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2,937,067

NEW PROCESS FOR THE COLORATION OF SYNTHETIC MATERIALS AND THE INDUSTRIAL PRODUCTS RESULTING THEREFROM

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The present invention concerns a new process for the coloration of synthetic materials and the industrial products resulting therefrom.

The coloration by dyeing or by printing of synthetic fibres based on polyacrylonitrile gives rise to difficulties. At present, some particular members of different classes of dyes give results which can be made use of in industry namely; plastosoluble dyes, vat dyes, basic dyes, insoluble azo dyes formed on the fibres and acid dyes applied according to the cuprous ion process. Their application can be effected at 100° C. or at a higher temperature; application above 100° C. results in an improvement of the penetration, uniformity, speed of dyeing, and sometimes the yield of these dyes. Nevertheless, it has not been possible to extend the use of this method and therefore to enlarge the range of dyes which can be employed to colour products based on polyacrylonitrile.

Another solution has been proposed for this purpose. It consists in making copolymers containing, besides acrylonitrile, products capable of facilitating the dyeing or printing by loosening the internal structure of the fibre or providing chemical functions on which certain dyes can become fixed.

Finally, in French Patent No. 1,094,620 there is described a process for dyeing fibres based on polyacrylonitrile which consists in using the copper complexes of o:o'-dihydroxy monoazo dyes containing only one sulphonic group, in the presence of hydroxylamine sulphate.

It has now been found that the products of polymerisation or copolymerisation of acrylonitrile or vinylidene cyanide can be dyed in strong shades by means of dyes which are soluble or insoluble in water, other than those of the above-mentioned French Patent, by operating without copper salt in the presence of hydroxylamine in the free state or in the form of a salt thereof, at a temperature above 100° C. The tinctorial yield is, in general, superior to that which is obtained by first treating the fibre with hydroxylamine (for example, according to the process of U.S. Patent No. 2,792,276) or by carrying out the dyeing in the presence of hydroxylamine at a temperature below 100° C.

The products of polymerisation or copolymerisation of acrylonitrile or vinylidene cyanide may be in various forms such as, for example, fibres, threads, coarse fibres, fabrics or sheets. In view of this, they are on occasion treated with other products e.g. products resulting from a polymerisation, or mineral or organic products intended to modify the physical properties of the substance or its physical appearance. Certain copolymers may contain products whose object is either to loosen the internal structure of the macromolecular acrylic chains or to provide chemical functions assisting in the fixation of the dyes, for example basic functions able to combine with the sulphonic or carboxylic groups of the soluble or pseudo-soluble dyes. Among the products considered capable of being dyed may be mentioned the fibres or

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threads with the following trademarks: Orlon (Du Pont de Nemours), Crylor (Société Rhodiacéta), Pan (Cassella Farbwerke Mainkur), Dralon (Farbenfabriken Bayer), Acrilan (Chemstrand Corporation), Dynel (Carbide & Carbon Chemicals Corporation), Darlan (B.F. Goodrich Co.).

The coloration can be obtained by dyeing or printing. The dyeing can be carried out by known methods, either by circulating the bath, the material being stationary, or by passing the material through the bath (vats, jigger, foulard), or by employing apparatus which combines both movements. In order to reach a temperature above 100° C., one can operate either in an aqueous bath open to the air whose boiling point has been raised by the addition of soluble salts, or in an autoclave. When working on the foulard, the fabric passes through the bath for some seconds and is then squeezed out between the rollers of the apparatus; the fixation of the dye is then carried out, with or without intermediate drying, by thermal treatment above 80° C.: the desired temperature is obtained by circulation of hot air, infra-red radiation, contact with a heated metal, by steaming by means of steam at normal pressure or under pressure, or by treatment at a temperature above 80° C. in an aqueous bath open to the air or under pressure, or by any other suitable means. Printing of the polymers and copolymers in question can be carried out by means of the usual apparatus by the application of a paste containing a thickener: the fixation is effected by one of the methods indicated above for foularded fabrics.

