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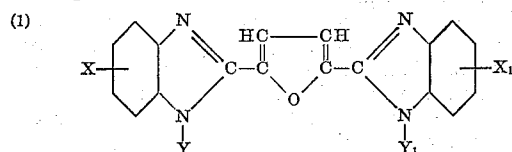
PROCESS FOR THE OPTICAL BRIGHTENING OF POLYACRYLONITRILE FIBERS

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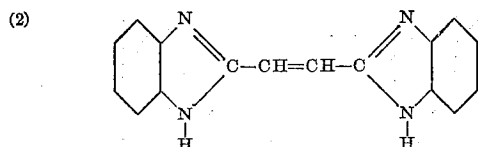
This is a continuation-in-part of our copending patent application Serial No. 563,457, now U.S. Patent No. 2,977,319 filed February 6, 1956.

The invention relates to a process for the optical brightening of polyacrylonitrile fibers which comprises treating said fibers with a compound of the formula



wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

The invention relates further to a process for the optical brightening of polyacrylonitrile fibers which comprises treating said fibers with the optical brightening agent of the formula



The present invention relates further to a composition of matter substantially consisting of polyacrylonitrile fibers having incorporated a small quantity of an optical brightening agent of the general Formula 1 or of the Formula 2.

The 2:5-di-[benzimidazolyl-(2')] -furans of the general Formula 1 can be made by heating an ortho-diamine of the benzene series, of which one amino group is primary and the other amino group is at most secondary and which may contain a chlorine atom or an alkyl group of low molecular weight in the benzene nucleus, with furan-2:5-dicarboxylic acid, and, when the ortho-diamine used as starting material contains two primary amino groups, if desired, treating the resulting 2:5-di[benzimidazolyl-(2')] -furan with an alkylating hydroxyalkylating, alkenylating or aralkylating agent.

The reaction is advantageously carried out at a temperature of at least 190° C. However, the dibenzimidazolyl-furans can also be obtained, as described for the known compound in U.S. Patent No. 2,463,264 patented March 1, 1949 by Charles Greanacher et al., by reacting the components together at a temperature below 190° C., for example, at about 150° C., but substantially lower yields are obtained.

In general, the two starting materials are advantageously used for the reaction in at least approximately the theoretical proportions, that is to say, that for every molecular proportion of furan dicarboxylic acid there are used 2 molecular proportions or an amount at most a

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few percent more or less than 2 molecular proportions, of the diamine. While the reaction can be carried out in a suitable high boiling solvent, this usually leads to less satisfactory results than when the reaction mixture consists solely of the two starting materials and, if desired, a small proportion of boric acid.

The presence of boric acid increases the yield quite considerably. The proportion of boric acid is advantageously about 0.5% to 5% calculated on the total weight of the reaction mixture.

Furthermore, it is of advantage to carry out the reaction in the absence of oxygen (air), for example, in vacuo or advantageously in an inert gas, such as nitrogen.

The procedure may, for example, consist in heating together the two starting materials at about 140 to 150° C. in the presence or absence of boric acid, if desired, after mixing them together in the solid state. The resulting melt is then gradually raised to about 200° C. While thus increasing the temperature, the elimination of water sets

in. The period during which the temperature is raised from 140° C. to about 200° C. should not be too long, as otherwise there is a risk of the melt thickening or even solidifying. The reaction is then advantageously completed at a temperature ranging from 200° C. to 230° C.

The water liberated during the reaction can be separated, and the progress and termination of the reaction can easily be followed by observing the evolution of steam.

The imidazole compounds so obtained can be isolated from the reaction mixture by the usual known methods.

An advantageous method consists in diluting the melt, while still hot, with a high boiling, inert, water-soluble organic solvent, precipitating the imidazole in the form of a salt, which is usually sparingly soluble in water, by adding a dilute mineral acid, for example, sulfuric acid or hydrochloric acid, and then separating the salt from the aqueous solution. From the salt the base can be liberated with the aid of an alkali, such as an alkali metal carbonate or ammonia.

Instead of using as starting materials for the manufacture of the furan compounds substituted at the imidazole nitrogen atoms, for example, those of Formula 1, diamines which contain a secondary amino group, the substituents in question (Y and/or Y₁; see above) may be subsequently introduced into 2:5-di-[benzimidazolyl-(2')] -furans unsubstituted at the imidazole nitrogen atoms, and one or both of the hydrogen atoms bound to nitrogen may be thus exchanged for substituents.

