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3,148,935

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3,148,935

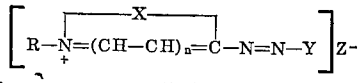
DYEING TEXTILE MATERIAL CONSISTING OF POLYACRYLONITRILE AND ITS COPOLYMERS

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Claims priority, application Germany June 25, 1955
3 Claims. (Cl. 8—41)

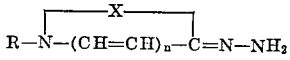
This invention relates to an improved process of dyeing textile material consisting of polyacrylonitrile and its copolymers.

We have found that textile material consisting of polyacrylonitrile and its copolymers can be dyed very fast, brilliant shades by using as the dyestuffs basic dyestuffs of the general formula

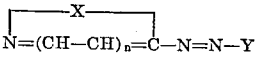


in which R represents an alkyl, aralkyl, aryl or cycloalkyl group, n is zero or 1, X represents a divalent atom or a divalent group which makes up the nitrogen-containing ring to a five-membered or six-membered ring, Y is the radical of an aromatic amine or enamine capable of being azo-coupled and Z^- is an anion.

A compound of this kind is already known (cf. Glauert, J. Chem. Soc. London, 1953, 3742); other members are obtained for example by oxidizing condensation of hydrazones of heterocyclic ketones of the general formula



in which R, n and X have the above significance, with aromatic amines or enamines capable of being azo-coupled in acid medium, or by allowing alkylating agents to act on dyestuffs free from sulfonic acid groups of the general formula



in which n, X and Y also have the above significance.

For dyeing with the basic dyestuffs of the said kind there are especially suitable flocks, fibres, threads, filaments, bands and woven or knitted fabrics of pure polyacrylonitrile or of copolymers of acrylonitrile with other vinyl compounds, such as vinyl chlorides, vinylidene chloride, vinyl fluoride, vinyl acetate, vinyl propionate, vinylpyridine, vinylimidazole, vinyl alcohol, acrylic acid esters, methacrylic acid esters and/or acrylamides, said copolymers containing above about 40 percent and preferably at least 75 percent (by weight) of acrylonitrile.

In principle, the dyeing can be carried out either in an acid bath or in a neutral or weakly alkaline bath, because

the basic dyestuffs of the said kind in general undergo no appreciable change in shade of color upon variation in the pH-value.

Consequently the pH-value may also be changed during the dyeing, and this may be advantageous in some cases. The baths are in general best exhausted at weakly acid pH-values. The most favorable dyeing temperatures vary according to the material to be dyed. In general the material is entered into the dyebath at about 40° to 60° C. and dyeing effected at the boil; however it is possible to dye under static pressure at more than 100° C., for example at 105° to 130° C. The co-employment of the usual dyeing assistants is sometimes advantageous but usually unnecessary.

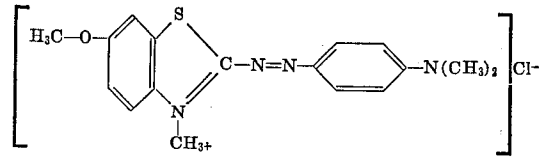
The dyestuffs can also be added to spinning solutions which contain polyacrylonitrile or copolymers of acrylonitrile with other vinyl compounds. The spun-dyed structures thereby obtained can be further dyed or shaded if desired with any desired dyestuffs, in particular those herein specified, in aqueous baths.

The dyeings obtained are distinguished by vivid, powerful shades and very good to excellent fastness, in particular in many cases by a fastness to light hitherto unattainable on polyacrylonitrile.

The following examples will further illustrate this invention but the invention is not restricted to these examples. The parts specified are parts by weight.