The number of dyes, soluble, pseudo-soluble or insoluble in an aqueous medium, which can be applied according to the present process is large. By way of example, there may be mentioned:

(1) The acid dyes and the direct non-metallisable dyes.

(2) The chromium complexes, called 1:1 that is, possessing one atom of metal attached to one molecule of dye. These dyes are generally used for dyeing wool in a strongly acid bath or for dyeing polyamide fibres.

(3) Metalliferous complexes, chiefly of chromium or cobalt, called 2:1, that is, possessing one atom of chromium or cobalt linked either to two molecules of dye, the same or different, or to one molecule of dye and to one molecule of colourless metallisable compound.

(4) The direct dyes comprising copper complexes of sulphonated polyazo compounds, or of polysulphonated monoazo compounds.

(5) The phthalocyanines and their soluble or insoluble derivatives.

(6) The dyes called chrome or mordant dyes; these can form complexes with different metals. The metal is generally chromium when these dyes are applied to wool or polyamide fibres. According to the present process, the chromium dyes are applied in the presence of soluble metal salts, of chromium, iron, nickel, cobalt, vanadium or manganese. It does not matter if oxidising salts such as dichromates, chromates, or permanganates are used which destroy the hydroxylamine. The complex can also be previously prepared before the dyeing, by the action of the dye on the metal salt, isolation of the complex and use immediately for coloration; in this case, it is not necessary to add a metal salt to the bath or the paste.

(7) The direct metallisable dyes; according to the present process these direct dyes are applied in the presence of soluble metal salts, of chromium, iron, vanadium, nickel, cobalt, tin, aluminium or manganese. It does not matter if oxidising salts which destroy the hydroxylamine are used. The complex can also be previously prepared, before the dyeing, by the action of the

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dye on the metal salt, isolation and use immediately for colouration; in this case, it is not necessary to add a metal salt to the bath or the paste.

(8) The leuco esters of vat dyes.

The dye baths or the printing pastes include the following elements:

The dye, the hydroxylamine or one of its salts, such as the neutral sulphate, the acid sulphate, the hydrochloride, or the phosphate, and possibly the following products: soluble metal salts when the dye is not itself a metal complex, acids or alkalis intended to produce the pH conditions which are most satisfactory for the substance to be dyed, wetting and dispersing agents of anionic or non-ionic type intended to improve the wettability of the material, the uniformity of the dyeing and the dispersion of incompletely soluble dyes, swelling agents such as ortho- or para-phenyl phenol, resorcinol, dimethylformamide, soluble lithium salts, calcium thiocyanate, intended to facilitate the penetration of the dye into polymers which are difficult to penetrate.

The colouration is effected by one of the previously mentioned processes of dyeing or printing at a temperature above 100° C. At 120–130° C. the results are always excellent and the bath is almost completely exhausted. The optimum temperature for the colouration is governed by the characteristics of the material to be coloured, which characteristics depend to a considerable extent on the method of manufacture of the latter. At the end of the dyeing or printing, it is expedient to subject the material to hot soaping, using soap or an anionic or non-ionic product, so as to purify the shade and remove particles of dye badly fixed on the surface.

The amounts of hydroxylamine or salt thereof and the amounts of metal salts vary according to the depth of the shade and the bath ratio; in practice, however, they range from 0.5% to 10% based on the weight of the material to be coloured.

The present process allows not only dyes of the same group to be used in combination but also dyes of different groups, and even metalliferous dyes with metallisable dyes in the presence of metal salts. Dyes which are soluble and insoluble in an aqueous medium can also be used in combination. Finally, two or more salts of the same metal or different metals can be added when dyeing with metallisable dyes.

A modification of the process of this invention consists in adding to the dyebath or to the printing paste, not hydroxylamine or one of its salts, but products capable of giving them under the conditions of application. A nitrite, such as sodium nitrite, and sodium bisulphite may be used and an acid, such as sulphuric acid, added before the colouration. The action of the acid on the bisulphite liberates sulphur dioxide, which reduces the nitrite, or nitrous acid occasionally formed, to hydroxylamine. Nevertheless, the conditions for the colouration are not the optimum conditions for the preparation of hydroxylamine, so that the tinctorial yields are less than when hydroxylamine or one of its salts is added directly to the bath.