The material to be improved by the use of the present process can exist in any stage of processing, it being obviously advantageous to treat it in the described manner at a stage when all other treatments have been completed which would have the effect of removing again the agent used according to the invention or would have an unfavorable effect upon it. The agents used can for example be added to the materials to be improved either before or during the shaping thereof. Thus they can be dissolved or finely distributed in a spinning mass before the spinning thereof.

Fibers can be used in the application of the present process which either consist of polyacrylonitrile alone or of fiber mixtures consisting to a substantial extent of polyacrylonitrile fibers, or of fibers consisting of copolymers containing other compounds in addition to polyacrylonitrile.

Especially valuable results are generally obtained with those 2,5-di-[benzimidazolyl-(2')] -furans of the general Formula 1 whose benzene radicals are substituted by low molecular alkyl groups, particularly methyl groups, which are preferably in the 5-positions of the benzimidazolyl-radicals.

If it is a question of improving textile fibers by the present process which can exist as staple fibers or mono-

filaments, in the crude state or in the form of yarns or fabrics, this operation is conducted with advantage in an aqueous medium in which the compounds to be used are dissolved or suspended. If desired dispersing agents can be added in the treatment for example soaps, polyglycol ethers of fatty alcohols or fatty amines, cellulose sulfite waste liquor or condensation products with formaldehyde of naphthalene sulfonic acids which may be alkylated.

It is of particular advantage, especially when the treatment of the fibers is exclusively for the purpose of improving the optical properties, to work in weakly alkaline to acid baths, preferably weakly acid baths, for example containing acetic acid or formic acid. It is likewise of advantage if the treatment takes place at elevated temperature, for example at the boiling temperature of the bath or in the neighbourhood thereof (about 90° C.). It is surprising that the compounds of the composition set forth above possess a good affinity for the fibers and can be fixed thereon in a similar manner to dyestuffs. In this connection it may be remarked that in the case of these synthetic fibers many optical improving and brightening agents which are of good applicability for other fiber materials, cannot be used for the reason that in this case they cannot be fixed on the fiber or do not give rise to the desired effect. The fastness to light of the materials treated according to the present process is also good, the effect persisting even after long exposure to light.

The quantity of the improving agent to be used, calculated on the material to be treated, can vary within wide limits. Even with very small quantities, in some cases for example, of 0.01 percent, a distinct and permanent effect can be attained. Although quantities of more than about 3 percent are in general not disadvantageous, they offer no advantages compared with the normal quantities.

As indicated above, the present process can advantageously be combined with other processing methods. Thus the compounds to be used according to the present invention can also be applied as follows:

(a) In admixture with dyestuffs or as additions to dye-baths or printing, discharge or reserve pastes. Further also for the after-treatment of dyeings, prints or discharge prints, especially in the soaping process. Thus, for example, polyacrylonitrile fibers can be simultaneously dyed and improved as regards optical properties in an acid medium and are dyed in the same bath with azo dyestuffs which are free from sulfonic acid groups and which contain as salt-forming groups amino groups and form with acids in an acid medium salts which at the most are partially hydrolyzable, these dyestuffs being fixed on the fiber in the form of their salts.

(b) In admixture with chemical bleaching agents or as additions to bleaching baths.

(c) In combination with washing agents: The washing agents and brightening agents can be separately added to the washing baths to be used. It is also advantageous to use washing agents which contain brightening agents admixed therewith. As washing agents are suitable for example, soaps (sodium salts of higher fatty acids), salts of sulfonate washing agents, as for example, of sulfonated benzimidazoles substituted on the 2-carbon atom by higher alkyl radicals, also salts of monocarboxylic acid esters of 4-sulfophthalic acid with higher fatty alcohols or salts of fatty alcohol sulfonates, alkylaryl sulfonic acids or condensation products of higher fatty acids with aliphatic hydroxy- or amino-sulfonic acids. Non-ionic washing agents can also be used, for example polyglycol ethers which are derived from ethylene oxide and higher fatty alcohols, alkyl phenols or fatty amines.

