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(54) **Improved polyamide fibres.**

(57) Polyamide fibres having an improved dye light fastness and heat and light stability are obtained by applying to them by means of a conventional dyeing operation, an aqueous composition containing a water insoluble copper salt of an organic acid which protects the fibres and any dye which may be present from radiation within the range 280 to 400 Nm. The copper salt has an affinity for the polyamide fibres and is stable and not volatile under the process conditions used.

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IMPROVED POLYAMIDE FIBERS

The present invention relates to dyed polyamide fibres having an improved dye light fastness and stability to heat and light, and particularly to such fibres when assembled into fabrics. The present invention also relates to a process for the production of such improved fibres.

It is known to improve the dye light fastness and heat and light stability of polyamide fibres by incorporating copper compounds into the polyamide polymer prior to spinning. However, for certain end uses, eg for automobile fabrics, a very high degree of dye light fastness and stability is desired. This would require large amounts of copper to be incorporated into the polymer which would consequently cause severe problems during melt spinning. To overcome this problem, there have been made numerous suggestions to treat the fibre with copper salts during or after dyeing.

Soluble copper salts have a very low affinity for polyamide fibres, and whilst, in exhaustion dyeing (batch) their use may offer a significant improvement in dye light fastness and stability, in continuous dyeing processes they offer much less of an improvement. Exhaustion dyeing is common practice with certain qualities of fabric/yarn/fibre, but the process has mechanical and quality limitations which make a continuous dyeing process essential for some fabric types.

European Patent No. 0 018 755 describes an improved method for dyeing a copper salt onto polyamide fibres using copper phosphate, especially in a colloidal form, during an exhaust dyeing process. The use of copper phosphate in a continuous dyeing process has proved not to be effective. European Patent No 0 051 188 describes a method for increasing the light fastness of polyamide fibres by impregnating them with an aqueous dispersion of a copper complex derived from salicylaldehyde and cyclohexylamine, followed by drying the fibres and then heating them at a temperature of 180°C for 30 seconds. Whilst this method when used either in a batch or continuous process provides an improvement in dye light fastness properties and heat and light stability of the fabric, the improvement is not sufficient for several specialised end-uses of polyamide fibres.

Japanese Patent No 61-27794 describes polyamide fibres, especially those of nylon 66, in which there is co-polymerised 5-30 mole percent of an aromatic dicarboxylic acid such as terephthalic, isophthalic and naphthoic di acids. It is said that fabrics formed from such fibres have excellent acidic dye uptake properties, and that dyed fabrics have good light-fastness properties.

The present invention provides a process for improving the dye light fastness and heat and light stability of polyamide fibres in fabric from when dyed, particularly by continuous techniques, with metal complex dyes, in particular 1-2 metal complex dyes.

It is well known that nylon polymers, on exposure to ultraviolet light, degrade due to the direct effect of the radiation and that at about 290 Nm direct photolysis is known to occur which causes degradation of the polymer chain. Furthermore the effect of elevated temperatures on nylon polymers is well known, and that measurable degradation of the polymers takes place on exposure (in the absence of other radiation) to temperatures exceeding 65°C.

The mechanism of fading metal complex dyes in nylon polymer is not well understood but empirical data suggests that the fading of the dyes and the degradation of the polymer follow the same pattern. In general the dye light fastness of metal complex dyes in nylon polymers is significantly affected by UV radiation in the range 280 - 310 Nm (280 Nm being the practical lower limit of radiation used in most automotive light fastness testing) for a fixed temperature of exposure; and for a fixed radiation condition, the effect of a rise in temperature above 65°C is significant.

The purpose of the present invention is therefore to provide a substance which will both transport copper into the polymer in sufficient quantities to offer a high level of heat protection, and at the same time to shield the polymer against the effects of UV radiation, particularly in the 280 - 310 Nm range.

We have now found that one way whereby the thermal and light stability of polyamide fibres and fabrics may be improved is by applying thereto a water insoluble copper salt of an organic acid which protects the fibres and any dyes which may be present, at least in part, from radiation within the range 280 to 400 Nm, and especially 280 to 310 Nm, the salt having an affinity for the polyamide fibres and being stable and not volatile under the process conditions used. Surprisingly the copper salt has little effect on the colour of dyed fabric.

