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⑤④ **Electrically conductive fibre.**

⑤⑦ An electrically conductive material, particularly an electrically conductive fibre, comprises a polymeric material modified by reaction with the reaction product of a mono- or polyfunctional amine with cyanamide, dicyandiamide, guanidine or bisguanidine, or a salt thereof, and impregnated with copper sulphide. The fibre can be produced by a method which comprises

(a) treating a fibre with an aqueous solution of the said reaction product to form a modified fibre; and

(b) treating the modified fibre with an aqueous solution or solutions of a copper salt, a reducing agent and a sulphur-containing compound capable together of forming copper sulphide which is adsorbed onto the modified fibre. The fibre is useful in providing anti-static or static-dissipative properties in textile, paper and other products.

Description

ELECTRICALLY CONDUCTIVE MATERIAL

This invention relates to electrically conductive material and to methods for making such material. In particular it relates to electrically conductive fibres.

Electrically conductive acrylic fibres are used to provide antistatic properties in textile products such as carpets and clothing. The acrylic fibres are made conductive by impregnation with copper sulphide. One method for making those fibres is described in EP-A-35,406 in which acrylic fibre is treated with a copper compound such as copper sulphate and a reducing agent to adsorb copper ions onto the fibre, followed by treatment with a sulphur-containing compound which converts the copper ions to copper sulphide, thus producing an electrically conductive acrylic fibre.

A similar method is described in GB-A-1,372,656, except that the synthetic fibre, such as acrylic fibre, is treated firstly with a sulphur-containing compound, namely hydrogen sulphide, thioacetamide or thiourea, and secondly with a metal salt solution, for example aqueous copper sulphate.

Attempts have been made to adapt those methods for the production of a conductive cellulosic fibre. In US-A-4,378,226 cotton and rayon fibres are pretreated with acrylonitrile or dicyandiamide to introduce cyanic groups into the fibres before they are treated with the copper and sulphide compounds as described above. That method has the advantage that acrylonitrile and dicyandiamide are toxic and therefore hazardous to use. To our knowledge cellulosic fibres are not produced commercially by that method.

JP-A-61-32305 describes a conductive regenerated cellulosic fibre in which the regenerated cellulose is impregnated with copper sulphide without first being pretreated. We have not been able to produce a viscose fibre having adequate electrical conductivity by using the method exemplified in that patent application.

The present invention provides an electrically conductive material comprising polymeric material modified by reaction with Compound A (as hereinafter defined), and impregnated with copper sulphide. By Compound A we mean the reaction product of a mono- or polyfunctional amine with cyanamide, dicyandiamide, guanidine or bisguanidine, or a salt thereof.

The polymeric material according to the invention is preferably in fibrous form. This electrically conductive fibre can be produced by:

(a) treating fibre with an aqueous solution of Compound A to form a modified fibre; and

(b) treating the modified fibre with an aqueous solution or solutions of a water-soluble copper salt, a reducing agent, and a sulphur-containing compound capable together of forming copper sulphide, which is adsorbed onto the modified fibre.

By treating the fibre with Compound A prior to impregnating with the copper sulphide, a fibre with good electrical conductivity can be obtained. Com-

pound A is relatively non-toxic, containing no, or virtually no, cyano groups and therefore the process according to the invention has the advantage that it is non-hazardous.

The compounds comprising the group "Compound A" are known and may be prepared by the methods described for example in GB-A-657,753 and US-A-2,649,354 and US-A-4,410,652. Suitably the amine, which has one or more primary and/or secondary and/or tertiary amino groups and which may be in free base or salt form, is reacted with the other material in the absence of water at elevated temperature, optionally in the presence of a non-aqueous solvent. Preferably, the reaction is carried out in the absence of solvent and at a temperature of 140-160°C, and, for most combinations of reagents, ammonia is evolved. The reagents are preferably reacted in a molar ratio of 0.1 to 1 mole of cyanamide, dicyandiamide, guanidine or bisguanidine per mole of reactive amine groups, and, when dicyandiamide is reacted with a polyalkylene polyamine, the molar ratio of the reactants is more preferably from 2:1 to 1:2, particularly about 1:1.