The washing agents of the above specified type can also contain the customary washing agent additions, such as alkali metal carbonates, phosphates, pyrophosphates, polyphosphates, metaphosphates, silicates, perborates or percarbonates, so long as the brightening agents are com-

patible with such additions. It is also possible to prepare washing agents which consist solely or for the most part of inorganic compounds of cleansing effect and the brightening agents. The production of the mixtures of the washing agents and optical brightening agents takes place in a simple manner by mixing and/or grinding of the components together. In this case it may be of advantage to use or the other component in the dissolved or molten condition for the purpose of facilitating distribution.

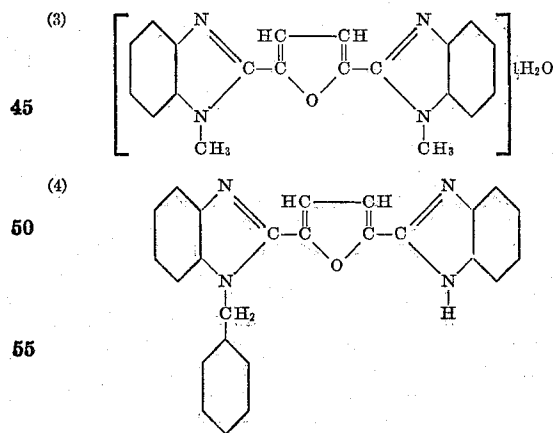
In general a small addition of the optical improving agents to the washing agents suffices. There are concerned, for example, quantities of 0.1 to 5 percent calculated on the washing agent. Also smaller quantities, for example, 0.01 percent or even less can be added. Also mixtures with other known brightening agents can be used. The washing agents are used as in the customary washing processes. In this manner materials to be cleansed can be simultaneously washed and brightened.

When the present process is combined with other treatment or improvement methods, for example those set forth above under (a) to (c), the combined treatment advantageously takes place with the aid of suitable constituted preparation. These stable preparations are characterized by a content of imidazoles of the type specified above, and also further textile treating agents, for example dyestuffs, chemical bleaching agents, finishing agents or especially washing agents.

The following examples illustrate the invention, the parts and percentages being by weight unless otherwise stated.

Example 1

Polyacrylonitrile fabric, for example "Orlon" is treated at a bath ratio 1:50 with 0.01 percent of 2:5-di-[benzimidazolyl-(2')] -furan for 30 minutes at about 90° C. in a bath containing per liter 1 gram of 85 percent formic acid. The material is then rinsed and dried. The resulting material possesses a higher white content than the untreated material. Similar effects are obtained when instead of 2:5-di-[benzimidazolyl - (2')] - furan the diimidazoles of the following formulae are used:



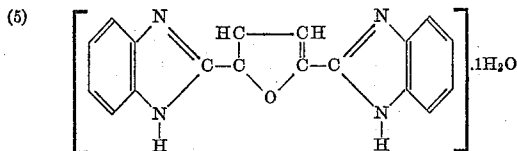
or when the α : β -di-[benzimidazolyl-(2')] -ethylene is used. The 2:5-di-[benzimidazolyl-(2')] -furan can be prepared in the following manner:

108 parts of 1:2-diaminobenzene, 78 parts of pure furan-2:5-dicarboxylic acid and 3 parts of boric acid are stirred for 70 minutes at 142-146° C. in a current of nitrogen. The temperature is then raised within 30 minutes to 210° C., which causes slow elimination of water. The mixture is then stirred for 1 hour at 210 to 220° C.

150 parts of glycol are then added, whereupon the temperature drops to 150° C. Immediately afterwards, 1000 parts of 2 N-hydrochloric acid are added, and the mixture is stirred for ½ hour at 90° C., allowed to cool, suction-filtered, and the filter cake is washed three times with 300 parts of water and then stirred for ½ hour at 70° C. in 2000 parts of water containing 100 parts of ammonia of

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30% strength. The yellow condensation product is allowed to cool to room temperature, suction-filtered and washed three times with 300 parts of water. After drying, about 105 parts of the condensation product of the formula



melting at 292.5–294° C. are obtained.

The water of crystallization can be removed by heating the product for 30 minutes at 230° C. under a pressure of 0.01 mm. Hg. The dehydrated product yields the following data:

Calculated: C, 71.99%; H, 4.03%; N, 18.66%. Found: C, 71.79%; H, 4.18%; N, 18.76%.

When the process described above is performed without the addition of boric acid, the yield obtained is by a few percent lower.