Therefore, according to one aspect of the present invention, there is provided a process for improving the dye light fastness and heat and light stability of polyamide fibres by applying to the fibres in the form of a fabric or a yarn by means of a conventional dyeing operation an aqueous composition containing a copper salt, the copper salt being a water insoluble organic salt which protects the fibres and any dye present, at least in part, from radiation within the range 280 to 400 Nm, has an affinity for polyamide fibres and is stable and not volatile under the process conditions used.

According to a further aspect of the present invention there is provided polyamide fibres in the form of a yarn or a fabric having an improved dye light fastness and stability to heat and light, which optionally has been dyed with a 1-2-metal complex dye, the fibres having a copper salt deposited on or beneath their surface, the salt protecting the fibres at least in part, from radiation within the range 280-400 Nm, and is a water insoluble salt of an organic acid. Optionally the fibres also have on or beneath their surface a free radical inhibitor and/or a conventional UV absorber which absorbs light within the range 280 to 400 Nm.

Fabrics suitable for treatment according to the process of the present invention include those which contain fibres formed from polycaprolactam or poly (hexamethylene adipamide) (nylon-6 and nylon-66).

The copper salt may be applied continuously to the fabric, and the treated fabric subsequently steamed and washed by any of the well known techniques. A convenient method of applying the salt is by padding or doctor blade application. The process may be preformed before or after a conventional dyeing process, or may form part of the dyeing process.

The copper salts for use in the present invention have an affinity for polyamides. By affinity, we mean that they are absorbed/adsorbed onto the polyamide fibres by either chemical reaction with the polyamide or by physical attraction to form a solid solution which produces a shift in the equilibrium of the partition of the salt between the polyamide and the aqueous medium in favour of the polyamide.

The copper salts must be largely insoluble in water and not decompose or volatilise to any appreciable extent during any of the processes to which the fabric is or may subsequently be subjected.

The salts suitable for use according to the invention are derived from copper but we have found that those in the cupric form, are more effective.

Copper salts to be used according to this invention include those of aliphatic or aromatic carboxylic acids or of organic acids with other acid groups such as sulphonic or phosphonic.

Particularly effective salts have been found to be those of the naphthoic acids and their substituted derivatives, and of benzoic acid and its substituted derivatives.

To be effective the salt must firstly be capable of being incorporated in the dye bath (or other bath) without affecting the stability of the bath or other chemicals in the bath. It must also be, itself, stable to the conditions in the bath and to subsequent processes. It must also be capable of being fixed on the fibres to give the required levels of copper in the finished fabric from what would be considered a reasonable dyebath addition (ie a minimum of 20% and preferably more than 50% of the salt should remain on or in the fibre after all the processes are completed). This property is governed not only by the chemical nature of the salt, ie its ability to form some chemical bond with the fibre or to dissolve physically in the fibre, but also by the physical form of the salt, in particular its particle size and surface area.

A large number of aliphatic and aromatic acid copper salts will fulfil this function and provide levels of copper on finished fibre up to 0.3% by weight Cu from baths containing 0.5 - 0.6% by weight as Cu in the form of a suitable salt such as copper benzoate. This level of copper provides a high level of protection to both the polymer and the dye in tests where the exposure temperature is 70°C or higher. In the tests where exposure temperatures are below 70°C, the copper offers very much less protection.

It was discovered that by using copper salts of some acids which themselves have strong UV absorption in the range 280 - 310 Nm the protection offered in both high and low temperature tests can be much better. However this is not true for all acids with absorption in the 280 - 310 region, in particular some anthroic acids and cinnamic acid offer no protection and in some cases the effect of exposure is worse than if no copper salt is present. We make the assumption that this phenomenon is a result of rapid decomposition of these acids in UV light possibly leading to the formation of chemical species which are destructive to dye and/or polymer.

The fulfilment of these requirements must also be coupled with the effectiveness of a particular salt to perform not only across a wide range of test conditions but also over a wide range of individual dyes and also across a wide spectrum of shades from mixed dyes.

