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3,279,944

PROCESS OF INCREASING THE TENSILE STRENGTH OF NYLON FILAMENT WITH CHLORINE OR BROMINE SUBSTITUTED LOWER ALKANES

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This invention relates broadly to certain new and useful improvements in the art of treating nylon filamentary material. More particularly the invention is concerned with a method of improving the tensile strength of filamentary material comprised of nylon filaments and with the products thereof. Still more particularly the invention is concerned with a method of improving the tensile strength of filamentary material comprised of nylon filaments which comprises contacting the said filamentary material with a tensile strength-improving treating agent consisting essentially of a compound represented by the general formula



wherein X represents a halogen selected from the group consisting of chlorine and bromine, n represents an integer which is at least 2, and R represents a saturated aliphatic hydrocarbon radical containing from 1 to 5 carbon atoms, inclusive, and at least 2 hydrogen atoms, said compound having a boiling point below the softening point of the said filamentary material. The filamentary material is maintained in contact with the said treating agent at a temperature ranging from ambient temperature up to the boiling temperature of the said treating agent but below the softening point of filaments of the said filamentary material for a period sufficient to increase the tensile strength of the said filamentary material. (The aforementioned "softening point" can be substantially the same as the melting point.)

The method features of the invention also include, as desired or as conditions may require, the additional step of removing excess treating agent from the treated filamentary material. The scope of the invention also includes the improved products resulting from the method of the invention.

Illustrative examples of compounds embraced by Formula I that can be used in practicing the present invention are:

Methylene dichloride
Methylene dibromide
Ethylene dichloride (1,2-dichloroethane)
Ethylene dibromide
1-bromo-2-chloroethane (ethylene chlorobromide, CH_2ClCH_2Br)
1,1-dichloroethane (ethylidene dichloride, CH_3CHCl_2)
1,1-dibromoethane
1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$)
1,1,2,2-tetrabromoethane
1,1,1,2-tetrachloroethane (CH_2ClCCl_3)
1,1,1,2-tetrabromoethane
1-bromo-2-chloropropane ($CH_3CHClCH_2Br$)
2-bromo-1-chloropropane ($CH_3CHBrCH_2Cl$)
1,1-dichloropropane (propylidene chloride, propylidene dichloride, $CH_3CH_2CHCl_2$)

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1,2-dichloropropane (propylene dichloride, $CH_2ClCHClCH_3$)
1,3-dichloropropane (trimethylene dichloride, $ClCH_2CH_2CH_2Cl$)
2,2-dichloropropane (isopropylidene dichloride, $CH_3CCl_2CH_3$)
1,1-dibromopropane
1,2-dibromopropane
1,3-dibromopropane
2,2-dibromopropane
1,2-dibromo-2-methylpropane [isobutylene dibromide, $(CH_3)_2CBrCH_2Br$]
1,2,3-tribromopropane (tribromohydrin, $CH_2BrCHBrCH_2Br$)
1,2,3-trichloropropane
1,5-dichloropentane [pentamethylene dichloride, $Cl(CH_2)_5Cl$]

It was known prior to the present invention to treat nylon (a synthetic linear polyamide) filamentary material with various treating agents to improve its useful properties, to condition it for a subsequent treatment, or for other reasons.

For example, U.S. Patent 2,251,508 discloses a process for increasing the coefficient of friction of a synthetic linear polyamide article in the form of a filament, yarn, fabric, ribbon, bristle, sheet, pellicle or the like, which comprises treating said article with an acid, e.g., sulfuric acid, or an acid halide, e.g., sulfuryl chloride, and then removing the treating agent from the article before the tenacity of the article has been reduced to a harmful degree.

U.S. Patent 2,341,423 discloses soaking an oriented filament of a synthetic linear polyamide in a solution of a phenol in a solvent that is a non-solvent for said filament and subsequently heating the filament in water. The treatment is said to improve the resistance of such filaments to sudden impact, more particularly their resistance to the fatigue of repeated impacts applied in a direction transverse to the length of the filaments.

U.S. Patent 2,876,524 discloses the treatment of "linear polyamide condensation polymers" (nylon) in yarn or other form with a substantially anhydrous hydrogen halide gas, e.g., gaseous hydrogen chloride. A permanent crimp, curl or other change of shape can be introduced, according to the teachings of this patent, into a nylon yarn by sorbing substantially anhydrous hydrogen halide gas on or in it, holding the fiber in the desired shape, and desorbing the gas with warming in vacuo.