Preferably, Compound A is the reaction product of dicyandiamide with a polyalkylene polyamine, especially diethylenetriamine.

Suitable methods for treating the fibre with Compound A are described in EP-A-151,370A and in European Patent Application No. 88810222.5 (based on GB 8708192), the disclosures of which are incorporated herein by reference. Conventional techniques, for example an exhaustion or padding process, can be used to apply Compound A to the fibre.

As described in EP-A-151,370A, Compound A can be applied using an exhaustion process by immersing the fibre in a bath containing an aqueous solution, which may be weakly acidic, of Compound A. The bath is then heated to from 50 to 100°C and an alkali such as sodium carbonate added to bring the pH value of the solution to from pH 8.5 to 10. The fibre is immersed in the bath for a time sufficient to fix Compound A onto the fibre, usually from 10 to 30 minutes. The fibre is then washed in water.

A similar method is described in the above-mentioned EP Application 88810222.5 except that the solution of Compound A is made more strongly alkaline, pH above 11, by the addition of a strong alkali such as sodium hydroxide rather than sodium carbonate, and the solution is maintained at a temperature below 50°C for cellulosic fibres, although higher temperatures can be used for applying Compound A to other types of fibre.

The concentration of the aqueous solution of Compound A with which the fibre is treated depends upon the desired level of Compound A to be fixed to the fibre. Preferably, the level of fixation is from 0.2 to 5.0 per cent, more preferably from 0.6 to 3.0 per cent Compound A w/wf (weight/weight of fibre). The nature of the fixation is not fully understood, although it is thought to involve chemical bonding to

the available hydroxyl groups in the cellulose, but the fixed compound is not removed by repeated washing. In general the method of E.P. 151,370A is used to apply lower levels of Compound A, in the region of 0.2 to 1.0 per cent w/wf, and the method of EP 88810222.5 is used to apply levels above 1.0 per cent w/wf, although lower levels can also be applied using the latter method.

The concentration of the solution is calculated according to the desired level of fixation of Compound A. In addition it is preferred to treat the fibre with an excess of Compound A in order to achieve even take-up of the compound on the fibre. Any unfixed compound can be subsequently removed by washing. Usually the concentration of the solution is from 0.5 to 20 per cent Compound A w/wf, and preferably from 1.5 to 10 per cent w/wf. The treated fibre is then washed, neutralised with acetic acid, for example, and rinsed with water.

After being treated with Compound A, the resulting modified fibre can be dried before being treated with the copper salt, reducing agent and sulphur-containing compound. However, it is preferred to treat the modified fibre with these compounds without first drying the fibre so that the electrically conductive fibre is produced in one continuous process.

The modified fibre is preferably treated with the copper salt, reducing agent and sulphur-containing compound simultaneously. Alternatively, the treatment with the sulphur-containing compound can be a separate step from the treatment with the copper salt and reducing agent.

Advantageously, a sulphur-containing compound is chosen that is also a reducing agent, so that a separate reducing agent may be dispensed with.

Where the treatments with the copper salt, reducing agent and sulphur-containing compound are simultaneous, the modified fibre is immersed in an aqueous solution containing a copper salt, a reducing agent and a sulphur-containing compound capable of reacting with the copper salt to form copper sulphide, and the bath is preferably heated to from 50 to 100°C, although higher temperatures can be employed. Treatment times can be from 10 minutes to 3 hours. The resulting fibre, which is impregnated with the copper sulphide, is then preferably rinsed with a mild oxidising agent to prevent any further reaction with the reducing agent, washed in water and dried.