For these purposes we have found the copper salts of the following acids to be effective

benzoic acid

the monochloro and dichlorobenzoic acids

the mononitrobenzoic acids

the mono-aminobenzoic acids

acetyl salicylic acid
phthalic, isophthalic and terephthalic acids
1 and 2 naphthoic acid
3 acetoxy 2 naphthoic acid

but the most effective acid of those which have been examined is abietic acid (1, 12 - dimethyl - 7 - isopropyl - 1, 2, 3,4, 5, 6, 10, 11, 12, 13 - decahydro phenanthrone carboxylic acid), the copper salt of which offers a very high affinity and an ability to perform over a wide range of tests and shades.

Copper (Cu + +) has the ability with many of these (and other) acids to form acid and basic salts and also to form a wide range of hydrates and addition compounds. Some of these compounds have been examined because in aqueous suspension made by direct double decomposition precipitation, they have different physical forms.

A number of acids were used to prepare normal and basic salts and also solutions containing an excess of the acid and attempts were made to prepare mixed salts from two different acids. The performance of the basic/acid/mixed salts was in no case better than that of the simple salt and in some cases significantly worse.

This property of forming addition compounds, in particular the case of formation of addition compounds with amine containing substances, may explain the high affinity of these compounds for polyamide fibres.

The salts may be applied to fabric as an aqueous suspension. Where the process of the invention is to be carried out in conjunction with pad dyeing of the fabric, the salt may be added in the form of an aqueous suspension to the dye liquor, or as a solution in an appropriate organic solvent. Alternatively the salt may be formed in situ in the dye liquor by adding the acid or a soluble salt thereof and a soluble copper salt.

The insoluble copper salt of the acid to be used in the process according to the invention must have a chemical and/or physical affinity for polyamide fibres and during the process it is fixed on the fibres to give a level of salt which is capable of withstanding severe washing processes used in a continuous dyeing process. Fabrics treated according to the present process and which contain at least 500 ppm of copper have been shown to have improved heat and UV light stabilities. Those containing 1200 to 1500 ppm of copper have very good stabilities.

The exhaustion of the copper salts on polyamide fabrics is controlled by the particle size of the insoluble salt, the smaller the particle size the greater the exhaustion in general. Salts prepared in a gelatinous form, especially those freshly prepared, have a very good exhaustion.

Cupric salts of the organic acids for use according to the present invention are unstable under certain conditions of alkalinity and acidity. It is therefore desirable that when an aqueous medium is used for their application to fabrics, the medium is maintained in the pH range of 4.5 to 11. At pH values below 4.5 decomposition of the cupric salts occurs and at values above 11 there is a tendency for copper oxide to be formed.

Further improvement in the light stability of treated fabrics may be obtained when the fibres thereof also contain an additional free radical inhibitor and/or a conventional UV light absorber absorbing in the 280 - 400 Nm region. These additional compounds may be included with the metallic salt during the treatment process, or may be incorporated into the fibres at an earlier, eg during spinning, or later stage.

A suitable process for improving the dye light fastness of polyamide fabrics by modification of the dyeing process is as follows. A dye bath liquor containing dye, thickener, antifrosting agent and wetting agent is prepared in the conventional way. To this is added sufficient soluble copper salt, eg the sulphate or acetate, to give a concentration of 0.1 to 5 gms per litre of cupric ions. The sodium salt of β-naphthoic acid, dissolved in water is slowly added to the liquor with stirring in an amount sufficient to give a concentration of 0.02 to 5 gms per litre. The copper salt of β-naphthoic acid is immediately precipitated in flocculent form. Preferably the dye bath is maintained at a pH value of 4.5 to 5.8 to prevent precipitation of the cupric ion before the addition of the naphthoic acid. The polyamide fabric is then dyed by the conventional continuous pad/steam/wash off process using the modified dye liquor. The dye light fastness of the thus dyed fabric may be tested by any of the well known accelerated methods, eg those using a xenon arc. It has been found that the fabrics treated according to the process of the present invention have a very significant improvement in dye light fastness and heat and light stability properties, particularly when exposure temperatures exceed 65°C. They are substantially superior to those obtained using the presently available commercial treatments or those described in the patent literature.

Alternative methods of preparing the copper salt include:

(a) adding a solution of the acid or a salt to a concentrated aqueous solution of copper sulphate whilst stirring at high speed to form a pre-mixture which is then added to the dye bath,

(b) ball-milling the pre-mixture formed in (a) above before adding to the dye bath.