The compound of Formula 3 can be prepared in the following manner:

15 parts of 2:5-di-[benzimidazolyl-(2')]-furan are dissolved in 80 parts of ethanol of 90% strength containing 8 parts of sodium hydroxide. A solution of 12.5 parts of dimethyl sulfate in 10 parts of ethanol is then stirred in at 75° C. dropwise in the course of 2 hours. The temperature of 75° C. is maintained for another hour, the solution is poured into 1000 parts of water, the precipitate is suctioned off and dried and yields about 14 parts of the compound of the Formula 3.

After having been recrystallized three times from aqueous ethanol, the product melts at 146–147° C. and gives the following analytical data:

$C_{20}H_{18}ON_4$: Calculated.—C, 69.35%; H, 5.24%. Found.—C, 69.24%; H, 4.95%.

The compound of the Formula 4 can be prepared in the following manner:

15.2 parts of 2:5-di-[benzimidazolyl-(2')]-furan are dissolved in 100 parts of 90% ethyl alcohol containing 6 parts of caustic soda. 8.2 parts of benzyl chloride are added with stirring in the course of 2 hours at a temperature of 75° C. The mixture is stirred for one hour, then poured onto water and the crystalline product is suction-filtered. The yield is 18.8 parts.

After recrystallization from aqueous ethanol the product melts with decomposition at about 250° C.

The α : β -di-[benzimidazolyl-(2')]-ethylene can be prepared in the following manner:

660 parts of o-phenylene diamine are heated with 116 parts of fumaric acid within 3 to 5 hours from 120 to 160° C. with the exclusion of air. As soon as the elimination of water subsides, the temperature is raised to about 190° C. and maintained for a short time until water no longer escapes. The whole is allowed to cool and the o-phenylene diamine in excess removed by extraction with alcohol, benzene or another solvent. The residue is dissolved in hot dilute hydrochloric acid and the condensation product precipitated from the solution by means of an alkaline agent, e.g. with ammonia, filtered and washed neutral with water.

Example 2

Polyacrylonitrile fabric ("Orlon") is treated at a bath ratio 1:40 with 0.03 percent, of 2:5-di-[benzimidazolyl-(2')]-furan for 1 hour at about 95° C. in a bath containing per liter 5 g. of 85 percent formic acid and 5 g. of an addition product from about 30 mols of ethylene oxide to a mixture of saturated fatty alcohols the majority of which has 18 carbon atoms. The material is then rinsed and dried. The resulting material possesses a higher white content than the untreated material.

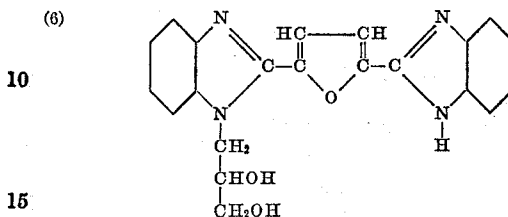
Similar effects are obtained when instead of 2:5-di-

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[benzimidazolyl-(2')]-furan a dimidazole of the Formula 2, 3 or 4 is used.

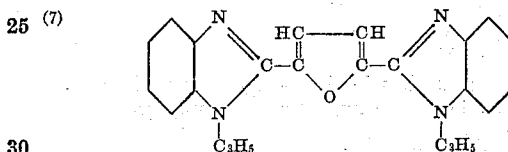
Example 3

Polyacrylonitrile fabric, for example "Orlon" is treated at a bath ratio 1:40 with 0.03% of the compound of the formula



in a bath containing per liter 1 gram of 85% formic acid, 2 grams of sodium chlorite and 2 grams of sodium nitrate. The material is then rinsed and dried. The resulting material possesses a higher white content than the untreated material.

Similar effects are obtained, when instead of the compound (6) the following compound is used:



The compound of Formula 6 can be prepared in the following manner:

10 parts of 2:5-di-[benzimidazolyl-(2')]-furan are dissolved in 70 parts of ethanol of 90% strength containing 8 parts of sodium hydroxide. A solution of 6 parts of 1-chloro-2:3-di-hydroxypropane in 10 parts of ethanol is then stirred in dropwise at 75° C. in the course of 2 hours. The temperature of 75° C. is maintained for another hour, and the solution is then poured into 500 parts of water, and the precipitate is suctioned off and dried, to yield about 12 parts of the condensation product of the Formula 6.

