

1

2,790,734

STABILIZATION OF NYLON THREADS AND FABRICS TO SUNLIGHT

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This invention relates to a process for treating nylon threads or fabrics to render such articles stable to the deteriorating effects of direct sunlight or ultra-violet sources. Nylon is one of a series of super-polymers having a molecular weight in the range of from 10,000 to 25,000 and made from a primary alkylene diamine and a dibasic aliphatic carboxylic acid. Hexamethylene diamine and adipic acid are primary constituents of commercial nylon. While such super-polymers have superior properties making them particularly useful as textile materials, nevertheless, they are subject to severe loss in tensile strength upon prolonged exposure to sunlight. The problem is particularly acute where nylon is used to fabricate window curtain material or automobile seat covers.

It is a principal object of this invention, therefore, to provide a method for treating nylon thread either prior to or subsequent to weaving into a textile material or article to render it less susceptible to the deleterious effects of sunlight, thereby improving the wear characteristics of the nylon.

Another object of this invention is to stabilize the tensile strength of nylon threads, or fabrics made therefrom, to the damaging action of sunlight.

Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the appended claims, the following description setting forth in detail certain illustrative embodiments of the invention, such disclosed means constituting, however, but a few of the various forms in which the principle of this invention may be employed.

It has been found that when nylon thread or fabric is treated with certain organic copper salts and cured at an elevated temperature, the property of resistance to loss of tensile strength upon exposure to actinic rays is conferred upon the material. More particularly, this invention comprises the method of inhibiting loss of tensile strength in nylon which comprises coating a nylon surface with a copper salt of an organic carboxylic acid and curing the coated nylon surface at a temperature of from about 250° F. to about 500° F. for a period of time up to about 10 minutes.

Treatment in accordance with this invention is effected in one of several ways, perhaps the most convenient of which is padding. By this process, the fabric or thread is immersed in a bath containing the active ingredient removing therefrom an amount sufficient to stabilize the nylon in the desired manner. Upon leaving the bath the saturated fabric or thread passes through a restricted passage, as between rolls, whereby excess liquid is removed from the material. In a modification of this process, one of a pair of rolls is partially immersed in a padding bath and as the material being treated passes through the pair of rolls, liquid is carried to the material by the bottom roll, any excess falling back into the bath.

2

Adjustment of the nip of the rolls determines the amount of liquid carried through by the material up to the limit of the ability of the material to pick up and retain a liquid.

The padding bath is usually prepared as an emulsion, although homogeneous solution systems or chemical precipitation means may be used to effect the coating of the nylon threads with the copper salt. Utilization of aqueous systems is a very satisfactory way of achieving the desired results of this invention because of the ease of handling water base materials, the avoidance of the fire hazard encountered with solvent systems, the ease of cleaning equipment after a run or to change the color, etc. It is also desirable to employ a resinous material as a binder for the copper salt in the treating compositions.

The threads, or fabrics made therefrom, which are improved with respect to tensile strength stability are those threads and fabrics which are made from polyamide type resins, e. g., nylon, either dyed or undyed. One form of nylon fabric which is particularly advantageously improved by the methods and compositions of this invention is nylon marquisette, widely used in the manufacture of window curtains. Other fabrics which are composed in whole or in part of nylon threads are greatly benefited by the process of this invention.

As previously indicated, the principal active ingredient in the treating baths of this invention is a copper salt of an organic carboxylic acid. While there appears to be high selectivity in the metallic ion (certain cobalt salts have also shown a lesser degree of improvement), the nature of the organic acyl radical is very much less critical. In general, the organic acidic materials which have been found useful herein contain at least 6 carbon atoms. No upper limit has been found and even polymeric acidic materials may be used to form the copper salts. Apparently it makes no difference whether the acidic base is aromatic or aliphatic or mixed aromatic-aliphatic. The presence or absence of substituent groups in the molecule also seems to exert little effect; hence halogen, oxygen, etc. may be present as substituent elements.

Specific examples of copper salts which may be used for treating nylon to improve the resistance thereof to loss of tensile strength upon prolonged exposure to sunlight include the copper salt of polyacrylic acid, copper caseinate, copper naphthenate, copper salt or petrex acids (resinous polybasic acids from terpene and maleic anhydride), copper stearate, copper oleate, copper benzoate, copper salicylate, copper phthalate, copper salt of carboxy methyl cellulose acids, copper-8-hydroxy quinolinolate, copper salt of linseed oil fatty acids, etc. Other copper salts which may be used will be evident to those skilled in the art.

