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[54] **SARAN RIBBON FOR DRY-CLEANABLE TEXTILES**
10 Claims, No Drawings

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ABSTRACT: Flat extruded saran filaments are provided for use in textile fabrics which may be dry cleaned in perchloroethylene without providing excessive shrinkage of the saran. The saran composition from which the flat filaments are formed must contain no more than 5 percent by weight of extractable organic additives based on the total quantity of the saran copolymer and the additives. The organic additives constitute a stabilizing plasticizer which is an ester of fumaric acid, maleic acid, itaconic acid or aconitic acid, and a light stabilizer; in addition, no more than about 0.5 percent of a nonextractable, primarily inorganic phosphate stabilizer is also used. The composition contains an additional quantity of about 5 percent of branched polyethylene.

SARAN RIBBON FOR DRY-CLEANABLE TEXTILES

The invention relates to saran ribbon for dry-cleanable textiles and, more particularly, to extruded saran monofilament of small thickness which is suitable for use in a fire-retardant textile fabric which may be dry cleaned in perchloroethylene without causing excessive shrinkage of the saran.

Saran is an old and well-known plastic which has a number of outstanding properties one of which is its noncombustability. Because of these properties its use has been suggested for many years in various areas and, among these, is its utilization as a textile fiber for use in various fabrics. Unfortunately, in addition to its outstanding properties, saran has a number of serious disadvantages; for example, it is extremely corrosive in the molten state and is difficult to handle and extrude. Until the present invention, it was impossible to successfully extrude saran filaments without at least about 7½ percent organic additives including plasticizers and stabilizers.

In recent years it has been suggested that saran filaments, particularly flat filaments, be used in the manufacture of various commercial fabrics, including draperies, because of the fireproof properties of the saran. Unfortunately, commercial draperies and other commercial fabrics must be capable of being dry cleaned and the common dry cleaning solvent in use today is perchloroethylene. It has been found that when saran fabrics are dry cleaned in perchloroethylene, the perchloroethylene extracts the organic additives, previously present in amount of 7½ percent to 10 percent, causing excessive shrinking of the saran. For this reason, it has not been commercially desirable to manufacture fabrics utilizing extruded saran filaments because of such excessive shrinkage after dry cleaning. The problem is particularly acute in the case of saran ribbon filaments, since these filaments have a very small dimension in one direction, i.e., they may be as little as 2 mils thick or even thinner, such small dimension permitting ready penetration of the perchloroethylene during dry cleaning, resulting in the extraction of almost all of the organic additives and the consequent excessive shrinkage of such filaments.

Many attempts have been made to solve the above problems such as through the selection of different plasticizers, different stabilizers, and various combinations of these materials. Nevertheless, in spite of all such attempts, it has heretofore been impossible to extrude such saran filaments without a minimum of 7½ percent of organic additive. Accordingly, before the present invention, the only successful approach to providing textile filaments intended for use in fabrics subjected to dry cleaning in perchloroethylene, was to form such filaments by methods other than extrusion, e.g. coagulation of a latex in film form followed by cutting the saran film into ribbon.

It is, accordingly, an object of the present invention to overcome the defects of the prior art, such as indicated above.

It is another object of the present invention to provide an extruded saran monofilament of small thickness which not only has the inherent fire retardant characteristics of saran, but which is also capable of being dry cleaned in perchloroethylene without causing excessive shrinkage.

It is another object of the present invention to provide a composition of saran which contains, at most, about 5 percent by weight of low molecular weight organic additives, which composition can be successfully extruded to form a commercial product.

It is another object of the present invention to provide a novel combination of ingredients including predominantly saran, which ingredients may be melt extruded to form a saran monofilament which is subsequently capable of being dry cleaned in perchloroethylene without causing excessive shrinkage thereof.

It is another object of the present invention to provide a flat saran monofilament which is satisfactorily stabilized, and yet is capable of being woven into fabrics without causing a build-up of stabilizer on the weaving equipment.

These and other objects and the nature and advantages of the instant invention will be more apparent from the following

description of an embodiment of the present invention, such description so fully revealing the general nature of the invention that others can, by applying current knowledge, readily modify such embodiment and/or adapt it for various application without departing from the generic concept, such adaptations and modifications accordingly being intended to be part of the generic invention.

The composition used to form the extruded saran monofilament of small thickness of the disclosed embodiment, suitable for use in a fire retardant textile fabric, which fabric is capable of being dry cleaned in perchloroethylene, consists essentially of 100 parts by weight of a uniform saran copolymer of about 85 percent by weight vinylidene chloride and about 15 percent by weight vinyl chloride; about 0.0013 to 0.0075 moles of an organic stabilizing plasticizer which is an ester of fumaric acid, maleic acid, itaconic acid or aconitic acid; about 0.76 to 2.65 parts by weight of an organic light stabilizer, the total quantity of organic light stabilizer and organic stabilizing plasticizer being no greater than 5 percent by weight of the above-mentioned ingredients; about 0.16 to 0.51 parts by weight of a primarily inorganic phosphate, which may, however, have certain organic groups, which phosphate is not perchloroethylene extractable; about 3 to 9 parts by weight of branched polyethylene. The ribbon filaments produced preferably have a thickness of about 2 to 2.5 mils and a width of about 25 to 30 mils.