Another variation of the process consists in adding hydroxylamine sulphate to the bath and liberating the base by the addition of sodium carbonate or a strong base, e.g. caustic soda or caustic potash.

The shades obtained are very varied and cover all those required in dyeing and printing; they display remarkable fastness both to light and to wet or other treatments.

The examples which follow, which are not restrictive and in which the parts indicated are parts by weight, describe processes of colouration in accordance with the present invention.

EXAMPLE 1

10 parts of polyacrylonitrile fibres are introduced into a bath comprising 200 parts of water, one part of hy-

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droxylamine sulphate and 0.2 part of the 1:1 chromium complex of the dye obtained by coupling the diazo derivative of 6-nitro-2-amino-1-hydroxy-4-benzenesulphonic acid with 1-phenyl-3-methyl-5-pyrazolone.

5 The temperature is raised to 120–130° C. and dyeing is carried out at this temperature for three quarters of an hour to an hour. The fibres are rinsed and washed with soap in the hot. An orange colour is obtained.

10 Table I summarises some examples of dyeing carried out by the same process.

Table I

15	1:1 Chromium Complex of the following azo dyes—	Colour obtained on polyacrylonitrile fibre of the Orion type
1-amino-2-hydroxy-4-naphthalene-sulphonic acid → 1-(4'-sulpho)phenyl-3-methyl-5-pyrazolone.		Rose.
20 2-amino-1-hydroxy-6-benzenesulphonic acid → β-naphthol.		Reddish-brown.
4-chloro-2-amino-1-hydroxy-6-benzenesulphonic acid → 1-(4'-sulpho)phenyl-3-methyl-5-pyrazolone.		Orange red.
1-amino-2-hydroxy-4-naphthalene-sulphonic acid → 1-hydroxy-8-naphthalene sulphonic acid.		Greenish blue.
25 6-nitro-1-amino-2-hydroxy-4-naphthalene-sulphonic acid → β-naphthol.		Very dark grey.
3:6-dinitro-2-aminophenol → naphthionic acid.		Olive green.
4-chloro-2-amino-1-hydroxy-6-benzenesulphonic acid → 1-hydroxy-4-naphthalenesulphonic acid.		Violet.
30 4-chloro-1-amino-3-benzenesulphonic acid → salicylic acid.		Yellow.
4-chloro-2-amino-1-hydroxy-6-benzenesulphonic acid → 2:4-dihydroxy-quinoline.		Reddish Bordeaux.

35 It is also possible to work as indicated in the first paragraph of Example 1 but replacing the hydroxylamine sulphate by the equivalent quantity of hydroxylamine hydrochloride. A lighter orange colour is obtained. In order to improve the tinctorial yield, it is enough to add to the dye bath a base such as sodium carbonate (0.5 to 1 part); the hydrochloric acid set free by the decomposition of the hydrochloride during the dyeing is thus neutralised.

EXAMPLE 2

45 In this example one operates according to the process described in the first paragraph of Example 1, but instead of the dye mentioned in the latter example, one of those in Table II below is used. The latter dyes, denoted by the name under which they are known on the market, are 2:1 complexes of chromium or cobalt.