Where the treatments with the copper salt, reducing agent and sulphur-containing compound are separate, the modified fibre may be first immersed in an aqueous bath containing a copper salt and a reducing agent and the bath preferably heated to from 50 to 100°C, to absorb copper ions onto the fibre. Treatment times can be from 10 minutes to 3 hours. Following this the fibre, optionally after intermediate washing, is immersed in a second bath containing a sulphur-containing compound to convert the adsorbed copper ions to copper sulphide. Treatment temperatures and times are within the ranges given for the treatment with the copper salt and reducing agent. The resulting fibre is then preferably rinsed with a mild oxidising agent to

prevent any further reaction with the reducing agent, washed with water and dried.

In both the simultaneous and the separate treatments, the concentration of copper salt in the solution is preferably from 5 per cent to 900 per cent w/wf (or from 2 to 300 g/l), more preferably from 10 per cent to 50 per cent w/wf. The concentration of the sulphur-containing compound is preferably from 5 per cent to 750 per cent w/wf (or from 2 to 250 g/l), more preferably from 30 per cent to 200 per cent w/wf.

Examples of suitable compounds for the copper salt include copper (II) sulphate, copper (II) chloride, copper (II) nitrate, copper (II) acetate and the like. Copper (II) sulphate is generally preferred.

Suitable sulphur-containing compounds include sodium sulphide, sodium thiosulphate, sodium metabisulphite, sodium hydrosulphite, thiourea dioxide, sulphurous acid and dithionous acid, or a mixture thereof. When sulphur-containing compounds such as sodium thiosulphate or sodium metabisulphite are employed, then these compounds also act as a reducing agent so that a separate reducing agent is not necessarily required. Examples of other reducing agents include metallic copper, glucose, formaldehyde, ferrous sulphate and the like.

As an alternative method, the modified fibre may be treated with another sulphur-containing compound such as thiourea, thioacetamide, Rongalite Z ($\text{ZnSO}_2 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O}$) or Formosul ($\text{Na}_2\text{SO}_2 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O}$) prior to being treated with the metal salt. It has been found that this pretreatment enhances the electrical conductivity of the resulting fibre in some instances. The subsequent treatment with the sulphur-containing compound may then be omitted, but it is preferred to include it so that the pretreatment is in addition to the above-mentioned steps.

In general the greater the amount of copper sulphide impregnated in the cellulosic fibre, the higher its conductivity, although too high a level of copper sulphide can reduce the fibre's physical properties, such as fibre strength. Preferably the modified fibre is impregnated with from 1 to 30 per cent copper sulphide w/wf, more preferably from 10 to 25 per cent w/wf, calculated from the copper content.

Although the exact form of the copper sulphide adsorbed onto the fibre is generally not known, the normal green and dark green/black colours of the resulting conductive fibre indicate that both copper (I) sulphide and copper (II) sulphide are usually present in the fibre.

A variety of different polymeric materials can be pretreated with Compound A and impregnated with copper sulphide to produce a conductive material according to the invention. Suitable polymeric materials include cellulose such as viscose or rayon or spun cellulose such as tencel, polyester, polyamide, acetate, silk, wool, polyaramid, or polypropylene, amongst organic polymers, and glass amongst inorganics, or mixtures thereof. Cellulosic material, especially viscose or cotton, is preferred.

The fibre which is to be treated with Compound A

and impregnated with the copper sulphide may be in loose fibre form, or as a yarn or fabric or any other suitable form. In addition, the fibre may be treated with Compound A in, for example, loose fibre form, and then made up into a yarn or fabric prior to being impregnated with the copper sulphide.

Products made from the conductive fibre may comprise solely the conductive fibre according to the invention or may be blended with other conductive fibres, for example carbon or metal fibres.

The conductive fibre of the invention has numerous applications in a variety of fields. It is particularly useful in providing anti-static or static-dissipative properties in textile, paper and other products, for example carpets both in the carpet tufts and in carpet backings, upholstery including automotive upholstery fabrics, and clothing. For anti-static applications, the conductive fibre is usually blended with other textile fibres. Alternatively, yarns formed from the conductive fibre are woven or knitted with non-conductive textile yarns. The proportion of conductive fibre is generally in the range of 0.1 to 20 per cent conductive fibre by weight based on the total fibre weight of the product, although higher proportions can be employed if desired.

