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PROCESS FOR THE MANUFACTURE OF RUBBER ELASTIC THREADS OF SULFOCHLORINATED POLYOLEFINS

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ABSTRACT OF THE DISCLOSURE

In the process for manufacturing rubber-elastic threads of sulfochlorinated polyolefins the improvement comprising shaping a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer to form threads in the presence of o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diaminohexane.

The present invention relates to a process for the manufacture of rubber-elastic threads of sulfochlorinated polyolefins.

It is known that the sulfochlorination of polyolefins yields products having good elastic properties.

It is further known to add vulcanization agents to solutions of sulfochlorinated ethylene/propylene copolymers, to spin these solutions and then to vulcanize the threads. The elastic threads obtained in this manner possess almost the same mechanical properties as those possessed by threads made of natural rubber or other types of synthetic rubber. As vulcanization agents which may be added to the spinning solution, there are known metal oxides (mono- or multivalent), mono- or polyamines and salts of an alkali metal or alkaline earth metal of weak, nonvolatile acids.

These vulcanization agents, however, have the grave drawback that they are either insoluble in the spinning solution such as, for example, the metal oxides and may, therefore, lead to incrustations of the spinneret or, as do the polyamines, they interlace the sulfochlorinated polyolefins already prior to the spinning process owing to their very good reactivity, which process the polyolefins gelatinize or precipitate and also incrust the spinneret. It is, furthermore, difficult to obtain from such solutions threads having a fine titer as required in the process of covering the threads for the manufacture of rubber-elastic woven, knitted, Raschel or plaited articles, for example fabrics for corsets and bodices as well as bathing suits and the like.

Now we have found that substantially improved, rubber-elastic threads can be obtained by spinning the sulfochlorinated polyolefins from their diamine-free solutions, in the presence of diamines to produce interlacing.

The spinning process can be carried out in apparatuses that are generally used, for example in a suitable dry spinning apparatus, or it can be carried out especially advantageously in an apparatus working according to the wet spinning process. In this case the diamine is added to the coagulation bath.

The sulfochlorinated polyolefins used may be sulfochlorinated homopolyolefins, such as sulfochlorinated

polyethylene as described, for example, in French Patent 1,167,042, or sulfochlorinated polypropylene as described, for example, in German Patent 1,015,603, but preferably sulfochlorinated olefin copolymers as described, for example, in Austrian Patent 203,709.

For the preparation of the spinning solution all solvents may be used which are inert towards diamines and which are not too difficultly volatile. In the preferred wet spinning process the solvents must, moreover, be miscible with the liquid in the coagulation bath.

Examples of suitable solvents are aromatic hydrocarbons, such as benzene or toluene, aliphatic hydrocarbons such as, for example, gasoline having a boiling point of 90° to 110° C., or halogenated hydrocarbons, such as chloro-benzene, chloroform, carbon tetrachloride being especially advantageous since the polyolefin for sulfochlorination is dissolved therein. However, mixtures of solvents may also be used. For the preparation of the solutions the comminuted polymer is advantageously stirred in a closed vessel with the calculated amount of solvent at a room temperature until it is completely dissolved. However, it is also possible to employ the polymer solution directly after the sulfochlorination (and after having blown out the gases which are still dissolved therein). Depending on the molecular weight at the polymer used, solutions of 5 to 25 percent strength are spun. The viscous solutions obtained are water-clear and colorless. The viscosity of the spinning solution is determined by the falling ball test usually employed in the viscose industry. With the use of steel balls (DIN specification 5401, diameter 2.5 mm.; type ±5, S.K.F.), the period of fall of the ball, at 20° C. and for a height of fall of 20 cm., shall be within the range of from 10 to 400 seconds, preferably within the range of from 20 to 100 seconds. In order to control the degree of polymerization, the relative or reduced viscosity of a solution of 1 percent strength of the polymer in carbon tetrachloride is determined at 20° C. The spinning solution may be spun not only through spinnerets of noble metal but also through glass spinnerets.

Depending on the required titer of the thread, the number of openings may vary from 5 to 150 openings, and the diameter of the opening may vary from 30 to 600μ.