50 The edition of the Colour Index from which the corresponding dyes are cited is the 1956 edition.

Table II

55	Dye	Colour on fibres based on—	
		polyacrylonitrile of the Orion type	copolymer of acrylonitrile and vinyl chloride of the Dynel type
60	Grey Cibalan BL (C.I. Acid Black 60)...	Bluish grey.	
	Orange Ortolane R (C.I. Acid Orange 39)...	Orange.....	
	Olive Irgalane BGL (C.I. Acid Black 64)...	Olive.....	
65	Brown Lanasyne RL (C.I. Acid Brown 28)...	Chestnut....	
	Bordeaux Cibalan GRL (C.I. Acid Red 213)...	Bordeaux....	
	Cobalt complex of the dye: 2-amino-4-sulphonamido-1-hydroxybenzene → β-naphthol.	Violet red...	
70	Orange Neopalatin GR (C.I. Acid Orange 71)...	Orange.....	
	Red Vialon fast B (C.I. Acid Red 225)...	Red.....	Red.
	Black Vialon fast R (C.I. Acid Black 63)...	Very dark grey	
	Yellow Vialon fast R (C.I. Acid Yellow 119)...	Reddish yellow	

EXAMPLE 3

In this example one operates as indicated in Example 1, but replacing the complex used by the copper complex of the dye obtained by coupling the tetrazo derivative of dianisidine with one molecule of 1-hydroxy-naphthalene-3:8-disulphonic acid and one molecule of 6-phenylamino-1-hydroxy-3-naphthalenesulphonic acid. A navy blue colour is obtained. Table III below summarises some examples of colours obtained with the metalliferous polyazo dyes according to the same process; these dyes are denoted by the commercial names under which they are known on the market.

Table III

Metalliferous polyazo dye	Colour obtained on polyacrylonitrile fibres	
	of Orlon type	of Crylor type
Brown Diazole Light BRN (C.I. Direct Brown 95).	chestnut..	yellowish brown.
Brown Diazole Light 8RL (C.I. Direct Brown 112).	red-brown	red-brown.
Ruby Diazole Light 2BL (C.I. Direct Red 83).	brown-red	brown-red.
Grey Diazole Light 6BL (C.I. Direct Black 71).	yellowish grey.	
Violet Diazole Light BLN (C.I. Direct Violet 48).		blue-grey.
Ruby Chlorantine Light RLL.....	ruby.....	

It is also possible to operate as has just been indicated by adding to the dye bath 0.8 to 1 part of sodium carbonate in order to liberate the hydroxylamine. According to this process there is obtained with the Brown Diazole Light BRN a yellowish brown colour on a polyacrylonitrile fibre of the Orlon type.

EXAMPLE 4

In this example one operates as indicated in the first paragraph of Example 1, but the dye of Example 1 is replaced by the disulphonated derivative of copper phthalocyanine, known under the trade name of Turquoise Diazole Light JL (C. I. Direct Blue 86). A jade green colour having excellent fastness to light and to washing is obtained.

Table IV below summarises some examples carried out by the same process with analogous dyes; these dyes are denoted by the names under which they are known on the market.

Table IV

Dye	Colour on polyacrylonitrile fibre of the Orlon type
Green Sirius Light FFGL.....	Green.
Alcian blue 8 GS.....	turquoise blue.
Blue Zapon fast HFL (C.I. Solvent Blue 25).....	blue.

Brilliant Blue Indanthrene 4G (C.I. Vat Blue 28) applied according to the same process in the form of the leuco derivative in the presence of hydrosulphite and caustic soda gives a greenish blue colour.

Brilliant Green Sulfogene J (C.I. Sulphur Green 14) is applied by reduction and solubilisation of the dye in an alkaline sulphide medium in the following manner: 0.2 part of concentrated settled sodium sulphide is mixed with 0.2 part of dye, 5 parts of pure boiling water are added and the mixture is stirred for 10 to 15 minutes to allow the reduction of the dye and its solubilisation to take place. This solution is poured into a bath comprising 195 parts of water, one part of hydroxylamine sulphate, and 0.3 part of sodium carbonate. 10 parts of polyacrylonitrile fibre of Orlon type are introduced and

one operates as indicated in the first paragraph of Example 1. A dark green colour is obtained.

Finely dispersed copper phthalocyanine is applied in the following way: 0.2 part of dye is made into a paste with one to two parts of hot water, and 20 parts of hot water are added. The dispersion obtained is poured into a bath comprising 180 parts of water and one part of hydroxylamine sulphate. 10 parts of polyacrylonitrile fibre of Orlon type are introduced and one operates as indicated in the first paragraph of Example 1. A turquoise blue colour is obtained.

