupling, which is very rapid, the composition diluted to 2500 parts by volume is heated to 95° C. and the dyestuff is precipitated by the addition of 100 parts of desulphated sodium chloride. The product is allowed to cool to 50° C. while stirring, and then filtered. After drying, the dyestuff is in the form of a yellow powder which dyes "Rilsan" from a slightly acid bath a yellowish orange shade having good fastness to wet tests and to light.

On replacing the 1-(2'-chloro-5'-sulpho)-phenyl-3-methyl-5-pyrazolone with the corresponding quantity of 1-(2',5'-dichloro-4'-sulpho)-phenyl-3-methyl-5-pyrazolone, a dyestuff is obtained which gives rather more reddish shades on "Rilsan" or "nylon."

Much redder shades are obtained with the ethyl esters of 1-(4'-sulpho)-phenyl-5-pyrazolone-3-carboxylic acid and 1-(2'-chloro-5'-sulpho)-phenyl-5-pyrazolone-3-carboxylic acid.

Example 2

19.7 parts of amino-azobenzene are diazotized by the process described in Example 1; the clear solution of the diazo derivative obtained is introduced over 30 minutes into a solution of 1-naphthol-4-sulphonic acid obtained by dissolving 25.8 parts of this acid in 350 parts of water, filtering and adding 38 parts of sodium carbonate. The mixture is stirred for a further half-hour to finish the coupling process, which is almost instantaneous, and is heated to 90° C., the dyestuff separated by filtration, and dried. The latter is in the form of a bluish red powder which dyes "Rilsan" from a slightly acid bath a bright red shade having good fastness to wet tests and characterised by an excellent fastness to light.

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The replacement of the 1-naphthol-4-sulphonic acid by 1-naphthol-5-sulphonic acid gives a dyestuff which, under the same conditions, dyes "Rilsan" a much bluer shade, while the dyestuff obtained with 1-naphthol-6-sulphonic acid gives a brown shade.

Example 3

22.5 parts of amino-azotoluene are made into a paste in 210 parts of water and 46 parts of a 30% solution of hydrochloric acid. The next morning, ice is added to the mixture to lower the temperature to 7° C., and a solution of 6.9 parts of sodium nitrite in its own weight of water is introduced over a period of five minutes. The mixture is agitated for four hours without exceeding a temperature of 10° C. When coupling occurs, the excess nitrous acid is destroyed by the addition of sulphamic acid and the solution of the diazo derivative is introduced over 30 minutes into a coupling bath prepared by dissolving 32 parts of 1-(2'-chloro-5'-sulpho)-phenyl-3-methyl-5-pyrazolone in 350 parts of water by means of 9 parts of sodium carbonate, to which are added 38 parts of sodium carbonate. The mixture is again agitated for an hour to finish the coupling, diluted to a volume of 2,700 parts, heated at 95° C. until completely dissolved, salted out with 60 parts of desulphated sodium chloride and allowed to cool to 45° C. while agitating. The precipitated dyestuff is filtered off and dried, and is in the form of a yellow powder which dyes fibres consisting of a polycondensation product of ω -aminoundecanoic acid from a slightly acid bath an orange shade more reddish than that of the dyestuff described in Example 1, and has good fastness to wet tests and to light.

On replacing the 1-(2'-chloro-5'-sulpho)-phenyl-3-methyl-5-pyrazolone by the corresponding quantity of 1-(2',5'-dichloro-4'-sulpho)-phenyl-3-methyl-5-pyrazolone, a dyestuff is obtained which gives more reddish shades. With the ethyl ester of 1-(2'-chloro-5'-sulpho)-phenyl-5-pyrazolone-3-carboxylic acid a pure reddish orange shade is obtained.

Example 4

The solution of the diazo derivative of aminoazobenzene prepared according to Example 1 is introduced over 15 minutes into a solution of 2-acetyl-amino-8-naphthol-6-sulphonic acid prepared by dissolving 29.5 parts of this acid in 400 parts of water by means of 8 parts of sodium carbonate, and adding 40 parts of sodium carbonate. The bath is diluted with water to twice its volume, heated to 90° C., and the dyestuff separated by filtration is dried. The powder obtained is a very bluish red and dyes "Rilsan" a ruby shade having good fastness to wet tests and a satisfactory fastness to light.

The replacement of 2-acetyl-amino-8-naphthol-6-sulphonic acid by 2-ethoxycarbonylamino-8-naphthol-6-sulphonic acid or 2- ω -methoxy-ethoxycarbonylamino-8-naphthol-6-sulphonic acid leads to dyestuffs giving similar shades on "Rilsan."

Example 5

22.5 parts of amino-azotoluene are diazotized according to the process described in Example 3; the diazo derivative obtained is introduced over a period of 20 minutes into a solution of 1-naphthol-4-sulphonic acid prepared by dissolving 28.5 parts of this acid in 350 parts of water, filtering and adding 38 parts of sodium carbonate. The mixture is agitated for 30 minutes, heated to 90° C., and, after filtering, the dyestuff is dried. The latter dyes "Rilsan" a very bright bluish-red shade, having very good fastness to the various wet tests and an exceptionally good fastness to light.

Example 6

19.7 parts of amino-azobenzene are diazotized by the process described in Example 1 and the solution of the diazo derivative obtained is run over 15 minutes into a solution of 2-naphthol-8-sulphonic acid prepared by dis-

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solving 23.5 parts of this acid in 350 parts of water by means of sodium carbonate, and addition of 38 parts of sodium carbonate. After an hour's agitation, the bath is heated to 95° C.; the dyestuff is separated by filtration and dried. It dyes "Rilsan" in a weakly acid medium a bluish-red shade having good general fastness.