The conductive fibre has electro-thermal properties which can be utilised in a variety of applications, for example electric blankets, floor heating, electrically heated clothing, pipeline and cable cladding, thermal coverings, thermal shieldings and the like. It has been found that, for a given electrical power input, the fibre according to the invention increases in temperature over time up to a specific temperature, after which time no appreciable increase in temperature occurs. Thus the conductive fibre is especially useful in applications which require automatic thermo-static control.

The invention is illustrated by the following Examples. Unless otherwise stated, all parts and percentages are by weight and, when based on the fibre weight, are based on the total dry weight of the fibre.

Example 1

In this Example viscose fibre is modified by reaction with the sulphate salt of the reaction product of dicyan diamide and diethylenetriamine. In this and subsequent Examples this sulphate salt is referred to as "Compound A1". A method for its preparation is given in EP-A-151,370A mentioned above, on page 19, Example 1.

1.7 decitex, 50 mm staple viscose fibre was immersed in a bath containing an aqueous solution of Compound A1. The liquor to goods ratio was 30:1 and the concentration of Compound A1 was 1.65 per cent w/wf. The temperature of the bath was raised from room temperature to 70°C and sodium carbonate added to increase the pH of the solution to pH 9.0 - 9.5. The viscose fibre was immersed in the bath for 20 minutes with agitation, after which the fibre was cooled and washed thoroughly with water.

The resulting modified viscose fibre was then immersed in a second bath containing an aqueous solution of 37.5 per cent w/wf copper (II) sulphate and 336 per cent w/wf sodium thiosulphate. The

liquor to goods ratio was 30:1. The bath was heated at a rate of 2°C/minute to raise the temperature of the solution from room temperature to 85°C. The fibre was treated with the solution for 30 minutes at 85°C, after which it was cooled, washed with warm water and then cold water, hydroextracted and dried.

The resulting fibre contained 0.72 per cent Compound A1 as determined by Kjeldahl Nitrogen Analysis. The fibre was dark green/black in colour, indicating the presence of adsorbed copper sulphide, and had an electrical resistivity of 20 ohms per square, measured on a Vermason Plate Electrode.

Example 2

1.7 decitex, 50 mm staple viscose fibre was immersed in a bath containing an aqueous solution of 1.65 per cent Compound A1 at a liquor to goods ratio of 20:1. After 5 minutes 1 g/l of sodium hydroxide was added and the temperature of the bath raised to 40°C. Treatment was continued for 10 minutes, after which the bath was cooled and the fibre washed thoroughly with cold water.

The resulting modified fibre was then treated with copper (II) sulphate and sodium thiosulphate and described in Example 1.

The resulting fibre contained 0.64 per cent Compound A1. The fibre was dark green in colour and had a resistivity of 50 ohms per square, measured on a Vermason Plate Electrode. It contained 5.6% w/wf of Cu.

Example 3

1.7 decitex, 37 mm staple viscose fibre was treated with Compound A1 as described in Example 2.

The resulting modified fibre was then immersed in a second bath containing an aqueous solution of 300 g/l copper (II) sulphate and 100 g/l sodium thiosulphate. The temperature of the bath was raised to 85°C and the fibre was immersed in the solution for a further 45 minutes, after which the bath was cooled and the fibre washed thoroughly with water.

The resulting fibre as black in colour and had a resistivity of 16 ohms per square, measured on a Vermason Plate Electrode.

Example 4

A wound yarn package of 16s cotton count 100 per cent cotton yarn was immersed in a bath containing an aqueous solution of 5.5 per cent Compound A1 at a 20:1 liquor to good ratio. The bath was initially at room temperature and after the package had been immersed for 5 minutes 3 g/l of sodium hydroxide was added. The bath temperature was then raised to 40°C and the treatment continued for a further 10 minutes, after which the bath was cooled and the fibre washed with water.