EXAMPLE 5

In this example one operates as in the first paragraph of Example 1, but the dye of Example 1 is replaced by the dye obtained by coupling the diazo derivative of aniline with 1-(4'-chloro-6'-sulpho)phenyl-3-methyl-5-pyrazolone, and in addition to hydroxylamine sulphate, 0.2 part of a soluble non-oxidising chromium salt, such as chromium fluoride or acetate, is added to the dye bath. An orange-red colour is obtained.

Table V summarises some examples of dyeing carried out by this process with other mordant dyes called "chrome dyes."

Table V

Chrome dye	Colour obtained on polyacrylonitrile fibre	
	of Orlon type	of Crylor type
Anthranilic acid $\longrightarrow$ 1-(4'-sulpho)phenyl-3-methyl-5-pyrazolone.	yellow....	
Salt of trimethyl-trisulleyl-carbinol.....		violet.
1-amino-5-nitro-2-hydroxy-4-naphthalenesulphonic acid $\longrightarrow$ α -naphthol.		very dark grey.
4-nitro-2-aminophenol $\longrightarrow$ m-phenylene-diamine $\longrightarrow$ sulphanilic acid.		yellowish brown.
Sulphanilic Acid $\longrightarrow$ Salicylic acid.	yellow....	yellow.
Anthranilic acid $\longrightarrow$ 2-hydroxy-6-naphthalenesulphonic acid.	bluish red.	

EXAMPLE 6

In this example one operates according to the process described in the first paragraph of Example 1, but the dye of Example 1 is replaced by one of those known on the market under the names mentioned in the following table.

Table VI

Dye	Colour on polyacrylonitrile fibre of Orlon type
Yellow Diazole Light 5J (C.I. Direct Yellow 25).....	yellow.
Rose Diazole Light 2B (C.I. Direct Red 75).....	rose.
Orange Diazole Light RN (C.I. Direct Orange 49).....	orange.
Fast yellow Diazole 2F (C.I. Direct Yellow 28).....	yellow.
Fast scarlet Diazole 5BS (C.I. Direct Red 14).....	scarlet.
Pure blue Diazole 6B (C.I. Direct Blue 1).....	blue.
Chrysophenine J extra (C.I. Direct Yellow 12).....	yellow ochre.
Orange Diazole BR (C.I. Direct Orange 20).....	orange.
Orange Diazole Brilliant JN (C.I. Direct Orange 1).....	Do.
Fast orange Diazole S (C.I. Direct Orange 26).....	Do.
Scarlet Diazole B (C.I. Direct Red 37).....	red.
Rose Diazole R (C.I. Direct Red 31).....	rose.
Fast red Diazole F (C.I. Direct Red 1).....	red.
Fast bordeaux Diazole 3B (C.I. Direct Red 16).....	bordeaux.
Brown Diazole M (C.I. Direct Brown 2).....	brown.
Violet Diazole BS (C.I. Direct Violet 22).....	violet.
Blue Diazole 3R (C.I. Direct Blue 3).....	blue.
Black Diazole ER (C.I. Direct Black 4).....	very dark grey.
Orange Cuprodiazole Light BR (C.I. Direct Orange 98).....	orange.

EXAMPLE 7

In this example one operates according to the process described in the first paragraph of Example 1, but the dye of Example 1 is replaced by one of those known on the market under the names mentioned in the following table.