The treating bath, whether of the emulsion, solvent, or chemically precipitated type, should contain from about 0.1% to about 1.0% by weight of the copper salt.

A typical formulation of a padding bath of the emulsion type is as follows:

EXAMPLE I

Part I:	Parts
Butylated melamine-formaldehyde	50%
solids in 50-50 xylol-butanol solvent	76
Copper resinate	24
Part II:	
Water	91
Styrene-maleic anhydride condensate	10.5
Morpholine	10.5
Glyceryl monoricinoleate	6.5
Whitening agent (TiO ₂)	181.5
Part III:	
Water	1293.3

3

Part I is made by dissolving the copper salt in the xylol-butanol solution of alkylated melamine-formaldehyde condensate.

Part II is the emulsifying and suspending system having dispersed therein, if desired, a whitening agent such as rutile titanium dioxide.

Part I is mixed into Part II, yielding an oil-in-water emulsion which is a concentrated form of padding material. This must then be diluted with water (Part III) to yield a suitable padding bath. In general the amount of such diluent (water or solvent) used will be such as to provide a concentration of copper salt in the final padding bath of from about 0.1% to about 1.0%. The above formulation provides a concentration of copper resinate of 0.18%.

EXAMPLE II

A typical solvent-type padding bath is simply a very dilute solution of the copper salt in a solvent. For example, copper naphthenate may be dissolved in a 50-50 xylol-butanol mixture to a concentration of 0.5% by weight. Any of the available copper salts of organic acids dissolved in a suitable solvent to a concentration of from about 0.1% to about 1.0% will provide a suitable padding bath. Obviously a polyamide solvent will be avoided.

The solvent type copper salt solutions may also contain a suitable resinous material, such as the alkylated melamine-formaldehyde condensates exemplified above in the emulsion type bath. Any resinous material capable of hardening and adhering to nylon may be used, if desired. It has been found that resinous materials are not required in this treatment, but better resistance to laundering is achieved if such resins are used to bind the copper salt to the nylon.

EXAMPLE III

Another process of coating the polyamide surface to protect against the deleterious effect of sunlight is by chemical precipitation. Padding equipment is used in this case as in the preceding cases, but two baths are involved. The first bath coats the nylon with a water solution of a reactive organic carboxylic acid salt, e. g., the ammonium salt. This coating is dried and the nylon passed through an aqueous solution of copper sulphate which causes water insoluble copper salt to form on the nylon surface. The surface is then dried and cured as aforesaid.

EXAMPLE IV

Another example of an emulsion type padding bath is as follows:

	Parts
Butylated melamine-formaldehyde condensate-----	1.6
Ethyl cellulose (10 cps. standard ethoxy)-----	1.8
Copper stearate-----	0.4
Xylol -----	2.2
Emulsifying agent (ethylene oxide condensate)-----	1.2
Dibutyl phthalate-----	0.25
NH ₄ OH -----	0.15
Water -----	91.3

This emulsion (oil-in-water type) was used to pad nylon marquisette at a wet pick-up of 55%. Stated in another way, each gram of nylon marquisette fabric on passing through the padder retained 0.55 gram of emulsion. Upon curing, it was observed that the sample yellowed slightly. The cause was later found to be the emulsifying agent. Studies have shown that the ammonia or morpholine salts of styrene-maleic anhydride condensates are superior emulsifying agents in that the yellowing tendency is avoided.

4

Although only trace amounts of copper salt are deposited on the polyamide fabric, copper stearate has a grey-green color and is desirable, when using on undyed nylon, to employ a whitening agent to mask the color.

A very desirable copper salt from the color standpoint is the copper salt of a monovinyl benzene-maleic anhydride condensate also used as an emulsifier-thickener. It has a very pale blue color and requires far less whitening to mask its color. Moreover, there appears to be less tendency to yellowing at curing temperatures. This copper salt is more difficult to disperse, however.