The resulting modified cotton package was immersed in a second bath containing an aqueous solution of 34.5 per cent w/wf copper (II) sulphate and 310 per cent w/wf sodium thiosulphate. The liquor to goods ratio was 14:1. The temperature of the bath was raised from room temperature to 85°C and the treatment continued for 1 hour. The bath

was then cooled and the package washed thoroughly with water.

The resulting yarn package was black in colour and had a resistivity of less than 10 ohms per square, measured on a Vermason Plate Electrode.

Example 5

A weft knit 100 per cent cotton interlock fabric was immersed in a bath containing an aqueous solution of 1.65 per cent Compound A1 at a 20:1 liquor to goods ratio. The temperature of the bath was raised to 70°C and sodium carbonate added to increase the pH value of the solution to pH 9.0 - 9.5. Treatment was continued for 20 minutes and then the bath was cooled and the fabric washed with water.

The resulting modified fabric was immersed in a second bath containing an aqueous solution of 18.75 per cent w/wf copper (II) sulphate and 114 per cent sodium thiosulphate at a liquor to goods ratio of 30:1. The bath temperature was raised to 85°C and the fabric was immersed for 30 minutes, followed by cooling and washing with water.

The resulting fabric was dark green in colour and had a resistivity of 210 ohms per square, measured on a Vermason Plate Electrode.

Example 6

A weft knit 100 per cent cotton interlock fabric was treated with Compound A1 as described in Example 5 and then treated with copper (II) sulphate and sodium thiosulphate as described in Example 3. The resulting fabric was black and had a resistivity of less than 10 ohms per square, measured on a Vermason Plate Electrode.

Example 7

A weft knit 100 per cent cotton interlock fabric was treated with Compound A1 as described in Example 2.

The resulting modified fabric was then immersed in a second bath containing an aqueous solution of 8.0 per cent Formosul for 1 hour at room temperature, after which the fabric was hydroextracted.

Following the Formosul treatment, the fabric was immersed in a third bath containing an aqueous solution of 300 g/l copper (II) sulphate and 100 g/l sodium thiosulphate for 1 hour at 50°C. The bath was then cooled and the fabric washed with water.

The resulting fabric was black and had a resistivity of 21 ohms per square, measured on a Vermason Plate Electrode.

Example 8

A 200 decitex spun viscose yarn was treated with Compound A1 by immersing the yarn in an aqueous solution of 5.5 per cent w/wf Compound A1. After 5 minutes the bath temperature was raised to 40°C and 2.25 per cent w/wf sodium hydroxide added. Treatment was continued for 20 minutes, after which the fibre was rinsed with cold water, neutralised with 1 ml/l acetic acid and rinsed.

The resulting modified yarn was then immersed in a second bath containing 30 per cent w/wf copper (II) sulphate pentahydrate and 180 per cent w/wf

sodium thiosulphate. The liquor to goods ratio was 20:1. After 5 minutes the temperature of the bath was raised gradually to 85°C and the yarn immersed in the heated solution for 2 hours. The yarn was then rinsed with water and washed with an 0.25 g/l aqueous solution of a mild oxidising agent, iron (III) chloride, at 50°C for 30 minutes, after which the yarn was given a final rinse and dried.

The resulting yarn was green/black in colour, had a copper content of 7.5 w/wf and a resistance of 780 ohms per cm.

Example 9

A 200 decitex spun viscose yarn was treated with Compound A1 as described in Example 8.

The modified yarn was then immersed in a second bath containing an aqueous solution of 16 per cent w/wf copper (II) chloride and 180 per cent w/wf sodium thiosulphate. After 10 minutes the temperature of the bath was raised to 85°C and the yarn treated for 2 hours at this temperature. The yarn was then rinsed thoroughly and dried.

The resulting yarn was green/black in colour and had a resistance of 760 ohms per cm.

Example 10

A 200 decitex spun viscose yarn was treated with Compound A1 as described in Example 8.

The modified yarn was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate, 140 per cent w/wf sodium metabisulphite and 40 per cent w/wf sodium hydrosulphite. After 10 minutes the temperature of the bath was raised to 85°C and the yarn treated at this temperature for 2 hours, after which the yarn was washed and dried.