Example 1

A fabric of 100 parts of polyacrylonitrile fibres is introduced at about 50° C. into a dyebath containing in 4000 parts of water 0.7 part of the dyestuff of the formula

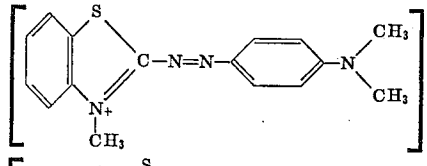
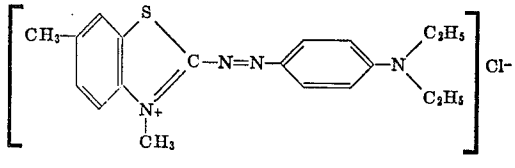


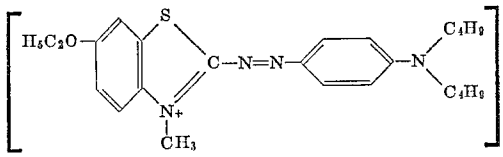
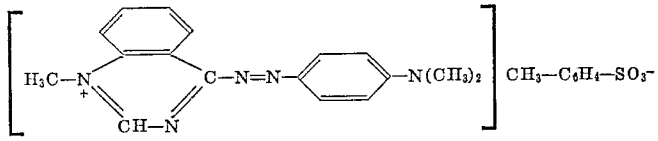
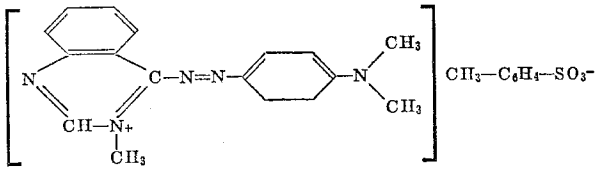
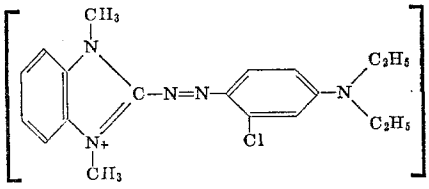
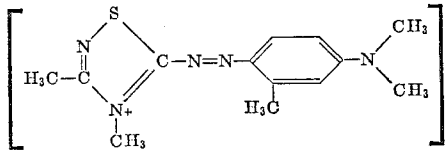
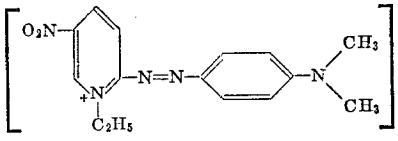
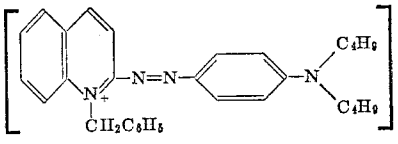
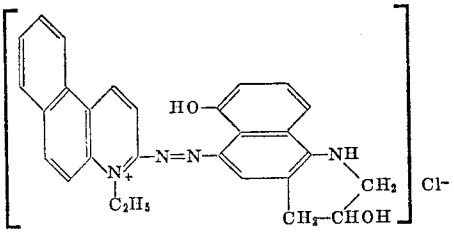
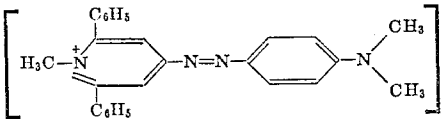
and 5 parts of 30 percent acetic acid. The whole is heated during the course of about 30 minutes to the boiling temperature and dyeing continued for 90 minutes in the boiling bath. The fabric is then rinsed and dried. A powerful, very level, pure blue dyeing of excellent properties is obtained.

Instead of acetic acid, for example 3.6 parts of 96 percent sulfuric acid may also be used. When dyeing from a neutral bath, somewhat less dyestuff is taken up.

If the dyeing is commenced in a weak ammoniacal bath and continued with the gradual addition of small amounts of acetic or sulfuric acid, very powerful dyeings are obtained with extensive exhaustion of the dyebath.

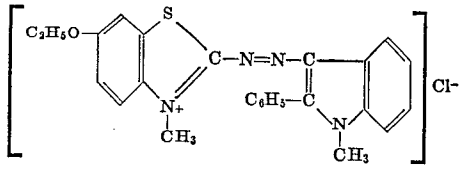
For the dyeing there may be used in an analogous manner the dyestuffs set out in the following table, which also indicates the shade of color obtained:

Dyestuff	Dyeing on fibres of polyacrylonitrile
	Blue violet.
	Reddish blue.

Dyestuff	Dyeing on fibres of polyacrylonitrile
	Pure blue.
	Violet.
	Do.
	Red violet.
	Blue violet.
	Violet.
	Green blue.
	Green.
	Red.

Example 2

100 parts of a fabric of a copolymer of 95 percent of acrylonitrile and 5 percent of butyl methacrylate are dyed in the manner described in Example 1 with a dyebath which consists of a solution of 0.8 part of the dyestuff of the formula

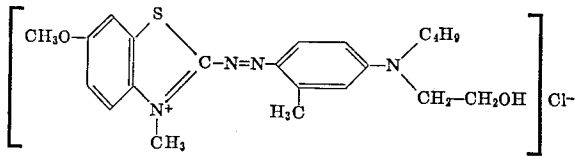


in 4000 parts of water. A very fast red-violet dyeing is obtained.

Dyeing can be effected in an analogous manner with the other dyestuffs in the table in Example 1.

Example 3

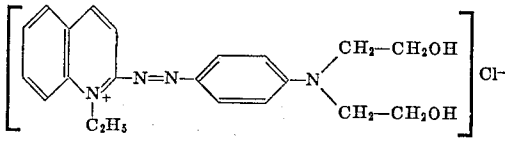
100 parts of pure polyacrylonitrile monofil are dyed in a pressure vessel for 60 minutes at 125° C. with a solution of 0.8 part of the dyestuff of the formula



in 2000 parts of water with the addition of 5 parts of 30 percent acetic acid. A powerful pure blue dyeing of excellent fastness is obtained.

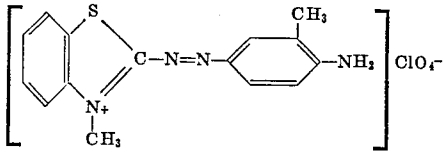
Example 4

To a spinning solution, consisting of a solution of 1000 parts of polyacrylonitrile in the necessary amount of dimethylformamide, there is added a solution of 10 parts of the dyestuff of the formula



in dimethylformamide. By spinning, a material is obtained which is dyed fast blue.

With the dyestuff of the formula

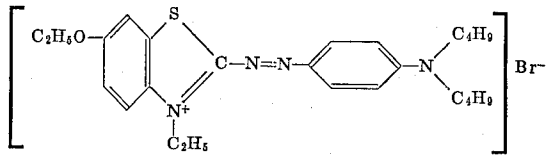


fibres dyed fast bluish red are obtained.

Example 5

100 parts of fibres of a copolymer of 40 parts of acrylonitrile and 60 parts of vinyl chloride are moved for 90 minutes at 85° C. in a dyebath which contains, in 3000

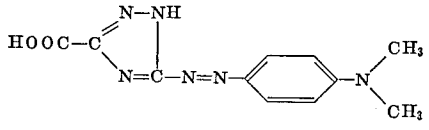
parts of water, 0.7 part of the dyestuff of the formula



5 parts of 30 percent acetic acid and 3 parts of the reaction product of 24 mols of ethylene oxide on 1 mol of sperm oil alcohol. The fibrous material is dyed pure blue; the dyeing is extremely fast.

Example 6

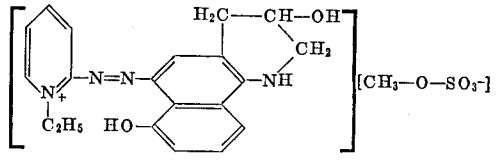
100 parts of fibrous material of a copolymer of 90 percent of acrylonitrile, 5 percent of vinyl acetate and 5 percent vinylpyridine are dyed for 90 minutes at the boiling temperature in a bath containing in 2000 parts of water 3 parts of 96 percent sulfuric acid, 2 parts of the reaction product of 25 mols of ethylene oxide on 1 mol of octadecyl alcohol and 1 part of the basic azo dyestuff obtained by reacting 18 parts of the dyestuff of the formula



with 35 parts of dimethyl sulfate in 200 parts of dimethylformamide at 110° C.

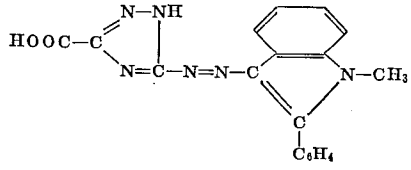
A powerful pure red dyeing of very good fastness to light and good fastness to moisture is obtained.

By using for the dyeing 0.8 part of the dyestuff of the formula

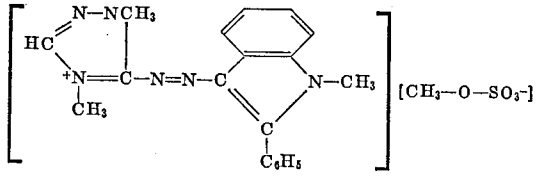


there is similarly obtained a very fast bluish green dyeing.

With the basic dyestuff obtainable by reacting with dimethyl sulfate the dyestuff of the formula

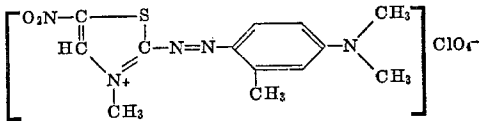
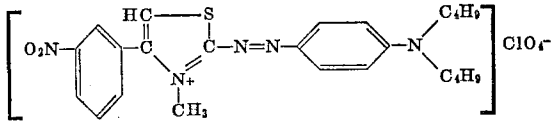
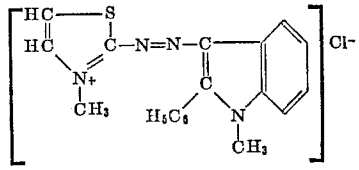
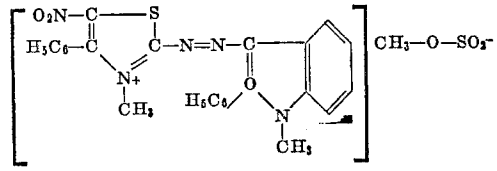
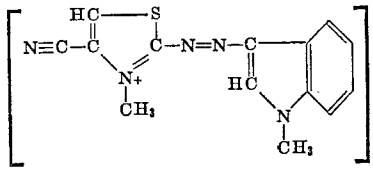
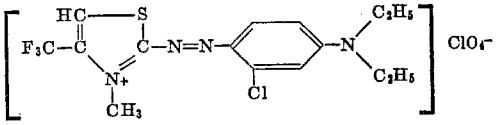


clear, fast reddish yellow dyeings are obtained in analogous manner.



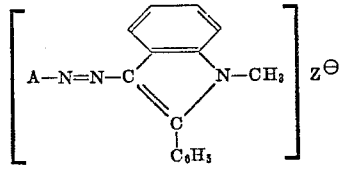
Example 7

Polyacrylonitrile fibres are dyed in the manner described in Example 1 with the dyestuffs enumerated in the following table, the dyeings therein listed being thereby obtained. All the dyeings are very level, powerful and extremely fast to light:

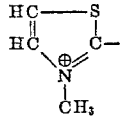
Dyestuff	Dyeing on fibres of polyacrylonitrile
	Blue.
	Do.
	Red.
	Do.
	Do.
	Blue.

What we claim is:

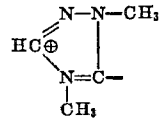
1. A textile material comprising an acrylonitrile polymer containing at least 40% by weight of acrylonitrile which is colored with a basic cationic dyestuff of the formula:



wherein A represents a member selected from the class consisting of

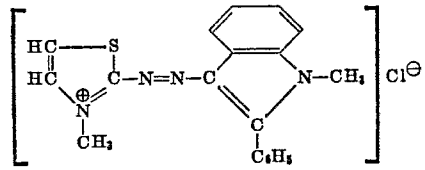


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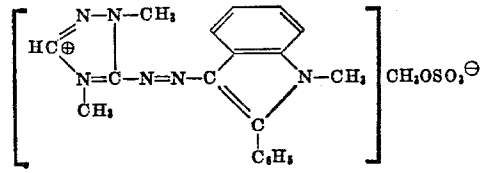


and $Z^{\ominus}$ represents an anion.

2. The colored textile material of claim 1 in w the dyestuff has the formula:



3. The colored textile material of claim 1 in w the dyestuff has the formula:



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9

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10

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