Saran itself is a well-known copolymeric plastic usually formed of approximately 85 percent vinylidene chloride and 15 percent vinyl chloride, although the proportion of vinyl chloride in the copolymer may lie anywhere in the range of from about 5 percent to about 15 percent, the remainder being vinylidene chloride. Many polymers of vinylidene chloride are described in the early U.S. Pat. Nos. 2,160,903; 2,160,904 and 2,160,931 through 2,160,948, The saran resins are generally crystalline, i.e., they have a relatively sharp melting point and may be extruded, quenched and oriented to form generally crystalline filaments. As pointed out in the Matlack et al. U.S. Pat. No. 2,605,244, the crystalline habit of saran makes compounding difficult since the polymer macromolecules prefer contact with each other and tend to reject foreign substances such as plasticizers and stabilizers.

The preferred saran copolymer for use in the present invention has a regular or uniform structure in the sense that the vinyl chloride groups are regularly spaced in the copolymer backbone without forming substantial blocks. This copolymer is preferably formed from a mixture of 85 percent by weight of vinylidene chloride and 15 percent by weight vinyl chloride. It has a melting point of slightly greater than 300° F.

In order to permit the extrusion of the saran, it is necessary to use at least a small quantity of plasticizer. The material so used in the present invention is a stabilizing plasticizer which is an ester of fumaric acid, maleic acid, itaconic acid, or aconitic acid. These known esters serve an important stabilizing function since, during extrusion of the molten saran, the polymer backbone undergoes dehydrohalogenation which results in color producing polyene segments. Since the dark color produced by such degradation is undesirable, the stabilizing plasticizers are provided to interrupt such color producing polymer segments.

This stabilization is accomplished by means of a Diels-Alder reaction between the maleate and the polyene segments produced by such degradation or dehydrohalogenation. Where fumarates are used, they isomerize to the cis-form and function in the same manner as the maleate. The aconitates and itaconates also react according to the Diels-Alder reaction with the polyene segments produced during extrusion.

Where the preferred stabilizing plasticizer, dioctyl fumarate, is used, it is preferably present in an amount of 1½ to 3½ percent by weight, based upon the weight of the composition exclusive of the polyethylene, and is most preferably present in an amount of 2.5 percent. However, because the alkyl group can vary considerably in the ester (it need not be dioctyl), it is desirable to express the proportion in moles per

The whole was passed into an oven at 150° C., and kept there for 1–2 minutes. Thereafter, onto the previous layer a second layer (foamed) was spread, which consisted of:

PVC, paste making resin, having a K-value of 72	100 parts (by weight)
dioctyl phthalate	80 parts (by weight)
azodicarbonamide	2 parts (by weight)
dibasic lead phthalate (stabilizing kicker)	2 parts (by weight)
TiO_2	5 parts (by weight)
polypropylene flakes	5 parts (by weight)

The initial thickness of this layer was 200 microns.

The whole was then passed into an oven at 200° C. and kept there for 1–2 minutes. The release paper was then removed. The system was then subjected to a slight tension in order to facilitate the separation of those components that were incompatible with each other; then the system was coupled to a cotton jersey fabric (with the second layer adjacent to the fabric), after preliminarily having spread on the fabric some plastisol of the first layer which served as a binder. Said coupling occurred in about 1 minute in an oven heated to 150–170° C.

The poromeric material thus obtained showed the following air transpiration rates:

Pressure (mm. Hg)	cm.³ of air Hr. cm.²

The release paper was then removed and the system was subjected to a slight tension and subsequently was coupled to a jersey fabric made of polyamide fibers, the second layer being adjacent to the fabric after preliminary having spread on the fabric some plastisol of the first layer which serves as a binder.

The poromeric material thus obtained shows the following air transpiration rates:

Pressure (mm.Hg)	cm.³ of air hr. cm.²
20	2.0
40	80
60	121
100	205
150	270

Example 3

On a device for the preparation of artificial leather substrate of release paper was spread coated with a plastisol consisting of (layer 1, compact):

PVC, paste making resin with a K-value = 70	100 parts (by weight)

truder and the filaments are pulled down through an airgap where partial orientation and modification to the cross sectional dimensions desired occur. The ribbons are then passed to an orientation zone where they are stretched approximately 4:1. Subsequent to orientation, an annealing is carried out at about 205° F. Where a slight degree of shrinkage is permitted.