U.S. Patent 2,993,826 discloses specific compositions for bonding together nylon in the form of slabs, fibers, yarns and netting; and further teaches that "Chlorinated hydrocarbons such as methylene chloride or ethylene chlorohydrin are satisfactory stabilizers" of a "liquor" used in the aforementioned bonding operation and which consists of a solution of a polyamide in, by weight, 80 parts methanol and 10 parts water.

The known prior art, exemplified by the foregoing U.S. patents, in no way teaches or even remotely suggests that the tensile strength of filamentary materials comprised of nylon filaments could be improved by contacting it with a treating agent of the kind and in the manner set forth broadly in the first paragraph of this specification and more specifically hereinafter.

It is a primary object of the present invention to pro-

vide a relatively simple and economical method of improving the tensile strength of filamentary material comprised of nylon filaments.

Another object of the invention is to provide articles, e.g., nylon hosiery, nylon fabric gaskets, etc., comprising treated filamentary material composed of nylon filaments and which has increased tensile strength as compared with the untreated filamentary material.

Still other objects of the invention will be apparent to those skilled in the art as the description of the invention proceeds.

The foregoing objects of the invention are attained by treating, as hereinbefore described, filamentary material comprised of nylon filaments with a lower alkylene polyhalide, specifically a lower alkylene polychloride or polybromide such as the dichloride and the dibromide, and which contains at least two hydrogen atoms. Such polyhalides are embraced by Formula I. Thus when X in Formula I represents Cl, the compounds can be represented by the general formula



and when X in Formula I represents Br, the compounds can be represented by the general formula



R and n in Formula II and III have the same meanings as previously have been given with reference to Formula I.

Any filament material comprised of nylon filaments can have its tensile strength improved by treating it in accordance with the present invention. The filamentary material can be in the form of mono- or multifilaments. It can be in the form of threads, yarns, ropes, tapes, ribbons, bands, rovings, knitted, woven or felted fabrics in dyed or undyed form, or in any other form in which filamentary material is available in finished, semi-finished or unfinished form.

By the term "nylon" as used herein and in the appended claims with reference to "nylon filaments" or "filamentary material comprised of nylon filaments" is meant those filaments now well known to those skilled in the art and in the trade under the generic name of "nylon."

Nylon filamentary materials are produced, for example, from synthetic linear polyamides such as those described in, for instance, U.S. Patents 2,071,250; 2,071,253, 2,130,948; 2,251,508; 2,341,423; 2,876,524; 2,993,826; and in patents referred to in the aforesaid patents, as well as in many others. The aforementioned polyamides, which are linear polymers containing amide groups as an integral part of the main chain of atoms in the polymer molecule, are produced in some cases from polyamide-forming reactants only. In other instances they are prepared from reaction mixtures containing, in addition, other reactants that yield linear polymers.

There are several different types of synthetic linear polyamides, and filamentary materials made from any of them are amenable to treatment in accordance with the present invention. One type is derived from suitable diamines by reaction with suitable dibasic carboxylic acids or their amide-forming derivatives. Another type is derived from polymerizable monoaminomonocarboxylic acids or their amide-forming derivatives. Interpolyamides, which are polyamides derived from a mixture of polyamide forming materials capable of yielding more than one polyamide if reacted in suitable combination, represent another type. Also amenable to treatment by the technique of the present invention are filamentary materials derived from synthetic linear polyamides containing other groups, e.g., ester groups. Examples of such polyamides are those prepared from adipic acid, hexamethylenediamine and a glycol, e.g., ethylene glycol, hexamethylene glycol, etc., or mixtures of different glycols.

More specific examples of nylon filamentary materials that can be treated to increase their tensile strength in accordance with this invention are those produced from

polyhexamethylene adipamide (i.e., the polymer derived from hexamethylenediamine and adipic acid), polytetramethylene adipamide, polydecamethylene adipamide, polytetramethylene sebacamide, polyhexamethylene sebacamide, polyamides of the amino-acid type, e.g., aminoundecanoic acid, etc., and polyamides or interpolyamides containing azelaic acid and/or decamethylenediamine as ingredients; also, polyamides derived from epsilon-caprolactam.

For additional information concerning the composition of the nylon filamentary materials which are amenable to treatment in accordance with the present invention, reference is made to the prior patents and publications known to those skilled in the art, including the patents mentioned specifically hereinbefore.