(c) adding the acid in dry powder form to a concentrated aqueous solution of copper sulphate, and ball milling the product to form a pre-mixture, and

(d) fusing a mixture of copper oxide and the acid and dissolving the thus produced salt in a suitable solvent (eg benzyl alcohol), and adding the solution, after the addition of an emulsifying agent, to the dye bath.

(e) fusing and milling with water to produce a fine suspension and adding the suspension and a dispersion agent to the dye bath.

The invention is further described with reference to the following examples.

Four test procedures which are in general use in the Automotive Industry to test the light stability of fabrics were selected for the experiments. These cover a range of temperature, radiation intensity and wavelength, humidity and other conditions. These tests are:-

1. The British Leyland Test which uses a Hanau "Suntest" machine with a 1 ½ kw unfiltered xenon burner and in which the samples are wrapped in polyethylene sheet before exposure. This machine has no temperature or humidity controls but is used for a commercial fabric acceptance specification.

2. The Ford (Europe) test, which uses a Hanau "Xenotest 1200" machine with three 4½ kw unfiltered xenon burners. This test is operated at an air temperature of 50°C and 80% RH, the black panel temperature being 75°. In both this and the British Leyland test, the wavelengths of radiation transmitted by the energy source is down to approx 275 Nm.

3. The FAKRA test (used by Audi/Volkswagen) which uses the Xenotest 1200 machine as above but in which a combination of soda-lime glass and infra red reflecting glass filters are used, effectively reducing the radiation below 310 Nm to a very low level. Operation is at an air temperature of 60°C and a RH of 20%, the black panel temperature being 83°C.

4. The General Motors test which uses an Atlas CI65 machine having a 6½ kw Xenon burner filtered with a borosilicate glass filter which eliminates radiation below 285 Nm. The machine operates on alternate light and dark cycles (3.8 hour light 1 hour dark). During the light cycle the air temp is 65° at 50% RH, with a black panel temp of 89°C. During the dark cycle indirect sprays operate giving an air temp of 38°C and 100% RH.

In order to study the light stability of nylon fabrics treated according to the present invention, fabrics were continuously exposed to UV light under conditions of temperature, radiation intensity and wavelength, and humidity required by the above described tests.

A range of samples were dyed in the laboratory using woven velvet having a polyamide pile and a cotton back. The pile of one was made from yarn spun from ICI Fibres product 3.3 dtex T323 the other from 3.3 dtex T123 fibres. Both types of fibre are made from polyamide 6.6, the former being semi-dull the latter being bright fibre.

The dyings were carried out over a range of conditions using dye combinations from the following list.

	CI Acid Number
Irgalan Yellow 3RL	Yellow 162
Irgalan Yellow GRL	Yellow 116
Irgalan Red Brown RL	Brown 226
Irgalan Bordeaux EL	Red 251
Irgalan Black RBL	Black 132
Erionyl Grey M-2G	Black 131
Irgalan Blue 3GL	Blue 171
Erionyl Blue MRW	Mixture
Irgalan Navy B	Blue 229
Erionyl Scarlet M2R	Red 316
Lanasyn Black SGL	Black 222
Lanasyn Dark Brown SGL	Brown 298
Lanasyn Dark Brown SBL	Brown 289

Irgalan & Erionyl - trade marks of Ciba-Geigy.
Lanasyn - trade mark of Sandoz.

The quantity and type of chemical auxiliaries were varied as was the type, quantity, method of preparation and method of addition to the dye bath of the copper salt.

The following examples demonstrate the effectiveness of the copper salts according to the invention.

EXAMPLE 1

A velvet cloth having a pre-dyed cotton back and an undyed pile made from 6.6 polyamide fibres of 3.3 decitex spun to 2/30 worsted count was dyed to seven shades. The dyes used were combinations taken from the following dyes.

Irgalan Yellow 3RL
Irgalan Yellow GRL
Irgalan Red Brown RL
Irgalan Bordeaux EL
Irgalan Black RBL
Erionyl Grey M2G

The shades, in the pale to medium depth range were based on commercial shades described as.