The resulting yarn was olive green in colour and had a resistance of 1.1×10^4 ohms per cm. It contained 2.9% w/wf of Cu.

Example 11

A 200 decitex spun viscose yarn was treated with Compound A1 as described in Example 8.

The modified fibre was treated in an 80 g/l aqueous solution of thiourea at room temperature for 1 hour, at a liquor to goods ratio of 50:1, after which it was hydroextracted.

Following the thiourea treatment, the yarn was immersed in a third bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 180 per cent w/wf zinc formaldehyde sulfoxylate for 2 hours at 85°C. The yarn was then washed and dried.

The resulting yarn was yellow/brown in colour and had a resistance of 6×10^5 ohms per cm.

Example 12

A 26 decitex, 100 mm stable viscose fibre was treated with Compound A1 as described in Example 8.

The modified fibre was then immersed in a second bath containing an aqueous solution of 20 per cent w/wf copper (II) sulphate pentahydrate and 20 per cent w/wf sodium thiosulphate for 2 hours at 85°C. The fibre was then washed and dried.

The resulting fibre was green/black in colour and had a surface resistivity of 120 ohms per square, measured on a Vermason Plate Electrode. It contained 6.2% w/wf of Cu.

Example 13

A 590 decitex viscose yarn was treated with Compound A1 as described in Example 8.

The modified yarn was then immersed in a second bath containing an aqueous solution of 10 per cent w/wf copper (II) sulphate pentahydrate and 5 per cent w/wf sodium thiosulphate for 1 hour at 85°C. The fibre was then washed and dried. The resulting yarn had a blackish green colour and a measured resistance of 6.2×10^3 ohms per cm. It contained 4.9% w/wf of Cu.

A similar yarn was treated in the second bath as described above except that the yarn had not been pretreated with Compound A1. This unpretreated yarn was a light greenish colour and had a resistance of greater than 10^7 ohms per cm (i.e. was not conductive).

Example 14

A sample of fabric woven from secondary cellulose acetate yarn (Dicel - available from Courtaulds Fibres Limited) was treated with Compound A1 by immersing the fabric in a bath containing an aqueous solution of 5.5 per cent w/wf Compound A1. After 10 minutes 2.25 per cent w/wf sodium hydroxide was added and the temperature of the solution raised gradually to 70°C. The fabric was immersed in the solution for 1 hour at this temperature and then the bath was cooled, and the fabric was rinsed and neutralised with 1 ml/l acetic acid and finally rinsed with cold water.

The modified fabric was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 30 per cent w/wf sodium thiosulphate at a liquor to goods ratio of 75:1. The temperature of the bath was raised to 85°C and the fabric treated for 2 hours, after which the bath was cooled and the fabric rinsed with water.

The resulting fabric was bluish green in colour and had a surface resistivity of 280 ohms per square, measured using a Vermason Plate Electrode.

The wash resistance of the conductive fabric was determined by washing the fabric at 80°C for 30 minutes in a solution containing 2 g/l of commercial detergent. The resistivity of the fabric was then measured and was still found to be less than 10^3 ohms per square.

Example 15

A fabric sample woven from cellulose triacetate yarn (Tricel - available from Courtaulds Fibres Limited) was treated with Compound A1 as described in Example 14.

The modified fabric was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 60 per cent w/wf sodium thiosulphate for 2 hours at 85°C. The fabric was then washed and dried.

The resulting fabric was dark green in colour and

had a surface resistivity of 2300 ohms per square.

Example 16

A 2.5 decitex, 38 mm staple polypropylene fibre was treated with Compound A1 as described in Example 14.

The modified fibre was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 180 per cent w/wf sodium thiosulphate for 2 hours at 85°C. The fibre was then washed and dried.

The resulting fibre was dark green in colour and had a resistivity of 1.5×10^4 ohms per square, measured using a Vermason Plate Electrode.

Example 17

A sample of fabric woven from polyaramid yarn (Kevlar - available from Du Pont) was treated with Compound A1 as described in Example 8.