The synthetic linear polyamides briefly described above and more fully in the aforementioned and other patents can be spun into filaments which, in turn, can be cold-drawn to produce molecularly oriented filaments, i.e., filaments which exhibit orientation along the fiber axis. From these oriented synthetic filaments are then produced finished nylon filamentary materials that may take such forms as, for example, continuous mono- and multifilaments, staple fibers, yarns, fabrics, ribbons, tapes, bands, ropes, threads, etc.

In carrying the present invention into effect, any suitable means can be employed in contacting the filamentary material comprised of nylon filaments with a halogenated compound of the kind embraced by Formula I or with a plurality (e.g., one, two, three, four or any desired number) of such compounds. The halogenated compound can be in the gaseous phase or the liquid phase or in a gaseous-liquid phase. If the halogenated compound is in the liquid phase, it can be effectively brought into contact with the nylon filamentary material by spraying, brushing, immersion, or other means well-known to those skilled in the art for effecting contact between a liquid and a solid. Contacting of the halogenated compound with the nylon filamentary material can be effected by continuous, semi-continuous or batch techniques, and at atmospheric, superatmospheric or subatmospheric pressures, or any sequential combination of such pressures.

In any of the aforementioned means for effecting contact between the nylon filamentary material and a tensile strength-improving treating agent comprising essentially or consisting essentially of a compound of the kind embraced by Formula I, the contacting temperature ranges, for example, from ambient temperature up to the boiling temperature of the said treating agent but below the softening point of filaments of the said filamentary material. The time of contact is in all cases a period that is sufficient to result in an increase in the tensile strength of the said filamentary material. Depending upon such influencing factors as, for example, the particular treating agent employed, the particular nylon filamentary material being treated, the contacting means used, the temperature at which contact is effected, the form of the treating agent (i.e., gaseous and/or liquid), and other influencing factors, it may range, for example, from less than a minute (e.g., about 1/4 minute) to 6 or 7 days or more.

When the treating agent is ethylene dichloride, good results have been obtained by immersing the nylon filamentary material in the liquid ethylene dichloride at its boiling temperature of about 84° C. (i.e., while maintaining the aforesaid dichloride under reflux) for a period ranging from about 24 hours to about 55 hours and then at ambient temperature for a period ranging from about 48 hours to about 64 hours. Similar results are obtained by maintaining the dichloride in contact with the nylon filamentary material while the former is in gaseous state throughout all or a part of the period of contact.

The present invention, although not limited thereto, is particularly applicable to the treatment of nylon fila-

mentary material in fabric (e.g., woven or knitted) form. A typical example of fabrics which are amenable to treatment in accordance with the present invention thereby to obtain an article comprised of nylon filaments having improved increased tensile strength as compared with the untreated article is nylon hosiery.

The treatment of nylon hosiery in accordance with the present invention can be effected at any stage in the manufacture of the hosiery, e.g., while it is in the grieg state, after knitting and grieg processing; or at any other stage before dyeing in a standard hosiery dyeing machine; during dyeing; or after dyeing.

Depending upon the particular use of the treated nylon filamentary materials of the present invention they can be used either with or without removal of excess treating agent from the filamentary material. For example, if the treated filamentary material, e.g., in fabric form, is to be used in an industrial application, e.g., as a gasket or sealing material, in some cases (if not in all) it may not be necessary to remove excess treating agent from the treated filamentary material. In other instances, e.g., in the case of nylon hosiery or other filamentary materials in fabric or other form wherein the nylon material is or may be in contact with the skin of the wearer, it may be necessary or desirable to remove the excess treating agent from the treated nylon filamentary material. This may be done, for example, by air-drying the treated material when using treating agents of low-boiling point, or by drying under heat in the case of those higher boiling treating agents which can be volatilized from the treated fabric material by drying at atmospheric pressure at elevated temperature or under sub-atmospheric pressure at normal or elevated temperatures. If desired, the higher boiling halogenated treating agents employed in practicing this invention can be removed by washing the treated filamentary material with a lower-boiling solvent for the halogenated agent but in which the nylon filamentary material is substantially insoluble, e.g., cold ethanol, diethyl ether, etc.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

Example 1

Nylon (specifically polyhexamethylene adipamide) cloth test strips (50 threads wide) are exposed to ethylene dichloride by immersion therein at boiling temperature for various periods of time followed by immersion at room temperature for differing time periods. The weight ratio of the nylon test strips to the ethylene dichloride is about 1:100. However, this ratio is not critical and may range, for example, from 1 part by weight of the nylon cloth to 1 to 1000 parts by weight of ethylene dichloride or other compound of the kind embraced by Formula I that is employed.