1. Flint Grey
2. Coffee Beige
3. Mink
4. Medium Dark Grey
5. Medium Sage
6. Light Driftwood
7. Light Saddle

The dye liquors per litre were made up as follows:

Part A

The dyes

5 gms Detergyl AG (Trade Mark of ICI) antifrosting agent, 2.5 gms of Mucitex TK XDR (Trade Mark of Schering Chemicals Ltd) thickener - viscosity modifier, and 450 ml water

The pH of this solution was reduced to 4 by the addition of acetic acid with stirring to develop the viscosity and then returned to 6.5 by the addition of sodium hydroxide solution.

Part B

Cupric sulphate pentahydrate
sodium salt of organic acid
500 ml water

The copper salts were made from cupric sulphate and the appropriate sodium salt by direct double decomposition precipitation. In the case of copper benzoate for example 5 gms of cupric sulphate were dissolved in 200 ml cold water and 5.8 gm of sodium benzoate were dissolved in 200 ml cold water. The benzoate solution was then added to the cupric sulphate solution with stirring to precipitate copper benzoate, and the pH adjusted to 6.5 with sodium hydroxide solution.

Suspension B was then added to a solution A to form the final dye liquor and, if necessary, the pH was adjusted to a value of 6.5, before the final volume was adjusted to 1 litre.

The dye liquor was then applied to the fabric to simulate continuous dyeing to give a liquor pick up of 400% and the samples steamed for 6 mins @ 100°C in a steamer operating at atmospheric pressure.

After steaming the samples were washed to remove all traces of unfixed dye and additive, hydro extracted, and finally dried for 5 mins at 160°C.

For each shade, the following copper salts were studied.

(a) none - comparative
(b) Copper sulphate 5 gms/l in final dye liquor - comparative

(c) Copper benzoate, equivalent to 5 gm/l of copper sulphate in final dye liquor
(d) Copper 4 nitrobenzoate equivalent to 5 g/l of copper sulphate
(e) Copper anthranilate equivalent to 5 g/l of copper sulphate
(f) Copper 2-naphthoate equivalent to 5 g/l of copper sulphate
(g) Copper abieate equivalent to 5 g/l of copper sulphate
(h) Copper abieate equivalent to 2 g/l of copper sulphate

Samples of these dyeings were then exposed to the conditions of the GM test method described previously (results given in Table 1) and to the conditions of the FAKRA test described previously (results given in Table 2.)

TABLE 1. GM Test conditions - 300 hours continuous light exposure-fade assessments against the Grey Scale

	SHADE						
TREATMENT	1	2	3	4	5	6	7
(a) None-comparative	2	1-2	1	1-2	1-2	1	1-2
(b) Copper sulphate-comparative	2	1-2	2-3	1-2	2-3	1	2-3
(c) Copper benzoate	4	3-4	4	2-3	3	3-4	4-5
(d) Copper 4-nitrobenzoate	4	3-4	4	2-3	2-3	3-4	4-5
(e) Copper anthranilate	4	3	4	4	2-3	3	3-4
(f) Copper 2-naphthoate	4	3-4	4	3	3	3	4
(g) Copper abieate	4-5	4	4	3-4	3-4	3-4	4-5
(h) Copper abieate	4-5	4-5	4-5	4-5	3-4	4-5	4-5

TABLE 2. FAKRA Test Conditions - 300 hours continuous exposure fade assessment against the Grey Scale

	SHADE						
TREATMENT	1	2	3	4	5	6	7
(a) None-comparative	2	1-2	1	1-2	1	1	1
(b) Copper sulphate-comparative	3	3	3	3	3	3	4
(c) Copper benzoate	4	4-5	3-4	3	3-4	3-4	4-5
(d) Copper 4-nitrobenzoate	4	4-5	3-4	3-4	3-4	4-5	4-5
(e) Copper anthranilate	3-4	4-5	3-4	3-4	3-4	4-5	4-5
(f) Copper 2-naphthoate	4	3-4	3-4	3	3-4	3-4	4-5
(g) Copper abieate	3-4	4	4	4	3	3-4	4
(h) Copper abieate	4	4-5	4-5	4-5	3-4	4-5	4-5

From the tables it can be seen that fabric treated according to the invention has a far superior UV light stability than fabric which has not been treated, or has been treated with copper sulphate.

EXAMPLE 2

Shade 3 (Mink) was dyed by the above technique using the following copper salts.