Table VII

Dye	Colour on polyacrylonitrile fibre of Orion type
Tartrazine (C.I. Acid Yellow 23).....	yellow.
Acid red light B (C.I. Acid Red 37).....	red.
Acid black 2JL (C.I. Acid Black 16).....	very dark grey.
Superaid orange 3J (C.I. Acid Orange 35).....	orange.
Superaid brown 4R (C.I. Acid Brown 23).....	brown.
Chrysoine (C.I. Acid Orange 6).....	orange yellow.
Alizarin green J (C.I. Acid Green 25).....	green.
Foulon yellow 7JL (C.I. Acid Yellow 44).....	bright yellow.
Foulon violet S 2B (C.I. Acid Violet 72).....	violet.
Acid yellow light 5R (C.I. Acid Yellow 3).....	orange.
Superaid yellow 5JL (C.I. Acid Yellow 22).....	yellow.
Pyrazolone yellow 3J (C.I. Acid Yellow 37).....	Do.
Xylene orange L (C.I. Acid Orange 17).....	orange.
Foulon Scarlet R (C.I. Acid Red 97).....	red.
Superaid brown R (C.I. Acid Brown 35).....	brown.
Fast Acid green BL (C.I. Acid Green 31).....	green.
Alizarin Cyanine green 5G (C.I. Acid Green 41).....	Do.
Acid Alizarin sky blue B (C.I. Acid Blue 78).....	blue.
Alizarin sapphire SE (C.I. Acid Blue 43).....	Do.
Fast Cyanine brilliant JL (C.I. Acid Blue 101).....	Do.
Fast Cyanine brilliant BL (C.I. Acid Blue 59).....	Do.
Orange II (C.I. Acid Orange 7).....	orange.
Foulon orange R (C.I. Acid Orange 79).....	Do.
Fast Acid red BRL (C.I. Acid Red 118).....	red.
Fast Acid red 4BL (C.I. Acid Violet 14).....	violet red.
Superaid red 2J (C.I. Acid Orange 19).....	red.
Superaid red J (C.I. Acid Red 181).....	Do.
Foulon red J (C.I. Acid Red 85).....	Do.

EXAMPLE 8

In this example one operates as indicated in the first paragraph of Example 5, the soluble chromium salt being replaced by stannous chloride. A bright yellow colour is obtained.

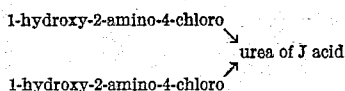
The colours obtained with the same dye in the presence of other soluble metal salts are indicated in Table VIII below:

Table VIII

Metal salt	Colour obtained on polyacrylonitrile fibre of the Orion type
Nickel acetate.....	reddish orange.
Cobalt nitrate.....	Do.
Aluminium sulphate.....	orange yellow.
Manganese sulphate.....	yellow.
Ferrous sulphate.....	beige.

EXAMPLE 9

In this example one operates as in Example 5, the dye of Example 5 being replaced by a direct copperable dye, for example, the dye



and the soluble chromium salt being replaced by stannous chloride. A chestnut colour is obtained.

In the presence of one of the soluble metal salts enumerated in Table IX below, the same dye gives the following colours:

Table IX

Metal salt	Colour obtained on polyacrylonitrile fibre of the Orion type
Chromium fluoride.....	red.
Nickel acetate.....	violet red.
Aluminium sulphate.....	bordeaux.
Manganese sulphate.....	red.
Cobalt nitrate.....	violet brown.
Ferrous sulphate.....	yellowish brown.

EXAMPLE 10

In this example, the metalliferous complex of a metal-lisable dye previously prepared before dyeing, is used. In this case therefore, it is not necessary to add a metal salt to the dye bath.

This metallic complex is prepared as follows: a solution of 10 parts of the so-called chrome dye described in the first paragraph of Example 5 in 100 parts of water is treated with a solution of 5 to 20 parts of a soluble metal salt, such as stannous chloride, in 50 to 100 parts of water. The precipitate instantaneously formed is filtered off on a Buchner funnel, washed with distilled water to remove excess metal salt or dye which has not formed a complex, and dried.

In order to dye polyacrylonitrile fibres, the procedure of Example 1 is used, the dye of Example 1 being replaced by the metalliferous complex prepared as above. A bright yellow colour is obtained.