The modified fabric was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 120 per cent w/wf sodium thiosulphate at a liquor to goods ratio of 40:1 for 90 minutes at 85°C. The fabric was then washed and dried.

The resulting fabric had a resistivity of 55 ohms per square, measured using a Vermason Plate Electrode.

Example 18

A 590 decitex polyester yarn was treated with Compound A1 by immersing the yarn in a bath containing an aqueous solution of 2.75 per cent w/wf Compound A1.

After 5 minutes 1.1 per cent w/wf sodium hydroxide was added and the temperature of the bath raised to the boil for 1 hour. The yarn was rinsed with water, neutralised in acetic acid and rinsed again.

The modified yarn was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 30 per cent w/wf sodium thiosulphate for 2 hours at the boil. The yarn was rinsed with water, hydroextracted and dried. The yarn was then washed in an aqueous solution of 2 g/l commercial detergent for 30 minutes at 85°C.

The resulting washed yarn had a greenish lustre and a resistance of 5×10^3 ohms per cm.

The treatment was repeated on another sample of 590 decitex polymer yarn except that the concentration of sodium thiosulphate was altered to 180 per cent w/wf. The resulting yarn was bluish grey in colour, indicating an unusual crystalline form of copper sulphide, and had a resistance of 195 ohms per cm.

Example 19

A 2 fold, 18s cotton count wool yarn was treated with Compound A1 by immersing in a bath containing an aqueous solution of 5.5 per cent w/wf Compound A1. After 5 minutes the bath was raised to 70°C and 1 g/l sodium carbonate added. Treatment was continued for 30 minutes at 70°C, the yarn was then rinsed with water, neutralised with

acetic acid and rinsed again.

The modified yarn was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 180 per cent w/wf sodium thiosulphate at a 50:1 liquor to goods ratio 2 hours at 85°C. The yarn was then rinsed with water and dried.

The resulting yarn was greenish black in colour and had a resistance of 2000 ohms per cm.

Example 20

A 4 ply, 74 decitex nylon 66 yarn was treated with Compound A1 as described in Example 18.

The modified yarn was then immersed in a second bath containing an aqueous solution of 30 per cent w/wf copper (II) sulphate pentahydrate and 180 per cent w/wf sodium thiosulphate for 2 hours at 85°C. The yarn was then washed with water and dried.

The resulting yarn was greenish black in colour and had a resistance of 500 ohms per cm.

Example 21

A weft knit 100 per cent cotton interlock fabric of 185 gm⁻² was treated with Compound A1 and impregnated with copper sulphide as described in Example 5. A sample measuring 10 x 6.0 cm was cut from the fabric and enveloped in expanded polystyrene to provide insulation against heat loss by convection.

The fabric sample enveloped in insulating material was connected to an electrical circuit comprising a universal avometer, a variable resistor and a variable voltage. The fabric sample was connected at each end to ensure uniform current density between the electrical contacts and uniform heating across the fabric sample. A thermocouple and digital thermometer were connected to the fabric sample to measure the temperature of the fabric over time for a given power input.

The circuit was connected with an electrical current of 0.2A and a voltage of 12V giving a power input of 2.4W. The temperature of the fabric was measured over 10 minutes at intervals of half a minute, and also after 20 minutes. The results are given in Table 1, which show that initially the temperature of the fabric rises rapidly until it has reached about 30°C. After this the temperature only increases slowly, the limiting temperature being about 34°C.

Table 1

Voltage = 12 V Current = 0.2A Power = 2.4W

	Time / Min.	Temperature / °C
5	0	24.0
	0.5	27.8
	1.0	30.1
	1.5	31.3
10	2.0	31.9
	2.5	32.3
	3.0	32.6
	3.5	32.8
15	4.0	33.0
	4.5	33.0
	5.0	33.0
	5.5	33.1
	6.0	33.2
20	6.5	33.2
	7.0	33.4
	7.5	33.4
	8.0	33.4
25	8.5	33.5
	9.0	33.6
	9.5	33.6
	10.0	33.7
	20.0	34.0
30		
35		
40		
45		
50		
55		
60		
65		

The experiment was repeated with a current of 0.4A and a voltage of 12V, giving a power input of 4.8W. The results are given in Table 2 and show a similar rate of increase in temperature to the results in Table 1, the limiting temperature being about 55°C.