(a)	none - comparative	
(b)	Copper sulphate - comparative	)
(c)	Copper benzoate	) Copper concentration
(d)	Copper anthranilate	) in final dye liquor
(e)	Copper 4 nitrobenzoate	) equivalent to
(f)	Copper 2 naphthoate	) 5 g/l of copper
(g)	Copper 3 chlorobenzoate	) sulphate
(h)	Copper isophthalate	)
(i)	Copper acetyl salicylate	)
(j)	Copper cinnamate	)
(k)	Copper 2-3 hydroxy naphthoate	)
(l)	Copper abieate	)
(m)	Copper abieate - equivalent to 2 g/l of copper sulphate	
(n)	Cibatex LP (phenyl benztriazole UV absorber (Ciba Geigy) 5 g/l	
(o)	Acralux PA (copper complex + UV absorber Bayer) 2.5 g/l	
(p)	Sunlife SN 500 (soluble copper salt) Japan 5 g/l	
(q)	Nylofixan AUTD (soluble copper salt Sandoz) 5 g/l	

Samples of these dyeings were tested by the four tests previously described. The results are given in Table 3 from which it can be seen that fabrics treated according to the invention have a superior stability to UV light to those treated with stabilisers of the prior art.

TABLE 3. Continuous exposure fade assessments of mink shade against the Grey Scale

	TEST CONDITIONS			
TREATMENT	GM	Ford	Fakra	BL
	300 hrs	96 hrs	300 hrs	200 hrs
(a) None-comparative	1	1	1-2	2
(b) Copper sulphate-comparative	2-3	3-4	3	2
(c) Copper benzoate	4	4	3-4	3
(d) Copper anthranilate	4	4-5	3-4	3-4

TABLE 3 continued

TREATMENT	TEST CONDITIONS GM 300 hrs	Ford 96 hrs	Fakra 300 hrs	BL 200 hrs
(e) Copper 4-hydroxybenzoate	4	4-5	3-4	3-4
(f) Copper 2-naphthoate	4	4	3-4	3
(g) Copper 3-chlorobenzoate	4	4	3-4	3
(h) Copper isophthalate	3	3-4	2-3	2
(i) Copper acetyl-salicylate	4-5	4-5	3-4	3-4
(j) Copper cinnamate	2-3	3	2	1-2
(k) Copper 2-3 hydroxy-naphthoate	4	4-5	4	2
(l) Copper Abieate	4	4-5	4	3-4
(m) Copper Abieate	4-5	4-5	4-5	4
(n) Cibatex LP	2	3	2	3
(o) Acralux PA	3	3-4	3-4	3
(p) Sunlife SN Ste	2-3	3-4	3	2
(q) Nylefixan AUTD	2-3	3-4	3	2

EXAMPLE 3

Shade 3 (Mink) was dyed by the technique described previously using an impure (commercial) source of abietic acid. Samples of the copper abieate were made using various proportions of copper sulphate to the commercial abietic acid, and also in a more concentrated suspension which was diluted before addition to the dye bath. The conditions were as follows, the copper sulphate being in the form of the pentahydrate.

(a) 1 part of copper sulphate was reacted with 1 part of the sodium salt of commercial abietic acid to give a dye bath having a copper concentration equivalent to 2 gm per litre of copper sulphate.

(b) 1 part of copper sulphate was reacted with 2 parts of sodium abieate to give a dye bath having a copper concentration equivalent to 2 gm per litre of copper sulphate.

(c) 1 part of copper sulphate was reacted with 3 parts of sodium abieate to give a dyebath having a copper concentration equivalent to 2 gm per litre of copper sulphate.

(d) 1 part of copper sulphate was reacted with 1 part of the sodium salt of commercial abietic acid to give a dye bath having a copper concentration equivalent to 5 gm per litre of copper sulphate.

(e) 1 part of copper sulphate was reacted with 2 parts of the sodium salt of commercial abietic acid to give a dye bath having a copper concentration equivalent to 5 gm per litre of copper sulphate.

(f) 1 part of copper sulphate was reacted with 3 parts of the sodium salt of commercial abietic acid to give a dye bath having a copper concentration equivalent to 5 gm per litre of copper sulphate.

(g) A suspension was made by mixing 80 gm of copper sulphate and 210 gm of sodium abieate in 1 litre of water, and a quantity of the resultant suspension was added to the dyebath to give a copper concentration equivalent to 2 gm per litre of copper sulphate.