EXAMPLE 11

In this example one operates as in Example 1, with the hydroxylamine sulphate being replaced by the mixture of the following constituents:

- 1 part of sodium nitrite
- 20 parts of sodium bisulphite (28° Bé. solution)
- 2 parts of concentrated sulphuric acid

A cream colour is obtained.

EXAMPLE 12

10 parts of fibres based on polyacrylonitrile are introduced into a bath comprising 200 parts of water and one part of hydroxylamine sulphate. The temperature is raised to 120–130° C., and is kept at this for three quarters of an hour to one hour. The fibres so treated are rinsed in water and introduced into a bath made up of 200 parts of water and 0.2 part of the dye used in Example 1. The temperature is taken to 120–130° C. and dyeing carried out at this temperature for three quarters of an hour to one hour. The fibres are rinsed and washed with soap in the hot. An orange colour is obtained.

EXAMPLE 13

(a) A strip of polyacrylonitrile fabric of Orion type is passed into a foularding bath containing the dye used in Example 1 and hydroxylamine sulphate in a ratio of 5 parts of hydroxylamine sulphate to one part of dye. After foularding, the fabric is squeezed out in such a way that one can fix 0.2 part of dye and 1 part of hydroxylamine sulphate for 10 parts of fabric.

The fabric is then introduced into a bath consisting of 200 parts of water. The temperature is taken to 120–130° C. and kept at this for about three quarters of an hour. The fabric is rinsed and washed with soap in the hot. An orange colour is obtained.

(b) Foularding is effected in the same manner as in (a) and the fabric is steamed for half an hour at normal pressure (102–103° C.). With or without intermediate drying, an orange colour is obtained.

(c) Foularding is effected in the same manner as in (a) and the fabric is steamed for half an hour under pressure (at 130° C.); with or without intermediate drying, an orange colour is obtained.

(d) Foularding is effected in the same manner as in (a) and the fabric is left for half an hour in a chamber heated to a temperature of 150° C.; with or without intermediate drying, a yellowish orange colour is obtained.

EXAMPLE 14

(a) A piece of polyacrylonitrile fabric of Orion type is printed by the roller process with a paste having the following composition:

	Parts
Dye used in Example 1.....	3
Glycerine.....	5
Hydroxylamine sulphate.....	15
Hot water.....	27
Starch-tragacanth thickener.....	50

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The fabric is steamed for half an hour at normal pressure (at 102–103° C.). With or without intermediate drying, and after rinsing and washing with soap in the hot, a reddish orange colour is obtained.

(b) Printing is effected as in (a), and the fabric is steamed for half an hour under pressure (130° C.). With or without intermediate drying, and after rinsing and washing with soap in the hot, a reddish orange colour is obtained.

EXAMPLE 15

Operating according to the process described in Example 14, (a) and (b), but replacing the dye of Example 14 by that described in Example 3, a violet blue colour is obtained by the variant (a) and a navy blue colour by the variant (b).

EXAMPLE 16

In this example one operates according to the process described in Example 14 under (a) and (b) but with a paste having the following composition:

	Parts
Dye used in Example 5.....	3
Glycerine.....	5
Hydroxylamine sulphate.....	15
Chromium acetate at 20° Bé.....	9
Hot water.....	18
Starch-tragacanth thickener.....	50
	100

A brownish red colour is obtained with or without intermediate drying.

EXAMPLE 17

(a) 10 parts of polyacrylonitrile of Orlon type, in the form of fabric, are introduced into a bath consisting of 200 parts of water and one part of hydroxylamine sulphate. The temperature is taken to 120–130° C. and kept at this for three quarters of an hour to an hour. The fabric thus treated is rinsed in hot water and dried in hot air. Printing is effected by the process described in Example 14 under (a), using a paste of the same composition. An orange colour is obtained by steaming at normal pressure (102–103° C.) or under pressure (130° C.).

(b) Operating according to the process described under (a), but replacing the polyacrylonitrile of Orlon type by a product from the copolymerisation of acrylonitrile and vinyl acetate or vinyl pyridine, known by the commercial name of Acrilan, a brownish orange colour is obtained by steaming at normal pressure (102–103° C.) or under pressure (130° C.).