At the end of the treating period the strips of cloth are removed from the ethylene dichloride treating agent and air-dried to remove excess ethylene dichloride. The test strips are then broken under tension and the results compared with control strips that had not been subjected to the ethylene dichloride treatment.

Because of a lack of low-range, tensile-test equipment of satisfactory sensitivity, improvisation was necessary.

The test strips were six to eight inches in length with a reduced center test section 50 threads in width. The test strip was suspended from a suitable clamp with a similar clamp attached to the bottom of the strip. A container was then attached to the lower clamp for loading purposes with sand, water or lead shot. The loading medium was slowly added to the suspended container until failure of the nylon test strip. The gross weight of the load was determined as the breaking strength of the test strip.

The results are summarized in the following table:

Specimen: Nylon Cloth Fabric (50 threads)	Breaking Load in Pounds		
	After Soaking in Ethylene Dichloride		
	Un-treated	For 24 hours at about 84.4° C. + about 48 hours at ambient temperature (about 20°-30° C.)	For 55 hours at about 84.4° C. + about 64 hrs. at ambient temperature (about 20°-30° C.)
Average of 5 determinations.....	9.9	13.3	13.6

This represents an increase in tensile strength by the foregoing treatment, in accordance with the present invention, of between about 34.3% and about 38.4%.

The polyamide of which the nylon used in this example is constituted is also known as Nylon 66.

Example 2

Same as in Example 1 with the exception that, instead of ethylene dichloride, there is used an equivalent amount, in individual tests, of one of the following halogenated hydrocarbons first at boiling temperature and then at room temperature:

Methylene dichloride
Ethylene dibromide
Ethylene chlorobromide
1,1-dichloroethane
1,1,2,2-tetrabromoethane
1,1,1,2-tetrachloroethane
1-bromo-2-chloropropane
2-bromo-1-chloropropane
1,1-dichloropropane
1,2-dibromopropane
1,3-dichloropropane
2,2-dichloropropane
1,2-dibromo-2-methylpropane
1,2,3-trichloropropane

Similar results are obtained.

Example 3

Examples 1 and 2 are repeated exactly with the exception that the nylon filamentary material is a nylon cloth produced from oriented filaments of a synthetic linear polyamide derived from epsilon-caprolactam (Nylon 6). Similar improvements in tensile strength are observed.

Example 4

Same as in Examples 1 and 2 with the exception that the maximum contacting temperature is about 100° C. and the nylon filamentary material, specifically nylon fabric, is in the form of a specimen cut from nylon hosiery, which is dried to remove excess treating agent after being brought into contact with the particular tensile strength-improving treating agent employed. Similar improvements in tensile strength are observed.

Example 5

Same as in Examples 1 and 2 with the exception that the nylon filamentary material is in the form of a continuous filament yarn. Similar results are obtained.

Instead of the particular nylon filamentary materials employed in the foregoing examples, one can use nylon filamentary materials which are produced from any of the other synthetic linear polyamides well known to those skilled in the art, numerous examples of which have been given hereinbefore, in the patents to which reference has been made previously herein, and in the patents and publications to which reference is made in the aforesaid patents.

Likewise, in place of the particular halogenated hydro-

carbons employed as tensile strength-improving treating agents in the foregoing examples, one can use any other halogenated compound of the kind embraced by Formula I, numerous examples of which have been given hereinbefore.

I claim:

1. A method for improving the tensile strength of nylon filamentary material which comprises contacting the filamentary material with a compound represented by the Formula $(X)_n-R$, in which X is a halogen selected from the group consisting of chlorine and bromine, n is an integer of from 2 to 4, and R is a saturated aliphatic hydrocarbon radical containing from 1 to 5 carbon atoms and at least two hydrogen atoms, said compound having a boiling point below the softening point of the filamentary material, and maintaining the filamentary material in contact with said compound at about the boiling temperature of said compound for at least about 24 hours and thereafter at about ambient temperature for at least about 48 hours.

2. A method as in claim 1 wherein X represents chlorine.

3. A method as in claim 1 wherein n represents 2.

4. A method as in claim 1 wherein X represents chlorine and n represents 2.

5. A method as in claim 1 wherein the compound represented by the Formula $(X)_n-R$ is ethylene dichloride.

6. A method as in claim 1 wherein the filamentary material is nylon fabric.

7. A method as in claim 6 wherein the nylon fabric is nylon hose.

8. A method for improving the tensile strength of nylon filamentary material which comprises contacting the filamentary material with ethylene dichloride at about 84° C. for between about 24 hours and about 55 hours and then at about ambient temperature for between about 48 hours and about 64 hours.

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