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[54] FLAME-RESISTANT POLYACYLOXALAMIDRAZONE FILAMENTS

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **D06m 13/50,** D06m 11/04

[58] **Field of Search** ..... 8/DIG. 21, 115.5; 260/78 SC, 260/DIG. 24

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

1,085,408	10/1967	Great Britain
1,139,279	1/1969	Great Britain

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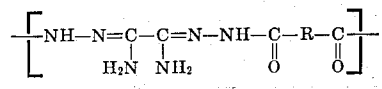
[57] **ABSTRACT**

Flame-resistant metal-containing polyacyloxalamidrazone filaments and a process for their production in which the filaments are treated with one or more solvent-soluble compounds of at least one of the metals zinc, tin, cadmium, barium, strontium, calcium, antimony and tantalum for a period of time sufficient to render the filaments resistant to flame.

16 Claims, No Drawings

FLAME-RESISTANT POLYACYLOXALAMIDRAZONE FILAMENTS

Filaments of polyacyloxalamidrazone having recurrent units of the formula:

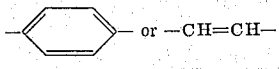


in which R represents a divalent hydrocarbon radical of two to 12 carbon atoms, e.g. a straight chain or branched chain saturated or unsaturated aliphatic radical of two to 12 carbon atoms or a cycloaliphatic, araliphatic or aromatic radical of six to 12 carbon atoms have been disclosed in Luxembourg Pat. Specification No. 55,732. These filaments are not flame-resistant although they do possess other desirable properties.

The object of the present invention is to provide a process for the production of flame-resistant polyacyloxalamidrazone filaments, especially those consisting essentially of polyterephthaloyloxalamidrazone and polyfumaroyloxalamidrazone.

It has now been found, in accordance with the invention, that a flame-resistant polyacyloxalamidrazone filament can be obtained by a process or method which comprises treating said polyacyloxalamidrazone with a solution of at least one solvent-soluble compound of one or more of the metals, zinc, tin, cadmium, barium, strontium, calcium, antimony or tantalum, for a period of time sufficient to render the filament resistant to flame, preferably so as to combine at least about 3 percent by weight of the metal with the polyacyloxalamidrazone filament.

The term "filament" is employed herein as including all types of filamentary or fibrous materials, e.g., continuous filaments, staple fibers, yarns, threads, fabrics, felts or any similar products. Especially satisfactory flame-resistant filaments are obtained by treating a polyacyloxalamidrazone in which the recurring acyl units consist predominately of terephthaloyl or fumaroyl radicals. Thus, it is especially desirable to employ those polyacyloxalamidrazone consisting essentially of recurring units of the above-noted formula in which R is one of the divalent radicals:



These particular polyacyloxalamidrazones retain good filamentary properties even with relatively large amounts of the metal additive and are most conveniently obtained from readily available initial materials.

Polyterephthaloyloxalamidrazone and polyfumaroyloxalamidrazone filaments can be produced, for example, according to the process described in Luxembourg Pat. No. 55,732, by spinning an aqueous alkaline solution of the polymer into a suitable precipitating or coagulating bath.

The preparation of the initial polymer, e.g., polyterephthaloyl- and polyfumaroyl-oxalamidrazones has been described in Luxembourg Pat. Specifications Nos. 54,747 and 57,177. These polymers are thus obtained in a conventional manner by the reaction of terephthaloyl or fumaroyl chloride with oxalic acid bisamidrazone. Polyterephthaloyl- and polyfumaroyl-oxalamidrazones having a reduced viscosity of 0.2 to 5.4 are already known, but filaments of these same polymers of higher molecular weight may also be used in the process according to the invention. It is not absolutely necessary to use filaments of pure polyterephthaloyloxalamidrazone or pure polyfumaroyloxalamidrazone, although this is preferable. One can equally well use filaments of polyacyloxalamidrazones which contain both the terephthaloyl and the fumaroyl radical as recurring acyl components. The preparation of such copolyacyloxalamidrazones has also been described in Luxembourg Pat. Specification No. 54,747. They are obtained by reacting terephthaloyl and fumaroyl chloride with oxalic acid bisamidrazone. Filamentary products such as yarns or the like which contain both polymers may also be used.

Furthermore, the process according to the invention may also be advantageously carried out using filaments of polyterephthaloyloxalamidrazone or polyfumaroyloxalamidrazone which in addition to the terephthaloyl or fumaroyl acyl units, also contain small quantities of other acyl units, preferably not more than about 5–10 molar percent with reference to the total acyl units.

Suitable metal compounds include any inorganic or organic salts and also complex compounds of the metals zinc, tin, cadmium, barium, strontium, calcium, antimony and tantalum. Such compounds should be either water-soluble or soluble in organic solvents which are substantially inert to the polyacyloxalamidrazone filaments, i.e. solvents which do not materially affect the desirable physical properties of such filaments.

Suitable solvents containing the metal in solution for the treatment of the polyacyloxalamidrazone filaments are such conventional solvents as water, including alkaline or acidic aqueous solutions, and many organic solvents, including for example: alkanols such as methanol or ethanol, dimethyl sulfoxide, hexamethyl phosphoric acid triamide, sulfolane (tetrahydrothiophene-1,1-dioxide), tetramethylurea, dimethyl formamide, pyridine and other organic amines. In some cases, chlorinated hydrocarbons, esters or ketones are also quite suitable. The metal compounds may also be used as solutions in mixtures of different solvents. The particular solvent is not a critical factor in achieving good results and a very wide range of selection is offered, the solubility of any particular metal compound in a given solvent being well-known or readily determinable. The following solutions are particularly convenient and suitable for carrying out the process according to the invention:

1. Solutions of tin compounds
   Aqueous stannous chloride solutions
   Ethanolic stannous chloride solutions
2. Solutions of zinc compounds
   Zinc chloride solutions in 2N ammonium hydroxide
3. Solutions of cadmium compounds
   Cadmium sulfate solutions in 2N ammonium hydroxide
4. Solutions of barium compounds
   Aqueous barium hydroxide solutions
   Aqueous ammoniacal barium chloride solutions
5. Solutions of strontium compounds
   Aqueous strontium hydroxide solutions
   Aqueous ammoniacal strontium chloride solutions
6. Solutions of calcium compounds
   Aqueous calcium hydroxide solutions
   Aqueous ammoniacal calcium chloride solutions
7. Solutions of antimony compounds
   Antimony trichloride solutions in dimethyl formamide
   Antimony trichloride solutions in tartaric acid
8. Solutions of tantalum compounds
   Tantalum (V) chloride solutions in dimethyl formamide.

Saturated or highly concentrated solutions of at least one of the metal compounds are preferably used, but dilute solutions may also be used. In general, solutions having a concentration of at least about 5 percent by weight of the metal compound or compounds is desirable in order to reduce the total time of treatment, but the concentration can vary over a wide range where a relatively long treatment or repeated treatments are considered to be feasible. It is advantageous to use the solution at approximately room temperature, but solutions at higher temperatures may also be used provided that the filaments are not seriously damaged or decomposed.

The treatment of the polyacyloxalamidrazone filaments with the solutions of the metal compounds may be carried out, for example, by dipping the filaments or threads into a vat or bath containing the metal in solution. Fibers or filaments may be introduced into the treatment bath, e.g. in a loose form or as yarn in the form of strands. Polyacyloxalamidrazone filaments wound on a spool may also be exposed to this treatment

with the dissolved metal compound in a conventional spool pressure washing process.

When the filaments are treated with solutions of the metal compound, the polymer such as the polyterephthaloyl- or pulyfumaroyl- oxalamidrazone which has been or is being formed as a filament reacts chemically with the metal compound and the polyacyloxalamidrazone actually binds the metal in complex form, for example as an enolate. The exact nature of this complex combination of the metal with the polymer cannot be fully established, but it can be assumed that complexing takes place through the oxygen atoms and/or other active sites on the polymer molecule.

The reaction rate and the quantity of metal taken up depend upon several factors. The rate at which metal is absorbed and bound to the polymer depends in part on the type of polyacyloxalamidrazone being used, the particular metal or metal compound, its concentration in the solution, the particular solvent or solvent mixture, the temperature and the pH of the solution. However, substantial amounts of the metal are taken up under a very wide range of conditions so that the determination and maintenance of these conditions offers no problems.

The filaments continue to take up metal from the solution in the course of the treatment until a saturation limit of the particular polyacyloxalamidrazone has been reached. The most suitable method for preparing a polyterephthaloyl- or polyfumaroyl- oxalamidrazone of a given metal content, and especially the determination of the necessary reaction time, can easily be obtained from a simple series of preliminary tests.

The flame-resistant filaments obtained by the process of the invention may also be produced by an alternative but somewhat less advantageous procedure. This procedure does not involve a treatment of the finished threads, filaments or fibers but with an alkaline solution of the polyacyloxalamidrazone. These alkaline solutions can be spun into a precipitating bath which, in addition to the acid and/or salts required for forming the thread, also contains the desired metal compound in solution. In this case, treatment of the polyacyloxalamidrazone filaments actually starts while they are in the process of being formed in the so-called spinning bath.

The metal-containing filaments produced by the process of the invention have an increasing flame-resistance with increasing amounts of the metal. Filaments of this type which have a characteristic minimum metal content for each metal can be classed as non-inflammable according to DIN 53 906 (German Industrial Standards). In the case of polyterephthaloyloxalamidrazone filaments, this minimum metal content is in the approximate range of 4 to 8 percent by weight. The minimum zinc content, for example, is approximately 5 percent by weight while the minimum tin content is approximately 3.5 percent by weight and the minimum calcium content is approximately 4 percent by weight. The minimum metal contents in polyfumaroyloxalamidrazone filaments are similar to those of polyterephthaloyloxalamidrazone. Filaments whose minimum metal content lies between about 3.5 to 8 percent by weight and whose content then extends up to the saturation limit of the polymer are not only "non-inflammable" according to DIN 53 906, but will also withstand prolonged action of the flames unharmed. The process according to the invention is therefore preferably used for producing filaments and fibers which have a metal content of about 3.5 percent to said saturation limit.

The flame-resistant or non-inflammable filaments produced by the process according to the invention have good textile properties. They can be easily worked up into yarns, mixed staple fiber yarns, woven fabrics, knitted fabrics, fleeces or the like. The strength and elongation values of filaments which have a metal content of about 15 to 50 percent by weight are generally only about 10 to 20 percent lower than the values of the corresponding metal-free polyacyloxalamidrazone filaments. Where the metal content is less than about 15 percent by weight, the filaments are only slightly inferior in strength and elongation to the corresponding metal-free polyacyloxalamidrazone filaments. The process according to the invention may be used, for example, for producing a polyterephthaloyloxalamidrazone thread with a zinc content of 15 percent by weight which then exhibits a dry strength of 17 Rkm, dry elongation of 15 percent, a wet strength of 6 Rkm, a wet elongation of 8 to 16 percent and a relative loop strength of 75 percent. (Note: Rkm = 9 × grams/denier).

The filaments, threads or fibers produced by the process of the invention are intensely colored, the color depending on the metal bound to the polymer, a property which makes additional coloring unnecessary. If desired, however, the filaments and fibers can also be colored with the usual dyes such as disperse dyes, metal complex dyes, substantive dyes, basic or acid dyes. Other conventional additives such as pigments, fillers and the like may also be used. Filaments which contain the metal zinc, tin, cadmium, barium, calcium and strontium are orange to brown in color. Those which contain antimony compounds are red while those which contain tantalum are yellow-orange.

The following examples will further serve to illustrate the invention.

EXAMPLES 1 TO 14

In Examples 1 to 14, a polyacyloxalamidrazone filament was used as produced by the following process.

A solution which after filtration and removal of air was found to have a viscosity of 9.5 seconds (falling ball test) was prepared by stirring 8 parts by weight of polyterephthaloyloxalamidrazone, 6 parts by weight of potassium hydroxide, 86 parts by weight of water and 0.45 part by weight of an ethoxylated coconut fatty amine for approximately 2 hours at room temperature. The spinning composition was spun into a 20 percent aqueous ammonium chloride solution maintained at a temperature of 30° C. the polyterephthaloyloxalamidrazone filaments obtained in this manner had the following textile properties:

Total yarn size:	190 dtex
Dry strength:	20.0 Rkm.
Dry elongation:	20.0%
Wet strength:	8.5 Rkm.
Wet elongation:	23.0%

The polyterephthaloyloxalamidrazone filaments were then dipped into a solution of the metal compound. Experimental conditions and results are represented in Table 1 below. Determination of inflammability was carried out by the standard method set forth in DIN 53 906 (German Industrial Standards).

EXAMPLES 15 AND 16

The polyfumaroyloxalamidrazone thread used in Examples 15 and 16 was obtained by spinning a solution of 8 parts by weight of polyfumaroyloxalamidrazone, 6 parts by weight of potassium hydroxide and 86 parts by weight of water into a 20 percent by weight aqueous ammonium chloride solution at 30° C. The resulting polyfumaroyloxalamidrazone filaments had the following textile properties:

Dry strength:	4.5 Rkm.
Dry elongation:	1.5 %
Absolute loop strength:	3.4 Rkm.
Swelling:	67 %

The polyfumaroyloxalamidrazone threads were then dipped into a solution of the metal compound. Experimental conditions and results are set forth in Table 2 below.

TABLE 1

Example No.	Metal compound	Solvent	Conc., percent by wt.	Time in hours	Quantity of metal taken up, percent by wt.	Properties of the thread according to DIN 53 906
1	$SnCl_2 \cdot H_2O$	Water	20	48	34.5	Non-inflammable.
2	$SnCl_2 \cdot H_2O$	2.5% aqueous NH_4Cl solution	34	00.1	12	Do.
3	$SnCl_2 \cdot H_2O$	Ethanol	5	24	16.2	Do.
4	$ZnCl_2$	$2nNH_4OH$	10	48	21.5	Do.
5	$ZnCl_2$	Same as above	20	64	36.2	Do.
6	$ZnCl_2$	do	23	0.75	5.1	Do.
7	$CdCl_2$	do	20	72	49.0	Do.
8	$3CdSO_4 \cdot 8H_2O$	do	20	48	29.4	Do.
9	$Ba(OH)_2$	Water	(1)	24	15.5	Do.
10	$BaCl_2 \cdot 2H_2O$	$2nNH_4OH$	10	29	12.5	Do.
11	CaO	Water	(1)	24	12	Do.
12	$CaCl_2$	$2nNH_4OH$	16	0.5	6.1	Do.
13	$Sr(OH)_2$	Water	(1)	29	11.8	Do.
14	$TaCl_5$	DMF	5	48	5.4	Do.

[1] Saturated.

TABLE 2

Example No.	Metal compound	Solvent	Conc., percent by wt.	Time in hours	Quantity of metal taken up percent by wt.	Properties of the thread according to DIN 53 906
15	$ZnCl_2$	$2nNH_4OH$	10	24	21.7	Non-inflammable.
16	$3CdSO_4 \cdot 8H_2O$	$2nNH_4OH$	10	24	27.5	Do.

From the foregoing examples, it will be apparent that especially good results have been achieved when treating or impregnating the filaments with basic aqueous solutions of the metals tin, zinc or calcium when considering the relatively short period of treatment and/or a relatively small amount of metal complexed with the polymer. However, good results were also achieved when using tantalum in a dimethyl formamide solvent (Example 14), even though the treatment solution contained as little as 5 percent by weight of $TaCl_5$. In this case, the filaments were rendered inflammable after taking up only 5.4 percent of the tantalum. Similar results are achieved with soluble antimony compounds as well as with other solvent-soluble compounds of the various metals set forth in the preceding tables.

In addition to the specific metal compounds illustrated only by way of example, it will be evident that it is possible to employ a very large number of compounds since it is only the metal which is taken up from the solution and attached by complex combination with the polyacyloxalamidrazone. For convenience and economy, it is therefore advantageous to select readily available solvent-soluble inorganic salts or bases of the metals even though organic compounds containing the metal in solvent-soluble form are also quite suitable. In all cases, a very flame-resistant or non-inflammable product can be obtained by a relatively simple and easily performed method.

In general, suitable solvent-soluble metal compounds include neutral-reacting and also basic or acid-reacting substances and can be listed as follows:

1. Inorganic compounds: halides and especially chlorides as well as bromides or iodides, sulfates, hydroxides, oxides nitrates, phosphates, etc.

2. Organic compounds: alcoholates, acetylacetonates, acetoacetates, carboxylates (tartrates, acetates, diaminotetraacetates), etc.

The invention is hereby claimed as follows:

1. A process for the production of a flame-resistant polyacyloxalamidrazone filament which comprises treating a polyacyloxalamidrazone filament with a solution of at least one solvent-soluble compound of a metal selected from the class consisting of zinc, tin, cadmium, barium, strontium, calcium, antimony and tantalum for a period of time sufficient to combine at least about 3 percent by weight of said metal in complex form with said polyacyloxalamidrazone filament.

2. A process as claimed in claim 1 wherein the amount of metal combined with said polyacyloxalamidrazone filament is about 3.5 percent by weight up to the saturation limit of the filament for the metal.

3. A process as claimed in claim 1 wherein the recurring acyl units of said polyacyloxalamidrazone consist predominately of at least one acyl radical selected from the class consisting of terephthaloyl and fumaroyl.

4. A process as claimed in claim 1 wherein said polyacyloxalamidrazone consists essentially of polyterephthaloyloxalamidrazone.

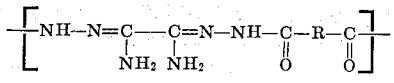
5. A process as claimed in claim 1 wherein said polyacyloxalamidrazone consists essentially of polyfumaroyloxalamidrazone.

6. A process as claimed in claim 1 wherein said treatment is carried out with the metal compound dissolved in a solvent selected from the class consisting of water, organic solvents and mixtures thereof.

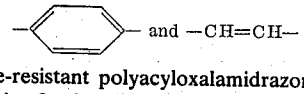
7. A process as claimed in claim 1 wherein an alkaline solution of said polyacyloxalamidrazone is spun into a precipitating bath to form said filaments, said bath containing said metal compound dissolved therein.

8. A flame-resistant polyacyloxalamidrazone filament containing in complex combination therewith at least about 3 percent by weight of at least one metal selected from the class consisting of zinc, tin, cadmium, barium, strontium, calcium, antimony and tantalum produced by the process of claim 1.

9. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 8 in which the polyacyloxalamidrazone consists essentially of recurring units of the formula



in which R represents a divalent radical selected from the class consisting of



10. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the amount of said metal contained therein is about 3 to 50 percent by weight.

11. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the amount of said metal contained therein is about 3.5 to 15 percent by weight.

12. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the metal is zinc.

13. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the metal is tin.

14. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the metal is calcium.

15. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the metal is barium.

16. A flame-resistant polyacyloxalamidrazone filament as claimed in claim 9 wherein the metal is strontium.

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