EXAMPLE 18

A piece of polyacrylonitrile fabric of Orlon type is printed by the roller process, with a paste having the following composition:

	Parts
Dye used in Example 1.....	3
Glycerine.....	5
Sodium nitrite.....	1.5
Sodium bisulphite (28° Bé.).....	7.5
Ammonium sulphate.....	6
Hot water.....	27
Starch-tragacanth thickener.....	50
	100

The fabric is steamed for half an hour either at normal pressure (102–103° C.) or under pressure (130° C.), a reddish orange colour being obtained.

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EXAMPLE 19

On operating as in Example 4, and using the following quantities of dye and hydroxylamine sulphate:

(a) 0.4 part of dye and 2 parts of hydroxylamine sulphate: a dark jade green is obtained.

(b) 0.02 part of dye and 0.5 part of hydroxylamine sulphate; a pastel green is obtained.

EXAMPLE 20

On operating as in Example 1, and replacing the dye of Example 1 by a mixture of the following dyes:

0.1 part of the dye used in Example 4, and

15 0.1 part of the dye used in Example 5

and adding 0.2 part of stannous chloride to the dye bath, a bright yellow green is obtained.

EXAMPLE 21

20 In this example one operates according to the process described in Example 1, the dye of Example 1 being replaced by one of those known on the market by the names mentioned in Table X below:

Table X

Dye	Colour obtained on polyacrylonitrile fibres
Solasol Brilliant Yellow JS (C.I. Solubilised Vat Yellow 4).	yellow.
Solasol Brilliant Yellow RS (C.I. Solubilised Vat Orange 1).	orange.
35 Solasol Orange RH (C.I. Solubilised Vat Orange 5).	Do.
Solasol Brilliant Rose RS (C.I. Solubilised Vat Red 1).	red.
Solasol Brilliant Violet 4 RS (C.I. Solubilised Vat Violet 1).	violet.
Solasol Blue SBS (C.I. Solubilised Vat Blue 6).	blue.
Solasol Dark Green JS extra (C.I. Solubilised Vat Green 3).	green.
40 Solasol Brown BRS (C.I. Solubilised Vat Brown 1).	brown.
Solasol Brown 2 RS (C.I. Solubilised Vat Brown 5).	Do.

We claim:

1. A process for colouring a synthetic material selected from the group consisting of the polymerisation products of acrylonitrile, the copolymerisation products of acrylonitrile, the polymerisation products of vinylidene cyanide and the copolymerisation products of vinylidene cyanide, which comprises simultaneously treating the synthetic material at above 100° C. with (1) a dye selected from the group consisting of the acid non-metallisable dyes, the direct non-metallisable dyes, the chromiferous dyes as 1:1 complexes, the metalliferous dyes as 2:1 complexes, the complexes of polysulphonated monoazo dyes and copper from the class of direct dyes, the complexes of the sulphonated polyazo dyes and copper from the class of direct dyes, the phthalocyanines, the derivatives of phthalocyanines, the chrome dyes (mordant dyes), the direct metallisable dyes and the leuco esters of vat dyes, and with (2) a member selected from the group consisting of hydroxylamine and its salts.

2. A process as claimed in claim 1 in which the dyeing is effected with a metallisable dye selected from the group consisting of the chrome dyes (mordant dyes), and the direct metallisable dyes, in the presence of a salt of a metal selected from the metals of the group consisting of chromium, iron, nickel, cobalt, tin, aluminium and manganese.

3. A process as claimed in claim 1 in which hydroxylamine is replaced by a mixture capable of providing it, comprising sodium nitrite, sodium bisulphite and an acid.

4. A process as claimed in claim 1 in which the amount of the member selected from the group consisting of hydroxylamine and its salts is from 0.5% to 10% based on the weight of synthetic material.

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5. A process as claimed in claim 2 in which the amount of the metal salt is from 0.5% to 10% based on the weight of synthetic material.

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