The monovinyl benzene-maleic co-polymer referred to above is conveniently produced by any one of several established ways. The ingredients may be mass polymerized by heating, for example, styrene and maleic anhydride at temperatures between about 100° F. and 300° F. for several hours or more. In certain instances it may be found desirable to employ a small amount, e. g., 0.1% to 1.0% by weight of divinyl benzene in the copolymerization reaction. A peroxide catalyst is often used and it is desirable that the materials be heated with care as by means of a water bath. Another method of producing these materials is by conducting the copolymerization in the presence of a solvent for the starting materials and the final product, such as, acetone. Instead of styrene, substituted styrenes including alkylated styrenes, such as, methyl, ethyl, propyl and butyl styrenes, or substituted styrenes, such as, chlorostyrene, or the like may be used to prepare the co-polymers. Instead of maleic anhydride, there may be used partially esterified maleic acid, such as, the half esters methyl maleate, ethyl maleate, iso-propyl maleate, sec-butyl maleate, etc. Further discussion of the production of these materials may be found by having reference to the patent to Barrett 2,537,018 dated Jan. 9, 1951; the patent to Seymour, 2,533,635 dated December 12, 1950; and the patent to Condo et al., 286,062, dated June 9, 1942. It has been found that when using divinyl benzene as a cross-linking agent in these co-polymers, substantially larger amounts than those indicated above tend to cause the printing paste to become too viscous.

Thus, the form of the bath, or the mode of coating the surface of the polyamide is not critical, although for convenience and safety reasons, the emulsion system is to be preferred. It is essential to the satisfactory practice of this invention that the polyamide surface, whether as an individual thread prior to weaving, or in a fabric composed of a plurality of threads, or as a wool mass, be coated with a composition capable of depositing a film containing a copper salt of an organic carboxylic acid of 6 to 22 carbon atoms, and that the thus coated surface be heat treated at a temperature of from about 250° F. to about 400° F. for a period of time ranging from a few seconds to several minutes. Quite obviously, the higher curing temperatures will require shorter curing times, a few seconds, i. e., 10-40 seconds being quite effective at 400° F. The converse is also true.

A surprising feature of this invention is that a relatively mild heat treatment step is required in order to develop the protective qualities of the coating on the polyamide surface. Why this is true is not known, but, as subsequent test data will show, unless the coated polyamide is cured, there is no permanent improvement in the tensile strength after exposure to ultra-violet light.

It is convenient at this point to illustrate the effectiveness of a variety of the more common copper salts for the purposes of this invention by comparing the results obtained from baths containing a variety of concentrations of copper salts with and without subsequent curing of the treated nylon. It will be understood that these examples are for illustrative purposes only and are not to be construed as limiting the invention to the precise scope thereof.

No.	Active Ingredient	Tensile Strength Before Exposure	Tensile Strength After Exposure	Hours Exposed	Bath Type	Curing Time, Minutes	Curing Temp., ° F.
1.	None.....	49.0	13	60	-----	3	-----
2.	None.....	49.0	-----	-----	-----	3	330
3.	0.5% Cu Salicylate.....	49.7	49.9	60	Solvent.....	3	330
4.	do.....	49.7	22.4	60	do.....	Uncured	-----
5.	0.25% Cu Benzoate.....	50.2	49.8	60	Emulsion.....	3	330
6.	0.25% Cu Petrexate.....	50.4	52.2	60	do.....	3	330
7.	do.....	50.4	25.3	60	do.....	Uncured	-----
8.	0.5% Cu Caseinate.....	48.7	44.0	60	Chem. Ppt.....	3	330
9.	do.....	48.7	22.1	60	do.....	Uncured	-----
10.	0.5% Cu Polyacrylate.....	50.4	50.0	60	do.....	3	330
11.	do.....	50.4	24.0	60	do.....	Uncured	-----
12.	1.0% Cu 8-hydroxy quinolinolate.....	48.0	48.4	60	Emulsion.....	3	330
13.	0.5% Cu 8-hydroxy quinolinolate.....	48.0	46.7	60	do.....	3	330
14.	0.5% Cu PVM/MA.....	53.0	52.4	60	Chem. Ppt.....	3	330
15.	do.....	53.0	28.4	60	do.....	Uncured	-----
16.	0.5% Cu Stearate.....	48.8	40.2	60	Emulsion.....	3	330
17.	do.....	48.8	40.1	100	do.....	3	330
18.	do.....	48.8	32.9	180	do.....	3	330
19.	0.6% Cu Stearate.....	50.2	51.3	117	do.....	3	330
20.	0.5% Cu Resinate.....	48.8	48.2	60	Solvent.....	3	330
21.	do.....	48.8	25.7	60	do.....	Uncured	-----
22.	0.3% Cu Resinate.....	48.2	47.1	60	Emulsion.....	3	330
23.	do.....	48.2	24.3	60	do.....	Uncured	-----
24.	0.25% Cu Resinate.....	48.3	20.5	60	Solvent.....	do	-----
25.	0.2% Cu Resinate.....	49.1	49.3	60	Emulsion.....	3	330
26.	0.1% Cu Resinate.....	47.6	34.2	60	do.....	3	330
27.	do.....	47.6	16.5	60	do.....	Uncured	-----
28.	1.0% Co Resinate.....	49.2	45.6	60	do.....	3	330
29.	0.16% Co Resinate.....	48.8	24.0	60	Solvent.....	3	330
30.	0.16% Co Resinate (bleached).....	48.8	38.7	60	do.....	3	330
31.	0.5% Cu Resinate.....	49.3	47.8	60	Solvent-Resin.....	3	330
32.	0.5% Cu Verseante.....	48.8	48.4	60	Chelate.....	3	330
33.	do.....	48.8	22.5	60	do.....	Uncured	-----