Example 7

The 2-naphthol-8-sulphonic acid in the previous example is replaced by 1-acetyl-amino-8-naphthol-4-sulphonic acid. A dyestuff is obtained which dyes "Rilsan" from a weakly acid bath a very bright red-violet.

Example 8

19.7 parts of amino-azobenzene are diazotized by the process described in Example 1 and the solution of the diazo derivative obtained is run over 20 minutes into a solution of 2-acetyl-amino-5-naphthol-7-sulphonic acid obtained by dissolving 30 parts of this acid in 400 parts of water by means of sodium carbonate and adding 40 parts of sodium carbonate. The bath is agitated for an hour, with the addition of 150 parts of desulphated sodium chloride, then slowly heated to 40° C.

After an hour's agitation at this temperature, the dyestuff is separated by filtration, then dried. It dyes "Rilsan" from a slightly acid bath a bluish-red shade of good general fastness.

The replacement of the 2-acetyl-amino-5-naphthol-7-sulphonic acid by 2-carboxy-acetyl-amino-5-naphthol-7-sulphonic acid leads to a dyestuff of a slightly more yellowish shade.

Example 9

22.5 parts of amino-azotoluene are diazotized by the process described in Example 3. The solution of the diazo derivative obtained is introduced over 20 minutes into a solution of 2-acetyl-amino-8-naphthol-6-sulphonic acid prepared by dissolving 29.5 parts of this acid in 400 parts of water by means of 8 parts of sodium carbonate and adding 40 parts of sodium carbonate. The mixture is agitated for an hour and the volume of the bath is doubled by the addition of the same quantity of water, heated to 95° C. and maintained at this temperature for an hour and a half, allowed to cool to 90° C. and the precipitated dyestuff is separated by filtration.

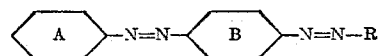
After drying, the dark red powder obtained dyes "Rilsan" from a weakly acid bath a very bluish red shade having good general fastness.

Example 10

A dyebath is prepared in the proportion 1/30 with 1% of formic acid and 0.5% of the dyestuff of Example 3, these quantities calculated with reference to the weight of the fibre. "Rilsan" fibres are introduced at 40° C., the bath is brought to the boil in 30 minutes, and the fibres dyed for an hour at this temperature. They are carefully rinsed with water. A very full-bodied, even, yellowish orange dyeing is thus obtained.

I claim:

1. Process for the coloration of condensation products of ω -aminoundecanoic acid which comprises using as the colouring agent a dyestuff of the general formula:

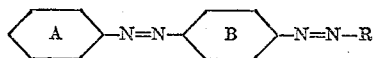


in which R represents a member selected from the group consisting of the monosulphonated 1-aryl-5-pyrazolones having a radical selected from the group consisting of the methyl, carbonamido and carbonalkoxy radicals in the 3 position, the naphthol monosulphonic acids and the

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acylamino naphthol monosulphonic acids, the colouring agent being applied from a dyebath having a pH between 3 and 4.

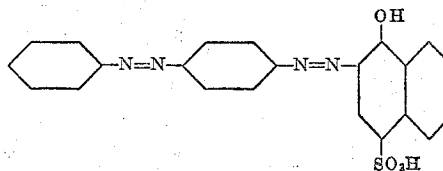
2. Process for the colouration of condensation products of ω -amino-undecanoic acid which comprises applying thereto, by dyeing in an acid medium and heating, a dyestuff of the general formula



in which the benzene nuclei A and B are substituted by members selected from the group consisting of the hydrogen atom and methyl groups and R represents a member selected from the group consisting of the residues of naphthol monosulphonic acids, acetylamino-naphthol-monosulphonic acids, ω -carboxy-acetylamino-naphthol-monosulphonic acids, alkoxy-carbonylamino-naphthol-monosulphonic acids, alkoxyethoxy-carbonylamino-naphthol-monosulphonic acids, 1-sulphophenyl-3-methyl-5-pyrazolones, 1-sulphophenyl - 3 - alkoxy-carbonyl-5-pyrazolones, 1-sulphophenyl-3-methyl-5-pyrazolones, 1-chlorophenyl-3-methyl-5-pyrazolones, 1-sulpho-phenyl-3-alkoxy-carbonyl-5-pyrazolones and 1-chlorophenyl-3-alkoxy-carbonyl-5-pyrazolones, said alkoxy radicals having up to two carbon atoms.

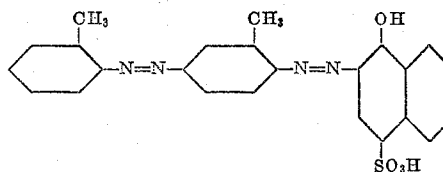
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3. Process as claimed in claim 2, in which the following dyestuff



10 is used.

4. Process as claimed in claim 2, in which the following dyestuff is used:



References Cited in the file of this patent

- Speil: Textile Chemicals and Auxiliaries, 2nd ed., 1957, page 20.
- 25 Colour Index, 2nd ed., 1956, vol. 1, pp. 1116-1117, 1142, 1155, 1157; vol. 2, pp. 2078, 2102, 2145, 2158; vol. 3, pp. 3214, 3219, 3223, 3231, 3232, 3235.