After having been recrystallized three times from aqueous ethanol, the product melts at 290.5–291° C. and gives the following analytical data:

$C_{21}H_{20}O_4N_4$: Calculated.—C, 54.21%; H, 5.13%; N, 14.37%. Found.—C, 64.58%; H, 5.50%; N, 14.28%.

When 13 parts of 1-bromo-propylene-(2) are used instead of 6 parts of 1-chloro-2:3-dihydroxypropane, the condensation with furan dicarboxylic acid yields about 15 parts of the compound of the Formula 7.

After having been recrystallized five times from aqueous dimethyl formamide, the product melts at 298.5–300° C. and yields the following analytical data:

$C_{24}H_{24}O_5N_4$: Calculated.—C, 69.24%; H, 5.77%. Found.—C, 69.22%; H, 5.60%.

Example 4

12 parts of 2:5-di-[benzimidazolyl-(2')]-furan are processed to a finely dispersed paste with 12 parts of an addition product from about 30 mols of ethylene oxide to a mixture of saturated fatty alcohols the majority of which has 18 carbon atoms and with 76 parts of water.

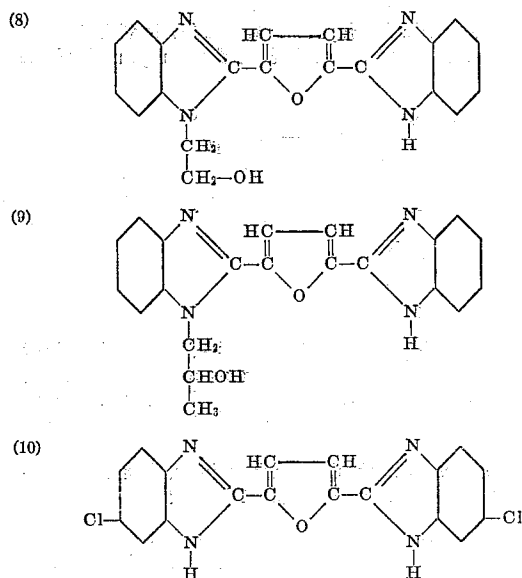
50 grams of "Orlon" fabric is treated for 30 minutes at 80–95° C. in a bath consisting of

- 1500 cc. water
- 3 grams formic acid 85%
- 3 grams sodium chlorite
- 0.1 gram of the above product,

then rinsed and dried. The material thus treated is whiter than a material which has been treated without the addition of the above product.

Similar effects are obtained when instead of the 2:5-di-

[benzimidazolyl-(2')]-furan a dimidazole of any of the following formulae is used:



or when the α : β -di-[benzimidazolyl-(2')]ethylene is used.

The compound of Formula 8 can be prepared in the following manner:

15 parts of 2:5-di-[benzimidazolyl-(2')]-furan are dissolved in 80 parts of ethanol of 90% strength containing 8 parts of sodium hydroxide. At the boiling temperature of ethanol a solution of 6 parts of 1-chloro-2-hydroxyethane in 10 parts of ethanol is added dropwise in the course of 1½ hours. The solution is stirred for ½ hour at 70° C. and then poured into 500 parts of water. The precipitated condensation product is suctioned off and dried, to yield about 16 parts of the compound of the Formula 8.

After having been recrystallized three times from aqueous ethanol, the product melts at 182–182.8° C.

$C_{20}H_{16}O_2N_4$: Calculated—C, 69.75%; H, 4.68%; N, 16.27%. Found—C, 69.80%; H, 4.66%; N, 16.49%.

When 6 parts of 1-chloro-2-hydroxypropane are used instead of 6 parts of 1-chloro-2-hydroxyethane the condensation with the furan-dicarboxylic acid yields about 11 parts of the compound of the Formula 9. Melting point: 150–151° C.

The compound of the Formula 10 can be prepared in the following manner:

10 parts of 4-chloro-1,2-diamino-benzene, 5.6 parts of 2:5-furan-dicarboxylic acid and 0.2 part of boric acid are heated with stirring to 210° C. in a current of nitrogen for 90 minutes, the mixture thickens after 30 minutes and solidifies after 45 minutes. The melt is dissolved by adding 20 parts of glycol, poured onto water and suction-filtered. The yield is about 9 parts.

After having been recrystallized three times from aqueous ethanol, the product melts at 306 to 307.5° C.