In determining the data in the preceding table, nylon 30 marquisette fabric pieces 5" x 12" were used. The material was dipped in the indicated padding bath and passed between rolls allowing a wet pick-up of 50-55% of the weight of the dry fabric, i. e., 1 gram of bath/2 grams of nylon marquisette. Curing was effected in an oven.

The tensile strength measurements were made on the nylon samples in a warp-wise direction only, using the Scott Tensile Strength Testing Machine. The measurement is made by breaking a 4" x 6" specimen between 1" x 1" clamps spaced 3" apart. The reading is in pounds. A more detailed description of the procedure is contained in Federal Specification CCC-T-191b—Method 5100. Unpadded nylon marquisette has a tensile strength under this method of between 49 and 51 lbs. Nylon marquisette which has been heated for three minutes at 330° F. in an oven has substantially the same tensile strength and in some cases is even a little stronger. After 60 hours exposure on a white background, the tensile strength of unpadded nylon runs between 10 and 15 lbs.

In the preceding table, reference has been had to Cu PVM/MA. PVM/MA is a co-polymer of polyvinyl methyl ether and maleic anhydride. In Examples XI and XII of Table I, the copper salt of this co-polymer was chemically precipitated on the nylon in the following manner. Ammonium hydroxide was added in excess to an aqueous solution of the co-polymer of appropriate concentration (0.5%). This was padded into the nylon marquisette and air dried. The nylon marquisette was then padded with a 0.5% copper salts solution. On a mol per mol basis, there is an excess of copper sulphate over what is needed to react with all of the ammonium salt of the co-polymer. The doubly padded nylon marquisette was then air dried, rinsed in cold water to remove the excess copper sulphate and again air dried.

Examples 29 and 30 refer to copper "Versenate." These are copper salts of ethylene diamine tetra-acetic acid. The "versenes" are sodium salts of ethylene diamine tetra acetic acid and are used as chelating agents for sequestering soluble metallic ions and maintaining them in non-ionic solution. The pad bath used in Examples 29 and 30 was made by dissolving 0.3% trivalent iron versene and 0.2% copper sulphate in water.

The solvent type baths were made by dissolving the designated percentage of copper salt in a 50-50 xylol-butanol solution. Where a solvent-resin bath is indicated, 75

butylated melamine formaldehyde in a weight ratio to the copper salt of 3:1 was used. Except for the presence of the resinous material, the resin-solvent baths would be the same as the solvent baths.

The chemical precipitation methods for depositing the copper salts on the nylon were all done in a similar manner. The ammonium salt of the organic acid was first made by means of aqueous ammonia and applied to the nylon sample. After drying the fabric was re-padded with a copper sulphate solution of sufficient concentration to contain an excess of copper sulphate over that required to precipitate the ammonium salt. The sample is then rinsed in cold water, dried and cured. The chemical precipitation method is generally used where the copper salt is difficult to disperse in a suitable vehicle.

Exposure to ultra-violet light was carried out in a Fadeometer using the white cardboard background. 50 hours of such exposure is equivalent to about 240 hours exposure without the background.

Table II below compares tensile strengths before and after 60 hours exposure to ultra-violet light at various curing times and temperatures. The active ingredient in each case was copper resinate applied to commercial nylon from a 0.5% solution in 50-50 xylol-butanol mixture.