Table 2

Voltage = 12 V Current = 0.4A Power = 4.8W

Time / Min.	Temperature / °C	
0	24.0	5
0.5	39.5	
1.0	46.6	
1.5	49.0	
2.0	50.3	10
2.5	51.0	
3.0	51.6	
3.5	52.0	
4.0	52.5	15
4.5	52.8	
5.0	53.0	
5.5	53.2	
6.0	53.4	
6.5	53.5	20
7.0	53.8	
7.5	53.9	
8.0	54.1	
9.0	54.4	25
9.5	54.4	
10.0	54.5	

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Claims

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1. An electrically conductive material comprising polymeric material modified by reaction with the reaction product of a mono- or polyfunctional amine with cyanamide, dicyandiamide, guanidine or bisguanidine, or a salt thereof, and impregnated with copper sulphide.

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2. A conductive material as claimed in claim 1, which is in fibre form.

3. A conductive material as claimed in claim 1 or 2, wherein the polymeric material is selected from cellulosic, polyester, polyamide, acetate, silk, wool, polyaramid, polypropylene, glass, or a mixture thereof.

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4. A conductive material as claimed in claim 3, wherein the polymeric material is cellulosic material.

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5. A conductive material as claimed in any preceding claim, wherein the amount of the said reaction product incorporated in the material is from 0.2 to 5.0 per cent w/wf.

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6. A conductive material as claimed in any preceding claim, wherein the said reaction product is the product of dicyandiamide and diethylenetriamine.

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7. A conductive material as claimed in any preceding claim, wherein the amount of copper sulphide impregnated in the material is from 1 to 30 per cent w/wf, preferably from 10 to 25 per cent w/wf, calculated from the copper content.

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8. A method for the production of an electrically conductive fibre which comprises:

(a) treating a fibre with an aqueous solution of the reaction product of a mono- or polyfunctional amine with cyanamide, dicyandiamide, guanidine or bisguanidine, or a salt thereof, to form a modified fibre; and

(b) treating the modified fibre with an aqueous solution or solutions of a copper salt, a reducing agent and a sulphur-containing compound capable together of forming copper sulphide, which is adsorbed onto the modified fibre.

9. A method as claimed in claim 8, wherein the said reaction product is the product of dicyandiamide and diethylenetriamine.

10. A method as claimed in claim 8 or 9, wherein the copper salt is copper (II) sulphate.

11. A method as claimed in any of claims 8 to 10, wherein the sulphur-containing compound is also the reducing agent.

12. A method as claimed in any of claims 8 to 11, wherein the sulphur-containing compound is sodium thiosulphate.



DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)		
X	EP-A-0 217 987 (NIHON SANMO DYEING CO., LTD) * Whole document * ---	1-5,7,8 -12	H 01 B 1/12		
X	EP-A-0 086 072 (NIHON SANMO DYEING CO., LTD) * Whole document * ---	1-12			
A	EP-A-0 035 406 (NIHON SANMO DYEING CO., LTD) * Whole document * ---	1-4,7, 10-12			
A	EP-A-0 160 406 (BRIDGESTONE) * Whole document * ---	1-4,7, 10-12			
A	DE-A-3 623 901 (MITSUBISHI RAYON) * Whole document * ---	1-3,7, 10-12			
A	US-A-4 661 376 (P.M. LIANG) * Whole document * -----	1-3,7			
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)		
			H 01 B		
The present search report has been drawn up for all claims					
Place of search THE HAGUE		Date of completion of the search 18-11-1988	Examiner DROUOT M.C.		
<table><tr><td>CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</td><td>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</td></tr></table>				CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document
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