The diamines having an interlacing action may be primary or secondary aromatic, araliphatic or aliphatic diamines, the latter being used with special advantage. The carbon chain of the diamines may also be interrupted by bridging members, for example by ether-oxygen or carbonyl groups. There are mentioned for example, the phenylene diamines, 4,4'-diaminobenzophenone, xylylene diamine, the diamino decanes, the 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine. Diamines having a chain of 2 to 6 carbon atoms, such as ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane are used with special advantage.

For the coagulation bath of the preferred wet spinning process there may be used as liquid for the coagulation bath short chain alcohols, such as methanol, ethanol, propanol, isopropanol, or low-molecular weight ketones, such as acetone or mixtures thereof. The diamines having an interlacing action are added to this coagulation bath.

To the diamine-containing coagulation bath there may be added substances binding hydrochloric acid, for example tertiary amines as trimethyl amine, triethyl amine or sodium bicarbonate to bind the hydrochloric acid forming between the polyolefin sulfochloride and the diamine in the modified Schotten-Baumann reaction.

The rubber-elastic threads obtained by the process claimed have a high tensile strength (0.5 to 0.7 gram/denier). In addition to coarse threads there may also be spun threads having a titer below 1 denier.

The threads have an excellent resistance against the action of light, heat and ozone. Thus the threads do not exhibit any impairment of their properties after having been subjected to a treatment in hot air at 100° C. for a period of more than 24 hours. A measurable deterioration of the property of the thread does not occur even if the threads are heated for short periods to 190° C. The threads withstand storage well; they do not yellow nor do they age; moreover, they are entirely odorless.

Owing to these properties, which are not possessed by natural rubber and different types of synthetic rubber, the novel rubber-elastic threads constitute an important advance in the art.

The novel threads may be processed advantageously not only in the bare state, but also in the covered state. Their use is not limited to the field of fine textiles such as, for example, fabrics for bodices, but they may be employed advantageously for industrial uses.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight:

EXAMPLE 1

A solution of 5.8 parts of a sulfochlorinated ethylene/propylene copolymer with 35 mole percent of propylene (reduced viscosity 3.1, measured in a solution of 1% strength in xylene, at 25° C.) containing 2.2% by weight of sulfur and 21.7% by weight of chlorine, in 94.2 parts of carbon tetrachloride was spun through a spinneret of gold and platinum having 30 openings of a diameter of 80μ each into a mixture of 95 parts of methanol and 5 parts of ethylene diamine. The coagulation bath flowed at a rate of 10 liters/hour in countercurrent to the thread. According to the falling ball test (steel balls having a diameter of 2.5 mm.), the viscosity of the spinning solution at 20° C. corresponded to a time of fall of the ball of 40 seconds. The portion of the coagulation bath through which the thread had to pass had a length of 100 cm. The spinning solution was expressed from an autoclave under a pressure of 1.9 atmospheres of nitrogen over a spinning arc into the coagulation bath which had a temperature of 16° C. and was then drawn off via three-roller-systems at a rate of 2.28 meters per minute. The time of stay of the thread in the coagulation bath was 26.3 seconds. The coagulated thread bundle was then washed in a bath having a length of 110 cm. and containing water of a temperature of 45° C., and wound up while it was drawn in a ratio of 1:1.5. At an elongation of 300%, the dried thread had a tensile strength of 0.54 gram/denier, an initial modulus of 0.078 gram/denier and a yield stress (in tension) of 0.019 gram/denier.

On analysis of the thread material there were found: 2.1% by weight S, 0.90% by weight N, 20.1% by weight Cl, which corresponds to the quantitative conversion of all existing sulfochloride groups with ethylene diamine.

EXAMPLE 2

A thread spun under the same conditions as those described in Example 1 was fixed in a drying cabinet with circulating air at 190° C. for 30 seconds while being drawn by 100%. At an elongation of 300%, the thread treated in this manner had a tensile strength of 0.72 gram/denier.