Table II

No.	Before Exposure	After Exposure	Cure Time, seconds	Cure Temp., ° F.
29.....	48.8	30.8	60	252
30.....	48.8	38.1	120	252
31.....	48.8	37.5	60	330
32.....	48.8	51.0	120	330
33.....	48.8	51.0	10	400
34.....	48.8	53.2	20	400
35.....	48.8	58.2	40	400

Reference has been made above to the use of whitening agents. The reason such agents are used at all is that the polyamide resins have a tendency to discolor upon heating. Yellowing invariably occurs with untreated nylon marquisette and a bleaching operation is indicated. Any bleaching operation should be carried out on the alkaline side since solutions having a pH below 6 tend to remove the copper salt. Accordingly, it is frequently desirable to utilize a whitening agent. Good hiding power, high tinctorial power, ready dispersibility, chemical inert-

ness, and low cost are desirable characteristics of a whitening agent. Titanium dioxide (rutile) is particularly satisfactory for this purpose although zinc oxide and basic lead carbonate may be used. The pigment is dispersed in the padding bath to a concentration of from 2 to 15%, about 2-5% being sufficient for most purposes.

In another embodiment of this invention the copper salts may be included in a padding bath for imparting color to nylon. Using from 0.1% to 1% of a copper salt in a padding bath containing a red pigment, the results in improved tensile strength were as noted above for undyed nylon.

It is not mandatory that a resinous material be used as a component of the treating bath although the inhibitive effect of the copper salt is present only so long as the copper salt is. Thus it is beneficial to use such a resinous binder and the most satisfactory are the water-soluble and water dispersible carbamide-aldehyde resins such as the urea, thiourea, melamine, etc.—aldehyde condensates. The melamine-formaldehyde resins and their "alkylated" analogues have been mentioned above. Urea-formaldehyde resins and thio-urea-aldehyde resins may also be used.

The alkylated melamine formaldehyde condensation products which are useful in accordance with this invention may be prepared by known methods. For example, reference may be had to the patent to Widmer, 2,197,357, and the patent to Swain, Re. 22,402. In general, these condensation products are prepared by reacting 2 to 6 mols of formaldehyde with 1 mol of melamine. The condensation product formed is believed to be mostly methylol-melamine.

When preparing the various alkylated melamine formaldehyde condensation products, it is frequently desirable to prepare first the methylated methylol-melamine and then, by an interchange process utilizing an aliphatic alcohol of the desired carbon atom content, e. g., 3 to 12 carbon atoms, obtain the corresponding "alkylated" methylol-melamine. Specific examples of such treatment are also given in the patent to Johnstone et al. Re. 22,566.

Specific examples of the alkylated melamine formaldehyde condensation products which may be used in accordance with this invention include propylated methylol-melamine, butylated methylol-melamine, hexylated methylol-melamine, cyclohexylated methylol-melamine, caprylated methylol-melamine, laurylated methylol-melamine, etc.

A preferred material for use in accordance with this invention is the butylated melamine-formaldehyde prod-

uct, primarily because of its ready availability on the market, and for this reason it has been used in the specific examples which will be understood as merely illustrative of the use of other such alkylated methylol-melamines.

Other resinous materials may be used including phenol-aldehyde resins, oil-modified alkyd resins, etc.

Other modes of applying the principle of this invention may be employed instead of those specifically set forth above, changes being made as regards the details herein disclosed, provided the elements set forth in any of the following claims, or the equivalent of such be employed.

It is, therefore, particularly pointed out and distinctly claimed as the invention:

1. The method of inhibiting loss of tensile strength in filamentous nylon which comprises coating a nylon surface with a copper salt of an organic carboxylic acid containing at least 6 carbon atoms and curing the coated nylon surface at a temperature of from about 250° F. to about 500° F. for a period of time up to about 10 minutes.
2. The method of claim 1 in which the organic carboxylic acid is an aliphatic carboxylic acid.
3. The method of claim 1 in which the organic carboxylic acid is an aromatic carboxylic acid.
4. The method of claim 1 in which the copper salt is copper resinate.
5. The method of claim 1 in which the copper salt is copper stearate.
6. The method of claim 1 in which the copper salt is copper benzoate.
7. The method of inhibiting loss of tensile strength in nylon fabric which comprises saturating said fabric with a padding composition containing from about 0.1% to about 1.0% by weight of a copper salt of an organic carboxylic acid containing at least 6 carbon atoms, and curing the padded nylon fabric at a temperature of from about 250° F. to about 500° F. for a period of time up to about 10 minutes.

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