(h) The suspension of (g) was added to the dye bath to give a copper concentration equivalent to 5 gm per litre of copper sulphate.

Samples of these dyeing were then tested by exposure to the General Motors test condition. Fading results are given to Table 4.

TABLE 4 - GM Test conditions - 300 hrs continuous exposure fade assessment of mink shade against the Grey Scale

Treatment			
Ratio of Copper Sulphate to Sodium Abieate		Copper concentration in finish dye liquor equiv. to copper sulphate (g/l)	Assessment
(a)	1 : 1	2	4-5
(b)	1 : 2	2	4
(c)	1 : 3	2	4
(d)	1 : 1	5	4
(e)	1 : 2	5	3-4
(f)	1 : 3	5	3
(g)	1 : 2.6) Concentrated	2	3-4
(h)	1 : 2.6) suspension	5	3
(i)	No copper additive (comparative)		1

Example 4

Samples of a warp-knitted cloth made from a continuous filament nylon 66 yarn were dyed by a conventional exhaustion method in a laboratory machine to give shades 1 to 3 of Example 1. The conditions were pH 6.5 for 1 hour at 100°C with a liquor/goods ratio 20:1 using 1% Sandogen NH (Trade Mark of Sandoz) as levelling agent to give the following fabrics having:

(a) no additive - comparative,
(b) 2% of copper sulphate penta hydrate (comparative),
(c) copper benzoate equivalent to 2% by weight on fabric of copper sulphate penta hydrate, and
(d) copper abieate equivalent to 2% by weight on fabric of copper sulphate penta hydrate.

Samples of the dyed fabric were exposed to the Ford test conditions, and the fading results are given in Table 5.

TABLE 5 Exhaustion dyeing - Ford test for 96 hours

TREATMENT		SHADE		
		1	2	3
(a)	Comparative	3	2-3	3
(b)	Comparative	3-4	3	3
(c)	Copper benzoate	4-5	4	4-5
(d)	Copper abieate	4	3-4	3-4

From the table it will be seen that fabrics treated according to the present invention have superior light resisting properties.

EXAMPLE 5

Dye liquors for shades 1, 2 and 3 were made up on a commercial scale (2000 litres) by the techniques previously described and copper benzoate incorporated in the liquors from a previously made concentrated suspension. The suspension was made by direct double decomposition to give 200 gms of copper benzoate per litre of suspension. This was added to the dye liquor at the rate of 5 gms of copper benzoate per litre of dye liquor.

These liquors were then applied to the previously described polyamide pile woven velvet fabrics made from ICI Type 3.3. dtex 323 - semidull fibre having a dyed cotton-back by a fully commercial process from a Kuster continuous dyeing machine using a doctor-blade applicator to apply the liquor at the rate of 200% on weight of fabric followed by steaming and washing in the same continuous machine. Light fastness tests of the treated fabric are given in Table 6.

EXAMPLE 6

Example 5 was repeated using a woven velvet fabric with undyed cotton backing made from ICI Type 3.3 dtex 123 bright fibre and incorporating in the dye liquors, direct-cotton dyes and an anionic blocking agent so that the cotton backing and polyamide pile were dyed simultaneously but no direct dye staining of the polyamide occurred.

Dyeing steaming and washing were as in example 5 but the washing process was followed by an after treatment (pad application) of Trinofix EW (Trade Mark of Ciba Geigy) at a concentration of 5 gm per litre to improve the wet fastness of the direct-cotton dyes.

Samples from examples 5 and 6 were tested for light fastness together with untreated controls in the three shades under BL and GM conditions as previously described. Light fastness tests of the treated fabric are given in Table 6.

TABLE 6. Light Stability of Polyamide Pile Velvet Fabrics

	BL (200 hrs)	GM (300 hrs)
Shade 1 Flint Grey		
(a) Control (no additive)	2-3	1-2
(b) polyamide dyed only - Example 5	4	3-4
(c) polyamide and cotton dyed together - Example 6	4	4
Shade 2 Coffee Beige		
(a) Control	1-2	1
(b) Example 5	3-4	3-4
(c) Example 6	3-4	3-4
Shade 3 Mink		
(a) Control	2	1-2
(b) Example 5	3-4	3-4
(c) Example 6	4	4

EXAMPLE 7

The improvements in the degradation properties brought about by these treatments are normally tested by abrasion tests such as the Martindale and Taber tests. However these tests when carried out on polyamide woven velvets are both lengthy and unreliable because the fabrics are so inherently resistant to abrasion. Strength tests offer no indication of the properties of the polyamide since the fabric strength is determined entirely by the backing yarn, in this case cotton. Thus in order to measure loss of strength on exposure to the tests, a conventional flat fabric was woven using for the warp and weft the same polyamide yarn as used for the velvet pile

Samples of this fabric were dyed by techniques previously described but using a conventional pad-mangle as the applicator, and the following treatments were carried out:

(a) untreated fabric.

(b) fabric dyed in shades 1, 2, 3 but without additive.

(c) fabric dyed in shades 1, 2, 3 with copper sulphate at a level of 2% on fabric weight.

(d) fabric dyed in shades 1, 2, 3 with copper benzoate at a level of 2% on fabric weight.

Samples of each fabric were then exposed under GM test conditions using a quartz outer filter in place of borosilicate which allows radiation down to 250 Nm for 50, 100, 150 & 200 hrs and the strength of 5 cm strips then measured on an Instron machine. The results are shown in Table 7 as percentage retained strength when compared with the unexposed untreated fabric.

TABLE 7. Percentage retained breaking load

Fabric Treatment	Exposure (hrs)	Retained breaking load (%) white fabric		
None - Untreated Control	0	100		
	50	67		
	100	44		
	150	26		
	200	12		
		Shade 1	Shade 2	Shade 3
None - dyed only (b)	50	82	74	86
	100	55	41	51
	150	37	30	31

TABLE 7 - Continued

Fabric Treatment	Exposure (hrs)	Retained breaking load (%) Shade 1	Shade 2	Shade 3
	200	19	16	20
Dyed and treated with copper sulphate (c)	50	88	81	87
	100	69	61	63
	150	49	44	49
	200	26	24	28
Dyed and treated with copper benzoate (d)	50	92	90	92
	100	77	71	81
	150	58	55	57
	200	34	31	34

Claims

1. A process for improving the dye light fastness and heat and light stability of polyamide fibres by applying to the fibres in the form of a fabric or a yarn by means of a conventional dyeing operation on aqueous composition containing a copper salt, the copper salt being a water insoluble organic salt which protects the fibres and any dye present, at least in part, from radiation within the range 280 to 400 Nm, has an affinity for polyamide fibres and is stable and not volatile under the process conditions used.

2. A process according to claim 1 wherein the aqueous composition is applied continuously to the fibres in the form of a fabric, followed by steaming the fabric and washing off residual material.

3. A process according to claim 1 or 2 wherein the copper salt is a salt of an aliphatic or aromatic carboxylic acid.

4. A process according to claim 3 wherein the copper salt is a salt of an acid selected from the group comprising benzoic acid, monochloro and dichlorobenzoic acids, mononitrobenzoic acids, mono-aminobenzoic acids, acetyl salicylic acid, phthalic acid, isophthalic acid, terephthalic acid, 1-and 2-naphthoic acids, 3-acetoxy-2-naphthoic acid and abietic acid.

5. Polyamide fibres in the form of a yarn or a fabric having an improved dye light fastness and stability to heat and light, which optionally has been dyed with a 1-2 metal complex dye, the fibres having a copper salt deposited on or beneath their surface, the salt protecting the fibres, at least in part, from radiation within the range 280-400 Nm and is a water insoluble salt of an organic acid.

6. Polyamide fibres according to claim 5 wherein the copper salt is a salt of an aliphatic or aromatic carboxylic acid.

7. Polyamide fibres according to claim 6 wherein the copper salt is a salt of an acid selected from the group comprising benzoic acid, monochloro-and dichlorobenzoic acids, mononitrobenzoic acids, monoaminobenzoic acids, acetyl salicylic acids, phthalic acid, isophthalic acid, terephthalic acid, 1-and 2-naphthoic acids, 3-acetoxy-2-naphthoic acid and abietic acid.

8. Polyamide fibres according to claims 5 to 7 wherein the fibres have deposited on or beneath their surface a conventional UV absorber which absorbs light within the range 280 to 400 Nm.