The following specific example will further clarify the nature of the present invention without limitation:

A composition is provided by mixing 95.75 percent by weight of uniform saran of 85 percent vinylidene chloride and 15 percent vinyl chloride having a melting point of slightly greater than 300° F. with 2.5 percent by weight dioctyl fumarate containing 0.25 percent by weight Victor 85X; and 1.5 percent by weight 2-hydroxy-4-n-octyloxybenzoylphenone. To this composition is added an additional 5 percent by weight of low density branched polyethylene (du Pont TE–4275) having a melt index of 3.7, a density of 0.923 and a melting point of 230°–250° F. The polyethylene being in fine particulate form [100 percent through a 50 mesh sieve (297 microns) and a maximum of 30 percent through a 100 mesh sieve (149 microns)]. The composition is passed through a screw extruder which reduces the mixture to a melt, and the mixture is melt extruded through a die having a plurality of rectangular openings with a 0.00225″×0.028″ cross section. The molten material is pulled through an airgap of about 1 inch where partial orientation and some modification of the shape of the filament occurs. The ribbon is then passed through a water quench bath at 105° F., passed through an orientation stand including a plurality of rollers where the ratio of input to output speed is approximately 3.9:1. Subsequently, the oriented filament is passed through an annealing water bath at 205° F. at 844 feet per minute. The ribbon emerges from the annealing bath at 820′ per minute and is carried onto chilled snubbing rolls.

The filaments so produced have a denier of 550, a cross section of about 2.5×28 mils a weight of 1.5 grams per denier, an elongation of 22 percent, and a shrinkage of 6 percent at 212° F. for 10 minutes.

The saran ribbon monofilament is woven together with other fibers to fabricate commercial fire-retardant draperies. These draperies, tested by an independent testing laboratory, undergo a shrinkage of only 0.5 percent after dry cleaning in perchloroethylene.

It is to be understood that the invention is not limited to the embodiment disclosed which is illustratively offered and that modifications may be made without departing from the invention.

What is claimed is:

1. Extruded saran monofilament of small thickness, suitable for dry-cleanable and fire-retardant textile fabric, consisting essentially of:

a. 100 parts by weight of a copolymer of about 85 percent by weight vinylidene chloride and about 15 percent by weight vinyl chloride in which the vinyl chloride groups appear regularly spaced in the copolymer backbone without forming substantial blocks;

b. about 0.0013 to 0.0075 moles of an organic stabilizing plasticizer of an ester of fumaric acid, maleic acid, itaconic acid or aconitic acid at least a portion of said stabilizing plasticizer being joined to said copolymer by means of a Diels-Alder reaction between said plasticizer and diene portions of said copolymer backbone produced by dehydrohalogenation occurring in said copolymer during extrusion thereof;

c. about 0.76 to 2.65 parts by weight of an organic light stabilizer which absorbs or screens ultraviolet light;

the total quantity of said organic light stabilizer and said organic stabilizing plasticizer being no greater than 5 percent by weight based on the total quantity of said copolymer, said stabilizer and said plasticizer;

d. about 0.16 to 0.51 parts by weight of a perchloroethylene nonextractable, primarily inorganic phosphate stabilizer; and

e. about 3 to 9 parts by weight of branched polyethylene.

2. An extruded saran monofilament in accordance with claim 1 of rectangular cross section having a thickness of about 2 to 2.5 mils and a width of about 25–30 mils.

3. An extruded saran monofilament in accordance with claim 2 wherein said polyethylene is present in an amount of about 5 percent by weight, said polyethylene having a melt index of about 3.7, a density of about 0.923 and a melting point in the range of 230°–250° F.

4. An extruded saran monofilament in accordance with claim 2 wherein said organic stabilizing plasticizer is present in an amount of 0.0045 to 0.0075 moles.

5. An extruded saran monofilament in accordance with claim 2, wherein said organic stabilizing plasticizer is dioctyl fumarate and is present in an amount of about 2.5 percent by weight based on the composition exclusive of the polyethylene.

6. An extruded saran monofilament in accordance with claim 2, wherein said organic light stabilizer is 2,4-dibenzoyl-resorcinol or a 2-hydroxy-4-n-alkyloxybenzophenone, wherein the alkyl consists of up to 18 carbon atoms.

7. An extruded saran monofilament in accordance with claim 2, wherein said organic light stabilizer is 2-hydroxy-4-n-octyloxybenzophenone and is present in an amount of about 1.5 percent by weight based on the composition exclusive of the polyethylene.

8. An extruded saran monofilament in accordance with claim 2, wherein said perchloroethylene nonextractable, primarily inorganic stabilizer is disodium phosphate, sodium pentacapryl tripolyphosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, sodium barium pyrophosphate, barium stearyl phosphate, barium lauryl phosphate, sodium metaphosphate or mixtures thereof.

9. An extruded saran monofilament in accordance with claim 2 wherein said perchloroethylene nonextractable, primarily inorganic stabilizer consists of a blend of about 88 percent by weight disodium phosphate and about 12 percent by weight of sodium pentacapryl tripolyphosphate, said blend being present in an amount of about 0.25 percent by weight based on the composition exclusive of the polyethylene.

10 An extruded saran monofilament in accordance with claim 2 comprising 95.75 percent by weight of said copolymer; 2.5 percent by weight of said organic stabilizing plasticizer which consists of dioctyl fumarate; 1.5 percent by weight of said organic light stabilizer which consists of 2-hydroxy-4-n-octyloxybenzophenone; 0.25 percent by weight of said perchloroethylene nonextractable, primarily inorganic stabilizer which consists of a blend of 88 percent by weight of disodium phosphate and 12 percent by weight of sodium pentacapryl tripolyphosphate; and an additional 5 percent by weight of said branched polyethylene.