Example 5

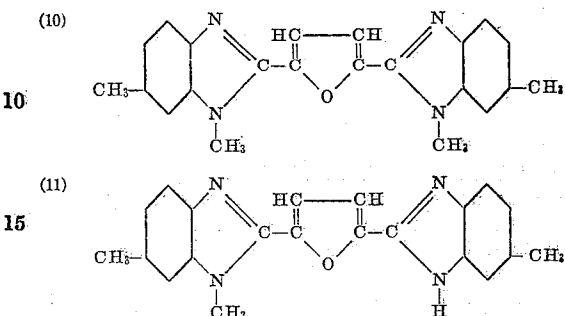
A soap is produced which contains 1 percent of 2:5-di-[benzimidazolyl-(2')]-furan. Polyacrylonitrile fibers, for example "Orlon," which have been washed with this soap, have a brighter appearance than material which has only been washed with usual soap.

A similar effect is achieved when instead of soap a synthetic washing material is used or one of the following composition:

- 33.3% of soap
- 11.0% of anhydrous sodium carbonate
- 14.0% of sodium pyrophosphate
- 7.0% of sodium perborate
- 3.0% of magnesium silicate

1.0% of 2:5-di-[benzimidazolyl-(2')]-furan
30.7% of water

Similar brightening effects are obtained when instead of 2:5-di-[benzimidazolyl-(2')]-furan the compounds of the following formulae are used in the washing agent:



20 or when the 2:5-di-[6'-methyl-benzimidazolyl-(2')]-furan or the α : β -di-[benzimidazolyl-(2')]ethylene is used. The compounds (10) and (11) can be prepared as follows:

24.4 parts of 4-methyl-1:2-diaminobenzene, 15.6 parts of furan-2:5-dicarboxylic acid and 0.5 part of boric acid are fused at 145–150° C. in a current of nitrogen. The temperature is then raised to 210–215° C. and the melt is stirred on for 2 hours at this temperature. 40 parts of glycol are then added to the melt, whereupon the temperature drops to 150° C. The melt is cooled to 100° C. and 200 parts of 2 N-hydrochloric acid are added. The mixture is then stirred for ½ hour at 90° C., cooled to room temperature, suction-filtered, and the filter cake is washed three times with 60 parts of water. The filter residue is then stirred for ½ hour at 70° C. in 200 parts of water containing 15 parts of ammonia of 30% strength. The yellow condensation product is allowed to cool to room temperature, suction-filtered and the filter cake is washed three times with 60 parts of water. After drying, about 24 parts of 2:5-di-[6'-methyl-benzimidazolyl-(2')]-furan are obtained. After having been recrystallized twice from aqueous ethanol, the product is analyzed and yields the following data:

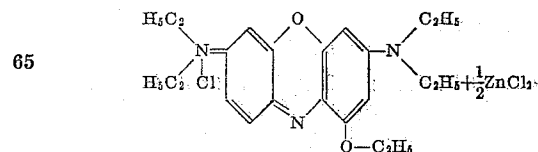
$C_{20}H_{18}O_2N_4$: Calculated—C, 69.35%; H, 5.24%; N, 16.18%. Found—C, 69.36%; H, 5.42%; N, 16.31%.

8 parts of 2:5-di-[6'-methyl-benzimidazolyl-(2')]-furan obtained as described above are dissolved in 50 parts of ethanol of 90% strength containing 4 parts of sodium hydroxide. A solution of 6 parts of dimethyl sulfate in 10 parts of ethanol is then added dropwise at 75° C. in the course of 1 hour. The solution is stirred for another ½ hour at that temperature and then poured into 500 parts of water, and the precipitate is suctioned off and dried, to yield about 6 parts of the compound of the Formula 10 and 2 parts of the Formula 11.

The product substituted at both nitrogen atoms melts at 236–237.5° C., whereas the product substituted at only one nitrogen atom melts at 272–272.5° C.

Example 6

"Orlon" fabric is treated for 1 hour at 90°–100° C. in a bath which contains (calculated on the fabric) 1% of the dyestuff of the formula



70 3% 2:5-di-[benzimidazolyl-(2')]-furan and 3% acetic acid of 86% strength. (Ratio of goods to liquor 1:40.)

After being rinsed and dried the fabric so treated has a pure greenish blue shade.

