

[54]	BRIGHTENING OF POLYACRYLONITRILE WET TOW	3,122,443	2/1964	Blankenship et al.	8/115.6
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[75]	Inventors: Gottfried Eigenmann, Therwil; Leo Kaiser, Aesch; Christian Luethi, Muenchenstein, all of Switzerland	3,271,321	9/1966	Stilz et al.	252/301.2 W
		3,274,184	9/1966	Thompson et al.	252/301.2 W
		3,401,048	9/1968	Okubo et al.	117/33.5 T
[73]	Assignee: Ciba-Geigy AG, Basel, Switzerland	3,597,364	8/1971	Okubo et al.	117/33.5 T
		3,627,758	12/1971	Weber Basel et al.	252/301.2 W
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[21]	Appl. No.: 260,786	3,711,472	1/1973	Siegrist et al.	117/33.5 T

[30] **Foreign Application Priority Data**
 June 18, 1971 Switzerland..... 8929/71

[52] **U.S. Cl.**..... 117/7, 8/115.6, 117/33.5 R, 117/33.5 T, 252/301.2 W, 260/240 CA, 260/240 B

[51] **Int. Cl.**..... C09b 23/14, C09k 1/60

[58] **Field of Search**..... 117/33.5 T, 33.5 R, 7; 252/301.2 W; 8/115.6; 260/240 CA, 240 B

[56] **References Cited**
UNITED STATES PATENTS
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[57] **ABSTRACT**

The invention relates to a process for optically brightening polyacrylonitrile fibres, which have been manufactured by the wet spinning process and are in the gel state by means of selected types of anionic optical brightening agents.

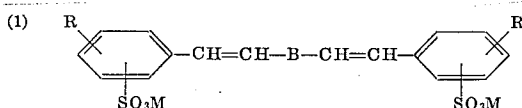
9 Claims, No Drawings

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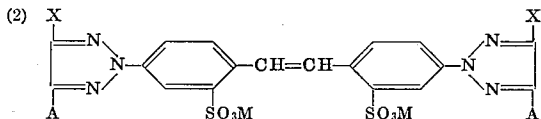
BRIGHTENING OF POLYACRYLONITRILE WET TOW

The present invention relates to a process for brightening optionally modified polyacrylonitrile fibres, which have been manufactured by the wet spinning process and are in the gel state, by means of selected types of compounds.

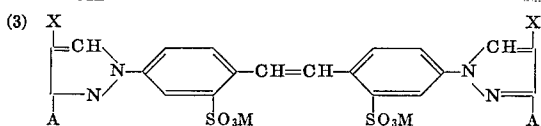
These types of compounds correspond to the formulae



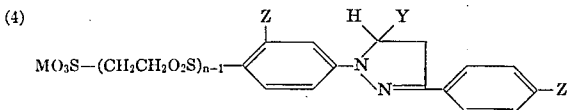
wherein B denotes 4,4'-biphenylene, 1,4-phenylene or 2,6-naphthylene, R denotes hydrogen, alkyl with 1 to 4 carbon atoms, halogen, $-\text{SO}_3\text{M}$ or alkoxy with 1 to 4 carbon atoms located in the ortho- or meta-position to the bridge member and M denotes a hydrogen, alkali metal, ammonium or amine salt ion, the solubility of these compounds in water at 90°C being at least 10 g/l, preferably at least 40 g/l,



wherein X denotes hydrogen or halogen and A denotes a phenyl radical which is optionally substituted by alkyl with 1 to 4 carbon atoms, halogen or a $-\text{SO}_3\text{M}$ grouping (with M = a hydrogen, alkali metal, ammonium or amine salt ion) and M denotes a hydrogen, alkali metal, ammonium or amine salt ion,



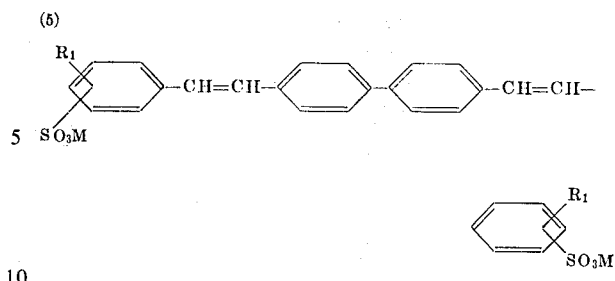
wherein X denotes hydrogen or halogen and A denotes a phenyl radical which is optionally substituted by alkyl with 1 to 4 carbon atoms, halogen or a $-\text{SO}_3\text{M}$ grouping and M denotes a hydrogen, alkali metal, ammonium or amine salt ion and



wherein Y denotes hydrogen, alkyl with 1 to 4 carbon atoms or phenyl, Z and Z₁, independently of one another denote hydrogen or chlorine, M denotes a hydrogen, alkali metal, ammonium or amine salt ion and n represents 1 or 2.

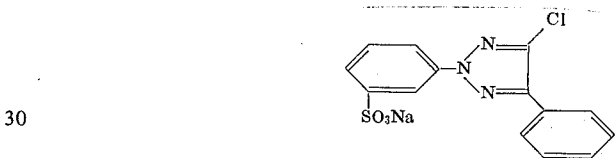
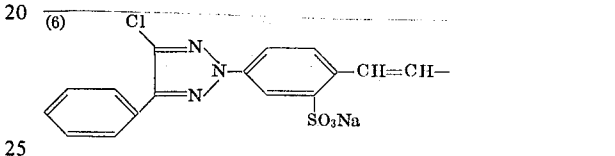
Within the framework of the formula (1), the compounds of the formula

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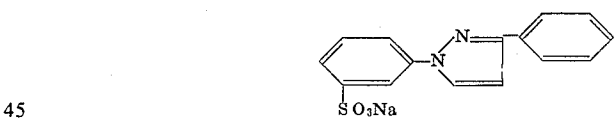
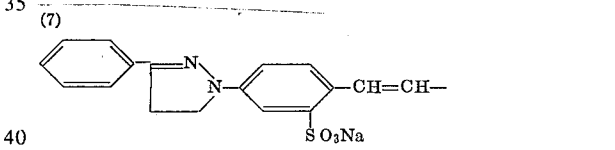


wherein R₁ represents hydrogen, alkyl with 1 to 4 carbon atoms, halogen or alkoxy with 1 to 4 carbon atoms located in the ortho- or meta-position to the bridge member and M denotes a hydrogen, alkali metal, ammonium or amine salt ion, should be particularly singled out.

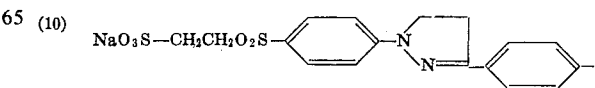
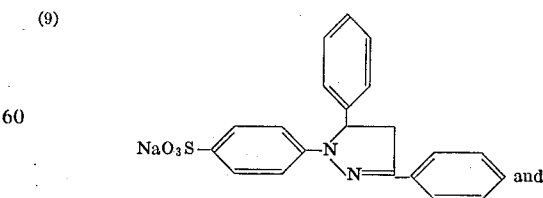
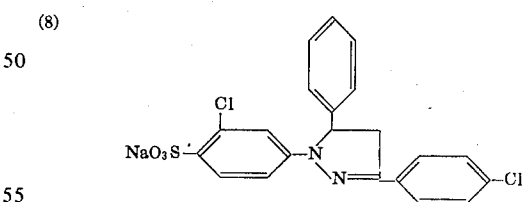
As an example of a compound of the formula (2) there may be mentioned the compound of the formula



and as an example of a compound of the formula (3) there may be mentioned the compound of the formula



whilst the compounds of the formulae



are embraced by the general formula (4).

According to the invention, the brighteners of the formulae (1) to (10) are applied to the fibre manufactured by the wet spinning process whilst the fibre is still in the gel state. In the gel state, the fibre still contains large amounts of water and is therefore strongly swollen. After the fibre formation (spinning process) and the washing process for removing solvents or solubilising agents, the fibre is stretched to orient the macro-molecules and is subsequently dried. This causes the gel state to disappear.

Processes for brightening polyacrylonitrile fibres which are in the gel state essentially consist of bringing the fibres, in the swollen state, into contact with the brightener solution either on a padder or in a bath. The latter can for example also be effected by moving the fibre or the hank of fibres through a brightener solution or suspension flowing in counter-current. The baths to be used are appropriately prepared by dissolving or dispersing the brightener in water and adjusting the resulting liquor to the desired pH value with acid and/or a buffer salt. This pH value is generally between 1 and 7, and is, for example, 1.5 to 5.5. The concentration of brightener in the bath is in most cases so chosen that after the treatment 0.005 to 0.5 percent, for example 0.05 to 0.2 percent, of brightener, relative to the dry weight of the fibre, is absorbed on the fibre. The treatment of the fibre in the brightener bath can be carried out at a bath temperature of below 50°C, for example at 10° to 30°C. In general, the duration of treatment of the fibre in the brightener bath is less than 2 minutes, preferably less than 40 seconds.

gory of derivatives of 4,4'-bis-[1,3,5-triazinyl-(2)-amino]-stilbene-2,2'-disulphonic acids show no significant effect.

EXAMPLE 1

A polyacrylonitrile tow obtained by the sodium thiocyanate wet spinning process, which has been rinsed and stretched but not dried, is immersed for 30 seconds into a solution of the following composition:

0.1	g/litre of 4,4'-bis-(2-sulphostyryl)-diphenyl (solubility at 90°C, approx. 260 g/l)
0.5	ml/litre of 98% strength sulphuric acid
	pH of the solution: 2
	Temperature: 20°C
	Liquor ratio 1 : 10

The tow is subsequently briefly rinsed in water and is dried in air at 95°C. The degree of whiteness of the polyacrylonitrile tow thus obtained is 190 [CIBA whiteness scale; see, for example, Fette, Seifen, Anstrichmittel Vol. 11, page 881 pp (1968)], compared with a degree of whiteness of 50 obtained in the absence of the 4,4'-bis-(2-sulphostyryl)-diphenyl.

The same result is obtained if the above brightener bath is adjusted to pH 5 with acetic acid, the sulphuric acid being omitted.

EXAMPLE 2

The experiments described in Example 1 are repeated, employing the compounds listed in Table I instead of 4,4'-bis-(2-sulphostyryl)-diphenyl. In this way, the degrees of whiteness indicated in Table I are obtained:

Table I

Compound	Solubility in water at 90°C	pH value of the bath	Degree of whiteness of the fibre according to the CIBA whiteness scale
4,4'-Bis-(2-chloro-5-sulphostyryl)-diphenyl	approx. 50 g/l	2	180
		5	175
1,4-Bis-(2-sulphostyryl)-benzene	>10 g/l	2	150
		5	150
2,6-Bis-(2-sulphostyryl)-naphthalene	>10 g/l	2	190
		5	190
4,4'-Bis-(3-sulpho-4-chlorostyryl)-diphenyl	approx. 2 g/l	2	<100
		5	<100
4,4'-Bis-(3-sulphostyryl)-diphenyl	>1 g/l	2	<100
		5	<100

The present invention also relates to the use of the brighteners of the formulae (1) to (10) for application onto polyacrylonitrile fibres which are in the gel state.

It is particularly surprising, in the present case, that the anionic brighteners of the indicated formulae give good effects whilst they fail when used for brightening polyacrylonitrile according to conventional methods (such as, for example, in the treatment of the previously stretched and dried fibre by the exhaustion process at 90°C), that is to say are not absorbed on the fibre, or are insufficiently absorbed to give a brightening which meets requirements.

A further surprising fact is that the anionic compounds of the indicated formulae are outstandingly suitable for the use according to the invention whilst, for example, anionic brighteners from the large cate-

The last two experiments show that with this class of compound sufficient solubility in water is a prerequisite for achieving a satisfactory brightening effect.

EXAMPLE 3

The experiments described in Example 1 are repeated, employing a compound of the formula (6), (8) or (9) instead of 4,4'-bis-(2-sulphostyryl)-diphenyl. The results thus obtained are listed in Table II:

Table II

Compounds of the formula	pH Value of the bath	Degree of whiteness of the fibre according to the CIBA whiteness scale
(6)	2	160
	5	150

Table II-Continued

Compounds of the formula	pH Value of the bath	Degree of whiteness of the fibre according to the CIBA whiteness scale
(8)	2	175
	5	170
(9)	2	120
	5	170

EXAMPLE 4

Similar results to those in Examples 1 to 3 are obtained if, under otherwise identical conditions, the process is carried out in a continuous apparatus by the countercurrent principle, with the continuously added liquor introducing 1.0 g of one of the abovementioned compounds per minute into the bath and the throughput of polyacrylonitrile wet tow in the opposite direction being 400 g per minute (expressed as dry weight).

EXAMPLE 5

Similar brightening effects of those in Examples 1 to 4 are obtained by working in a static bath in which the concentration of one of the abovementioned compounds is kept constant at 0.1 g/litre whilst the fibre material is continuously drawn through the bath.

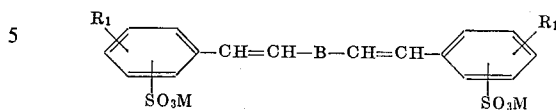
EXAMPLE 6

Similar brightening effects on polyacrylonitrile wet tows to those in Examples 1 to 5 are obtained if the polyacrylonitrile tow which has not been dried and is in the gel state is padded with a liquor which per litre contains 0.6 g of one of the abovementioned brighteners, the liquor uptake being 150 percent.

What we claim is:

1. A process for providing brightened polyacrylonitrile stretched fibres, comprising treating the fibres in

the gel state in a bath which contains at least one compound of the formula



10 wherein B is 4,4'-biphenylene, 1,4-phenylene or 2,6-naphthylene, R is hydrogen, alkyl with 1 to 4 carbon atoms, halogen, $-\text{SO}_3\text{M}$ or alkoxy with 1 to 4 carbon atoms located in the ortho- or meta-position to the bridge member and M denotes the hydrogen, alkali metal, ammonium or amine salt ion, the solubility of these compounds in water at 90°C being at least 10 g/l and drying the treated fibers.

2. A process according to claim 1 wherein B is 4-4'-biphenylene.

3. A process according to claim 1 wherein the fibres are stretched prior to said treatment.

4. A process according to claim 1 wherein the fibres are stretched after said treatment.

5. A process according to claim 1 wherein the treatment of the fibres is carried out at a temperature below 50°C.

6. A process according to claim 1 wherein the brightener concentration is so chosen that after the treatment 0.005 to 0.5 percent of brightener, relative to the dry weight of the fibres, has been applied to the fibres.

7. A process according to claim 1 wherein the duration of treatment of the fibres in the bath is less than 2 minutes.

8. A process according to claim 1 wherein the fibres are moved through the brightener liquor which is flowing in counter-current.

9. Polyacrylonitrile fibres which have been brightened according to the process of claim 1.

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