EXAMPLE 3

A solution of 8.0 parts of a sulfochlorinated ethylene/propylene copolymer with 35 mole percent of propylene (reduced viscosity 3.10, measured in a solution of 1% strength in xylene, at 25° C.) with 2.2% by weight of sulfur and 21.7% by weight of chlorine in 92 parts of chloroform was spun through a spinneret of gold and platinum (number of openings: 20, diameter of the opening: 200μ) into a mixture comprising 94 parts of methanol, 5 parts of ethylene diamine and 1 part of triethyl amine. The coagulation bath flowed at a rate of 20 liters/hour in countercurrent to the thread. The viscosity of the spinning solution amounted to 129 falling ball seconds at 20° C. The portion of the coagulation bath through which the thread had to pass had a length of 95 cm. The spinning solution was expressed into the coagulation bath under a pressure of 2.8 atmospheres of nitrogen. The thread was drawn off at a rate of 3.53 meters/minute. The coagulated and washed thread bundle was wound up at a rate of 4.73 meters/minute, and dried. The spinning thread was then either placed for 10 minutes in an acetic anhydride bath having a temperature of 30° to 50° C., washed on being withdrawn from the bath and dried, or it was allowed, after having been spun and dried in a desiccator, to stand over acetic anhydride at 20° C. for 24 hours. At an elongation of 211%, the thread prepared in this manner had a tensile strength of 0.4 gram/denier, an initial modulus of 0.05 gram/denier and a yield stress (in tension) of 0.02 gram/denier.

A thread having equally good elastic properties was obtained on using, instead of the polymer employed above, a sulfochlorinated ethylene/propylene copolymer having a content of C_3 hydrocarbons of 30 mole percent, an η_{red} value of 3.9 (measured as described above), a sulfur content of 1.1% and a chlorine content of 17.3%.

When carrying out the process according to the invention, it is quite generally advantageous to subject the spun thread to a subsequent heat treatment at temperaures wihin the range of from 70° to 200° C. This heat treatment may be carried out directly after the spinning process, or it may be carried out during or after the following washing process and during the drawing process. Owing to this heat treatment, the interlacing reaction is terminated and the surplus diamine removed, however, above all the strength of the thread is improved thereby.

It is advantageous, moreover, to treat the thread, after it has left the coagulation bath and after it has been washed, with a compound having an acylating action, such as acetic anhydride, to acylate free amino groups. This after-treatment prevents yellowing of the threads.

We claim:

1. In a wet spinning process for the manufacture of rubber-like elastic threads of sulfochlorinated polyolefins, the improvement comprising spinning a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer into a spinning bath consisting of methanol, ethanol, propanol, isopropanol or acetone which contains o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane.

2. In a wet spinning process for the manufacture of rubber-like elastic threads of sulfochlorinated polyolefins, the improvement comprising spinning a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer into a spinning bath consisting of methanol, ethanol, propanol, isopropanol or acetone which contains o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane, and an acid binding substance selected from the group consisting of tertiary amines and sodium bicarbonate.

3. In the process for manufacturing rubber-elastic threads of sulfochlorinated polyolefins the improvement comprising spinning a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer to form threads and contacting said threads with a member selected from the group consisting of o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane.

4. In the process for manufacturing rubber-elastic threads of sulfochlorinated polyolefins the improvement comprising spinning a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer to form threads, contacting the threads with a member selected from the group consisting of o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane, and subjecting the undrawn threads to a subsequent heat treatment at 70° to 200° C.

5. In the process for manufacturing rubber-elastic threads of sulfochlorinated polyolefins the improvement comprising spinning a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer to form threads, contacting the threads with a member selected from the group consisting of o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N,N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane, drawing the threads and subjecting the drawn threads to a subsequent heat treatment at 70° to 200° C.

6. In the process for manufacturing rubber-elastic threads of sulfochlorinated polyolefins the improvement comprising spinning a diamine-free solution of sulfochlorinated polyethylene, sulfochlorinated polypropylene or a sulfochlorinated olefin copolymer to form threads, contacting the threads with a member selected from the group consisting of o-, m-, and p-phenylene diamine, 4,4'-diaminobenzophenone, xylylene diamine, diamino decane, 2,2'-diamino-diethyl ether, N.N'-dimethyl-ethylene diamine, ethylene diamine, 1,3-propylene-diamine or 1,6-diamino-hexane, and subjecting the threads to a treatment with acylating agents.

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