Similar effects are obtained when instead of 2:5-di-[benzimidazolyl-(2')]-furan a compound of the Formula 8

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or 9 is used, or when the compound of the Formula 2 is used.

Fabric dyed in the same manner but without the addition of the di-imidazole compounds is less pure in color and less greenish.

Example 7

A mixed fabric of polyacrylonitrile fibers and wool is treated in a bath ratio 1:40 for 20 minutes at 80-90° C. with 2 percent of the compound of Formula 8 in a bath which contains 1 gram per liter of 95 percent formic acid. The resulting material possesses a higher white content than the untreated fabric.

Similar brightening effects are produced when instead of the compound of Formula 8 a compound of Formula 4 or 6 is used, or when the compound of the Formula 2 is used.

Example 8

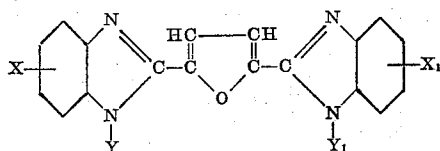
30 parts of 2,5-di-[benzimidazolyl-(2')]-furan are ground to a fine, homogenous powder in a suitable mixing and grinding apparatus, with 60 parts of sodium bisulfate and 910 parts of a condensation product of naphthalene sulfonic acid and formaldehyde.

Polyacrylonitrile fibers, for example "Orlon," are treated for 30 minutes at 90-95° C. at a bath ratio of 1:30 with 0.5 percent of this powder in a bath which contains 1.5 grams per liter of 85 percent formic acid, then rinsed and dried. The "Orlon" fiber thus treated has a higher white content than the untreated material.

Similar brightening effects are obtained when a compound of the Formula 2, 6 or 9 is used instead of 2,5-di-[benzimidazolyl-(2')]-furan.

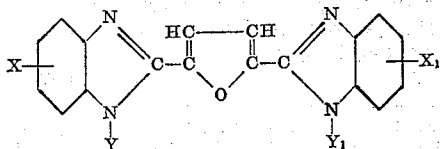
What is claimed is:

1. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of a compound of the formula



wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

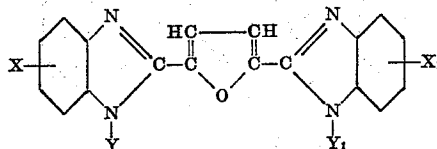
2. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium in a finely dispersed state from 0.01 to 3.0 percent, calculated on the weight of said fibers, of an optical brightening agent of the formula



wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

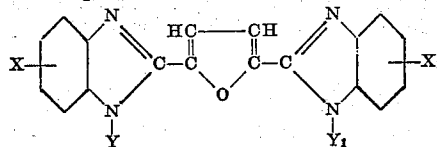
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3. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium in the presence of a dispersing agent from 0.01 to 3.0 percent, calculated on the weight of said fibers, of an optical brightening agent of the formula



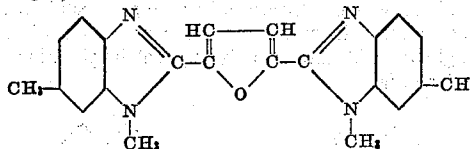
wherein X and X₁ each represent a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

4. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium in the presence of a washing agent from 0.01 to 3.0 percent, calculated on the weight of said fibers, of an optical brightening agent of the formula

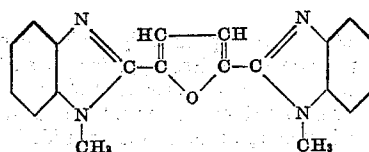


wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

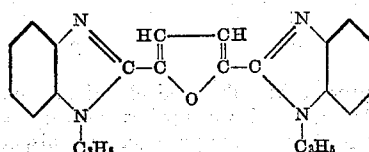
5. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the compound of the formula



6. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the compound of the formula

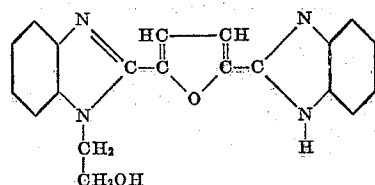


7. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the compound of the formula

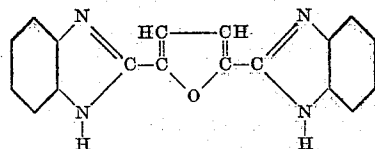


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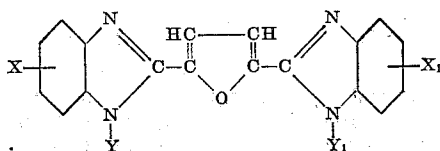
8. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the compound of the formula



9. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the compound of the formula

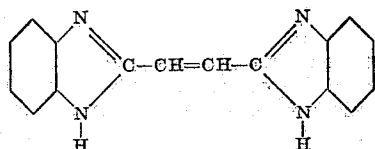


10. A composition of matter substantially consisting of polyacrylonitrile fibers having incorporated therein an optical brightening agent in a proportion sufficient to brighten said fibers, said optical brightening agent being of the formula

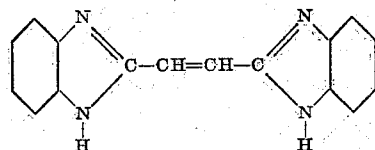


wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

11. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the optical brightening agent of the formula



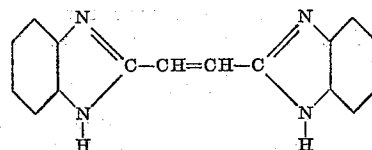
12. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium in a finely dispersed state from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the optical brightening agent of the formula



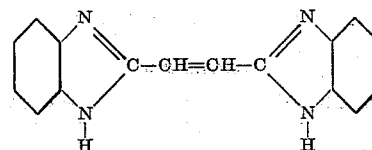
13. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium in the presence of a dispersing agent

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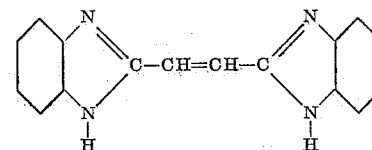
from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the optical brightening agent of the formula



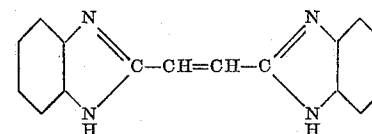
14. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium in the presence of a washing agent from 0.01 to 3.0 percent, calculated on the weight of said fibers, of the optical brightening agent of the formula



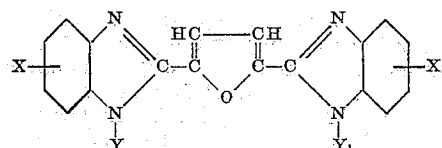
15. A composition of matter substantially consisting of polyacrylonitrile fibers having incorporated therein an optical brightening agent in a proportion sufficient to brighten said fibers, said optical brightening agent being of the formula



16. A process for the optical brightening of polyacrylonitrile fibers which comprises applying to said fibers in aqueous medium from 0.01 to 3.0 percent, calculated on the weight of said fibers, of a member selected from the group consisting of the compound of the formula

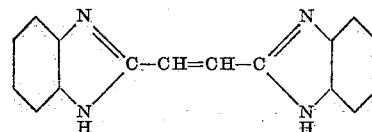


and a compound of the formula



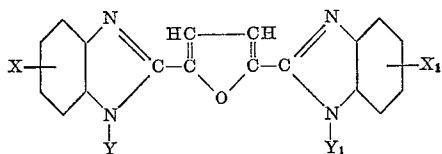
wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

17. A composition of matter substantially consisting of polyacrylonitrile fibers having incorporated therein an optical brightening agent in a proportion sufficient to brighten said fibers, said optical brightening agent being selected from the group consisting of the compound of the formula



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and a compound of the formula



wherein X and X₁ each represents a member selected from the group consisting of a hydrogen atom, a chlorine atom and a lower alkyl group having at most 3 carbon atoms and Y and Y₁ each represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group having at most 3 carbon atoms, a lower alkenyl group having at most 3 carbon atoms, a lower mono-hydroxy alkyl group having at most 3 carbon atoms, a lower di-hydroxy alkyl group having at most 3 carbon atoms and a benzyl radical.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

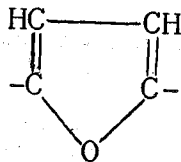
Patent No. 3,005,779

October 24, 1961

Franz Ackermann et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 8, after "use" insert -- one --; line 23, for "preparation" read -- preparations --; column 5, lines 6 to 12, formula (5), the center portion of the formula should appear as shown below instead of as in the patent:



Signed and sealed this 15th day of May 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents