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3,846,226

HIGH LUSTER, ANTISOILING ACRYLIC FIBERS

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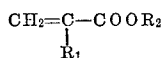
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5 Claims

ABSTRACT OF THE DISCLOSURE

A low density lustrous acrylic fiber of reduced soiling tendencies based on a fiber-forming first acrylonitrile polymer and incorporated therein as small discontinuous segments separated from said first polymer by void space from 1-10% of a second incompatible acrylonitrile copolymer containing 50-95 weight percent acrylonitrile and 5-50 weight percent of a monomer of the formula



wherein R_1 is hydrogen or methyl, R_2 is hydrogen, hydroalkyl, or $\text{fCH}_2\text{CH}_2\text{O}_n\text{R}_3$, wherein n is an integer of 1-50 and R_3 is hydrogen, alkyl, or aryl.

This invention relates to acrylic fibers having a combination of high luster, low light transmission, and reduced apparent soiling tendencies. More particularly, this invention relates to acrylic fibers wherein within the fiber structure defined by a fiber-forming first acrylonitrile polymer is distributed a small amount of a second acrylonitrile copolymer, incompatible with the first polymer, in the form of elongated discontinuous segments separated from the first polymer by void spaces and concentrated in the fiber core.

The tendency for fibrous materials to soil is well recognized and much attention has been directed to this problem. This problem is particularly acute when the fibers are employed in uses where frequent laundering or cleaning to remove stubborn soil is not practical, such as is the case with carpet fabrics. In such use, an initially attractive fabric may be quickly rendered unsightly, with the result that the routine cleanings do not remove soil effectively and due to the inconvenience and, therefore, infrequency of laundering, the carpet is in an unsightly condition throughout most of its service life.

Many attempts have been made to improve the resistance of acrylic fibers to soiling because of their attractiveness in carpet use. One such attempt was to incorporate an opacifying agent, such as titanium dioxide, into the fiber to reduce the light transmission of the fiber. In this way, the amount of soiling visible would appear to be reduced and, conversely, the fiber would appear to be less soiled. Such a technique actually effects only the amount of soiling visible but does not reduce the actual amount of soiling which occurs. The visible extent of soiling is referred to as "apparent soiling" while the true extent of soiling is referred to as "actual soiling" or "real soiling." Unfortunately, however, the incorporation of opacifying agents into the fiber causes a highly undesirable loss of fiber brightness and luster. The effect of such loss leads to fibers that are unattractive even before any soiling occurs.

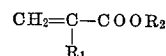
An alternative method proposed for improving soiling tendencies of fiber is the application of certain finishes upon the fiber surface. Such finishes as special forms of silica, metal salts, fluorocarbons, and hydrophilic finishes have been employed. Although such finishes tend to reduce the rate of true soiling upon extended use the extent of soiling is such as to require laundering or special cleansing treatments. Subsequent exposure of the cleansed fiber to soiling hastens the rate of soiling so that the frequency of special cleansing treatments after the initial

special cleansing treatment increases to the point where no advantage, or even disadvantage, is offered with respect to the use of no finish. The result may be due to a lack of adequate durability of the applied finish or may result from retention of the cleansing agents, which generally are soil scavengers, by the applied finish. Whatever the reason the problem of soiling is not adequately solved by use of anti-soiling finishes.

An improved process for applying what is described to be one of the most effective antisoiling finishes is disclosed in United States Patent 3,541,075, issued Nov. 17, 1970 to Baur et al. The finish is a combination of zirconium acetate and sulfamic acid which is applied to a freshly coagulated and washed filament prior to completion of the initial drying associated with fiber making. The actual improvement in soiling offered is very limited compared to other conventional finishes and no evidence is presented as to finish performance after special cleansing to remove accumulated soil.

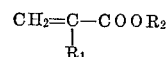
Accordingly, the various known methods of reducing soiling of acrylic fiber are unsatisfactory since each suffers from one or more deficiencies such as reducing luster, providing insufficient durability of antisoiling tendencies, or offering insufficient soiling reduction. Thus, there continues to exist the need for acrylic fibers or reduced antisoiling tendencies, whether apparent or actual, as well as processes for such fibers.

In accordance with the present invention, there is provided a low-density, lustrous acrylic fiber of reduced soiling tendencies comprising a fiber-forming first acrylonitrile polymer containing at least 70 weight percent acrylonitrile and the balance of one or more vinyl monomers and, as small discontinuous elongated segments within said first polymer separated therefrom by void space, from about 1 to 10 weight percent, based on the total weight of the fiber, of a second acrylonitrile copolymer incompatible with said first polymer and containing from 50 to 95 weight percent acrylonitrile and from 5 to 50 weight percent of a monomer of the formula



wherein R_1 is hydrogen or methyl and R_2 is selected from hydrogen, hydroxyalkyl of 2 to 4 carbon atoms and $\text{fCH}_2\text{CH}_2\text{O}_n\text{R}_3$, wherein n is an integer of about 1 to 50 and R_3 is selected from hydrogen, alkyl of 1 to 4 carbon atoms, and aryl of monocyclic structure having less than about 10 carbon atoms.

In accordance with the method aspect of the present invention, there is provided a process for preparing the above fiber which comprises the steps of: (a) preparing in an aqueous inorganic salt solvent a first solution of a fiber-forming first acrylonitrile polymer containing at least 70 weight percent acrylonitrile and the balance one or more vinyl monomers, said solution containing from about 8 to 20 weight percent of polymer; (b) preparing in an aqueous inorganic solvent of the same salt used in the first solution a second solution of a second acrylonitrile polymer containing from 50 to 95 weight percent acrylonitrile and 5 to 50 weight percent of a monomer of the formula

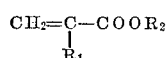


wherein R_1 and R_2 have the same significance given above, said second polymer being incompatible with said first polymer, said second solution containing from about 8 to 20 weight percent of polymer; (c) intimately mixing said first and said second solutions to form a spinning composition such that said second polymer constitutes from about 1 to 10 weight percent of the total polymer content of said mixture; (d) extruding said spinning com-

position into an aqueous coagulant to form wet-gel filaments; (e) washing the wet-gel filaments free of salt; (f) stretching the washed wet-gel filaments; (g) relaxing the stretched wet-gel filaments in an aqueous medium at a temperature greater than 90° C.; and thereafter drying the relaxed fibers at a temperature greater than 80° C.

As the fiber-forming first acrylonitrile polymer is employed one which contains at least 70 weight percent acrylonitrile, as previously indicated. Preferably, such polymer will contain at least 80 weight percent acrylonitrile or more. As vinyl monomers which may be employed with acrylonitrile are included such monomers as acrylic, alpha-chloroacrylic, and methacrylic acids, esters of the aforementioned acids, such as the methyl, ethyl, butyl, and beta-chloroethyl esters; vinyl chloride, vinyl bromide, vinylidene chloride, 1-bromo-1-chloroethylene; methacrylonitrile; acrylamide, methacrylamide, alpha-chloroacrylamide, and monoalkyl substituted derivatives thereof; methyl vinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate, and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and esters thereof; N-vinylcarbazole; vinyl furan; alkyl vinyl ethers; vinyl sulfonic acids, such as vinyl sulfonic acid, styrene sulfonic acid, methallyl sulfonic acid, p-methallyloxybenzene sulfonic acid, and salts thereof; ethylene-alpha-beta-dicarboxylic acids, their anhydrides, and esters such as diethyl citraconate and diethyl mesaconate; styrene and vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, and the like; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, vinylpyrrolidone, vinyl piperidone; and other mono-ethylenically unsaturated vinyl monomers copolymerizable with acrylonitrile. One or more of such monomers may be used with acrylonitrile to constitute the fiber-forming first acrylonitrile polymer.

The second acrylonitrile copolymer, as has been indicated, must be incompatible must be incompatible with the fiber-forming first polymer and must contain from 50 to 95 weight percent acrylonitrile and 5 to 50 weight percent of acrylic or methacrylic acid or special derivatives thereof. The required comonomer with acrylonitrile in the second polymer is one having the formula



wherein R₁ is hydrogen or methyl and R₂ is hydrogen, hydroxy alkyl of 1 to 4 carbon atoms, a polyether of the formula $\{\text{CH}_2\text{CH}_2\text{O}\}_n\text{R}_3$ wherein n is an integer of 1 to 50 and R₃ is hydrogen, alkyl of 1-4 carbon atoms, or aryl of monocyclic structure having less than about 10 carbon atoms. Examples of suitable comonomers include acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 4-hydroxybutylacrylate, 4-hydroxybutyl methacrylate, 2-(ω-methoxy-3,6,9,12,15,18,21,24,27-nonaoxa-nonacosyloxy)ethyl acrylate and 2-(ω-methoxy-3,6,9,12,15,18,21,24,27-nonaoxanonacosyl-oxy)ethyl methacrylate. The latter two monomers are polyether esters of acrylic and methacrylic acids wherein the value of n of the polyether structure is 11. Other ethers and hydroxy-containing substituents consistent with the structures given may also be employed.

It is to be understood that the various monomers used in forming the first and second polymers are copolymerizable according to conventional procedures, which are employed. It is essential that polymerization of the first acrylonitrile polymer be effected so as to obtain a fiber-forming polymer in accordance with conventional procedures. It is generally preferred that the second acrylonitrile copolymer also be capable of fiber forming, but such requirement is not essential since the second polymer merely serves as an additive within the fiber formed by the

first polymer. By the term "vinyl monomer" is meant a monomer copolymerizable with acrylonitrile and containing a single $-\text{CR}=\text{CH}_2$ radical wherein R may be hydrogen or a substituent group such as methyl for example.

In carrying out the process of the present invention, it is first necessary to prepare separate solutions of the two acrylonitrile polymers. As solvents for the polymers are used concentrated aqueous inorganic salt solutions conventionally employed to dissolve acrylonitrile polymers. Suitable salts which in concentrated aqueous solutions are capable of dissolving the polymers are, for example, zinc chloride, calcium thiocyanate, zinc thiocyanate, sodium thiocyanate, and lithium bromide. These salts may be used alone or in combination. Certain other salts, although alone not capable of dissolving the polymers, may be used to augment the solubilizing ability of the polymer-dissolving salts and may be used in such capacity. Such salt mixtures are described in U.S. Pat. 2,648,592. Preferably, the aqueous solvent will be a concentrated sodium thiocyanate solution in water, generally in the range of 40 to 60 weight percent based on the total weight of the aqueous solution. Since the separate polymer solutions are to be mixed to form a spinning composition, it is necessary to employ solvents based on the same salt or salt mixtures for the two polymers. The concentration of polymer in the solvent is in accordance with conventional procedures using concentrated aqueous salt solvent, generally about 8 to 20 weight percent polymer based on the total weight of the solution. It is generally preferable to match viscosities of the separate solutions as an aid in obtaining an intimate mixture thereof having adequate stability for routine extrusion.

After the two polymer solutions are prepared, a spinning composition is prepared by intimately admixing the solution of the second polymer with the solution of the first polymer. Sufficient of the second polymer solution is added to the first polymer to provide a spinning composition in which the polymer composition is about 1 to 10 weight percent of the second polymer and the balance of the first polymer. Preferably, the amount of the second polymer will be sufficient to provide from about 0.5 to 5 weight percent of the required monomer other than acrylonitrile present in the second polymer, based on the total weight of polymer present. The mixture obtained, due to the incompatibility of the two polymers will be colloidal in nature containing finely dispersed globules which provide a hazy appearance thereto.

In the special cases where the second polymer contains acrylic and/or methacrylic acid in free acid form, a preferred embodiment of the present invention is to convert the free acid groups to salt form subsequent to solution preparation but prior to mixing. This is readily accomplished by adding sufficient alkali, such as sodium hydroxide, to neutralize the free acid groups. Subsequently, after filament extrusion, as will be discussed, the acid groups are regenerated. Such treatment, of course, is not appropriately carried out when monomer contents other than the free acids are present as the required monomer other than acrylonitrile and is not required when acrylic and/or methacrylic acids are the required comonomers. However, when such embodiment is carried out when appropriate, the final fiber generally possesses enhanced luster while maintaining the desired low value of light transmission.

Once the spinning composition, as described has been obtained, it may be extruded into fibers without further modification. However, an important feature of the present invention is the fact that insoluble, solid additives may be additionally incorporated uniformly into the fiber without resulting in adverse delustering of the fiber formed. This result is highly surprising and totally unexpected. Useful insoluble, solid additives that may be uniformly incorporated within the fiber include such usual additives as anti-oxidants, pigments, ultraviolet absorbers, stabilizers, antistatic agents, softening agents, flame retardants,

and anti-bacterials. Typical additives include for example BaCd laurate, benzidine orange, sorbitan distearate, N-octadecylimidazoline, hexabromobenzene, salicylanilide, and the like. The amount of solid additive to be incorporated will generally be at a level which provides suitable fiber property modifications. Generally, the insoluble, solid additive may be employed at from about 0.1% to 30% by weight based on the weight of the polymers, preferably from about 1 to 20%, same basis. The solid additive is added directly to the spinning composition and uniformly dispersed therein by suitable mixing, such as high shear agitation. Dispersion of additive may be simultaneously effected.

After the spinning solution is prepared as described above, it is extruded into an aqueous coagulant to form wet-gel filaments in accordance with conventional procedures. The aqueous coagulant, as conventionally, is maintained below about 15° C. and preferably below about 5° C. A suitable coagulant is preferably an aqueous solution of a salt (or salts) used in preparing the polymer solvent but at a solution concentration below that necessary to dissolve the polymer, preferably at a solution concentration of about 12 weight percent based on the total weight of the aqueous solution.

After the wet-gel filaments are coagulated, they are subjected to water washing so as to remove salt completely. Where provision is made to form salts of the free acids present in the second polymer, provision is now made to acidify in conjunction with water washing, or in a separate step immediately thereafter to restore the free acid groups. Suitable acid addition may be made of hydrochloric acid, for example. Also, if desired, advantage may be taken of the cold drawability of the wet-gel filaments to effect a partial stretching of the filaments in conjunction with the water washing or in removal of the filaments from the coagulant bath preparatory to entering into water washing. Generally, such cold drawing or stretching will be limited to a stretch ratio of about 2. The term "stretch ratio," as employed herein, means the length of the stretched fiber relative to the original length of the extruded fiber, i.e. a stretch ratio of 2 means that the stretched filament is twice as long as the fiber initially extruded. Cold drawing may also be effected as a separate step, if desired.

Subsequent to water washing, the wet gel fiber is subjected to stretching in water at a temperature above about 90° C., as is conventional, to obtain fully oriented wet-gel filaments. Such stretching is generally accomplished so as to provide a total stretch ratio of up to about 15 and may be done in one or more stages.

After the wet-gel filaments have been subjected to the desired hot stretching, the stretched wet-gel filaments are next subjected to relaxation so as to remain in the wet-gel state. The fibers are exposed to hot water or steam in a free-to-shrink state. Water at a temperature greater than 90° C. or preferably saturated steam is used to effect relaxation, which is characterized by a degree of shrinkage. The hot-wet relaxation step is a conventional step that may be applied to wet-gel fibers or to dried fibers. In the present invention it is critical that this step be carried out prior to drying the filaments. That is to say that processing of the coagulated wet-gel fibers through water-washing, stretching, and hot-wet relaxation is carried out on wet-gel filaments which have never been dried to collapse the wet-gel structure, which is an irreversible structure. The extent to which relaxation is carried out is in accordance with conventional procedures and will vary depending on the stretch ratio, the relaxation conditions, and the time of exposure. The extent of relaxation is optional, but must be carried out on wet-gel filaments to achieve the results of the present invention. Sufficient relaxation is achieved when a minimal shrinkage of about 5% in the stretched filament length occurs, although much higher shrinkage may be obtained.

After the stretched filaments have been suitably relaxed

to provide relaxed wet-gel filaments the filaments are dried to collapse the wet-gel structure. Such drying is in accordance with conventional procedures. It is greatly preferred to dry the fibers under conditions of low humidity so as to enhance, the optical properties of the final fibers. Generally drying may be accomplished at temperatures in the range of 100–150° C., preferably 120–135° C. without need for humidity control. Subsequent to drying, the dried filaments may be further relaxed as previously described, but such processing is not essential to the present invention.

Fibers obtained by the present invention are characterized by a high degree of luster and low light transmission. The latter property provides a low degree of apparent soiling in service use, such as in carpet fabrics, while the former property provides the necessary brightness for aesthetic appeal in such use.

The invention is more fully illustrated by examples which follow, wherein all parts and percentages are by weight unless otherwise specifically designated. Two test procedures are employed in evaluating fiber properties and these procedures are given immediately below.

LUSTER TEST

Luster, through a real and important optical property, is complex and difficult to define concisely. One generally accepted definition describes luster as the difference in the amount and quality of light reflected at various angles of incidence. The amount of light reflected by fibers at the angles of greatest and least reflectance is measured against a reflectance standard. The difference in reflectances divided by the lower reflectance is a measure of the fiber luster.

A test sample is prepared by winding filaments on a flat plate under tension. The sample is placed in Color-Eye® (Model C, manufactured by Instrument Development Laboratories) suitably equipped with a device for rotating the sample and a calibrated vitrolite standard. The intensity of light reflected is measured relative to the standard while slowly rotating the sample so as to record the lowest reflectance value (Y_2) and the highest reflectance value (Y_1). The percent luster is then calculated from the following formula:

$$\text{Percent luster} = \frac{(Y_1 - Y_2) \times 100}{Y_2}$$

LIGHT TRANSMISSION TEST

Fine structure in fibers due to interfaces or inclusions tends to scatter light, thus reducing the transmission of light through the fibers. When such a structure is surface related, the fibers are delustered. When, however, as in the present invention, the structure is totally internal and of a certain nature, significant reductions in light transmission can be obtained without loss in luster and, in many cases, can provide an increase in luster over comparable fibers not having such structure. When fiber is immersed in a liquid of similar refractive index, surface scattering of light, such as that due to geometric factors, is eliminated and that which occurs can be assigned to the effect of internal scattering. In turn, scattered light is not transmitted through the fiber so that a measurement of relative light transmission of fiber immersed is an appropriate liquid can be considered a measure of its relative apparent anti-soiling properties. To determine light transmission, finely cut fiber is dispersed in a liquid of similar density and refractive index (in this case, dimethyl phthalate). The sample is placed in the light beam of a photometer calibrated to 100% light transmission for the liquid alone. Percent light transmission of the fiber-liquid dispersion is then determined. Normally, a fiber-liquid dispersion of 0.125 grams of fiber cut to less than 1/8 inch length in 25 cubic centimeters of liquid is used. Replicate determinations are made.

Example 1

As fiber-forming polymer there was employed a copolymer of 89.3% acrylonitrile and 10.7% methyl methacrylate. In 88.8 parts of a solution of 45% sodium thiocyanate and 55% water were dissolved 11.2 parts of the copolymer.

As additive copolymer there was employed one containing 78.7% acrylonitrile and 21.3% acrylic acid. In 90 parts of a solution of 45% sodium thiocyanate in 55% water were dissolved 10 parts of additive copolymer. A sufficient amount of concentrated sodium hydroxide was added to neutralize all of the free acrylic acid to the sodium salt.

To 900 grams of the solution of fiber-forming polymer were added 53 grams of the additive copolymer solution. The mixture was well blended to give a cloudy, uniform dispersion which was extruded through a spinnerette into an aqueous solution of 12% sodium thiocyanate maintained at 0° C. to form filaments. The freshly-formed filaments were continuously removed from the coagulant bath and washed on rollers with water adjusted to pH 1.5 with sulfuric acid to convert the sodium salt of the acrylic acid in the additive copolymer back to the free acid form. The wet-gel filaments were next advanced to another set of rollers where they were further washed with water at 70° C. to remove residual sulfuric acid and salt. The wet-gel filaments were then stretched at a stretch ratio of 10 in water at 99° C. and collected on a cone winder. The cone was subsequently stored in water at room temperature to preserve the filaments in wet-gel state. Skeins of the wet-gel filaments were placed in an autoclave and subjected to steam at 115° C. or 20 minutes in order to effect relaxation. The skeins were then dried in an oven for 20 minutes at 127° C. The luster and transmission values determined by the tests described above, are given in Table I.

Comparative Example A

The procedure of Example 1 was followed in every material detail except that no additive copolymer was employed. Luster and transmission values of this control fiber are also given in Table I, which follows:

Example	Percent	
	Luster	Light transmission
A-----	22.5	87.0
1-----	29.4	19.5

These results show that the luster of the fibers made by the invention is actually higher than the control while the light transmission is greatly reduced.

Example 2

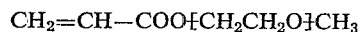
The procedure of Example 1 was followed except that the fiber-forming polymer had the following composition: 81.5% acrylonitrile, 8.8% methyl methacrylate, and 9.7% vinylidene chloride. The fibers obtained had a luster of 37.5% and a light transmission of 16.0%. Such fibers yielded fabrics having very attractive visual aesthetics while possessing improved anti-soiling tendencies.

Example 3

The procedure of Example 2 was followed in every essential detail except that the additive copolymer contained 30% 2-hydroxypropylmethacrylate and 70% acrylonitrile. The additive polymer was employed at 5% based on the weight of the fiber-forming polymer. The neutralization with sodium hydroxide and subsequent acidification were eliminated since the comonomer in the additive copolymer did not contain a free acid. The final fiber had a luster of 29.5% and a light transmission less than 10%.

Example 4

The procedure of Example 3 was followed in every material detail except that the additive copolymer contained 50% acrylonitrile and 50% of 2-(w-methoxy-3,6,9,12,15,18,21,24,27-nonaioxanonacosyloxy)ethyl acrylate. This latter comonomer corresponds to the structure



The final fiber had a luster of 29.4% and a light transmission of 19.5%.

Example 5

The procedure of Example 1 was repeated in every material detail except that 5% of hexabromobenzene (HBB), based on the total polymer weight, was uniformly dispersed in the spinning composition. Fiber properties are given in Table II.

Comparative Example B

The procedure of Comparative Example A was repeated in every material detail except that 5% of hexabromobenzene, based on the weight of the polymer was uniformly dispersed in the spinning composition. Fiber properties are also given in Table II, which also repeats the values of Example 1 and Comparative Example A.

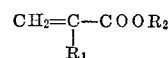
TABLE II

Example number	Additive copolymer	HBB added	Percent	
			Luster	Transmission
A-----	0	0	22.5	87.0
1-----	5	0	29.4	19.5
B-----	0	0	15.1	18.5
5-----	5	5	30.4	11.8

The results show that the fiber of the present invention is not delustered by the presence of an insoluble solid additive therein.

What is claimed is:

1. A low-density, lustrous acrylic fiber of reduced soiling tendencies comprising a fiber-forming first acrylonitrile polymer containing at least 70 weight percent acrylonitrile and the balance of one or more vinyl monomers and, as small discontinuous elongated segments within said first polymer separated therefrom by void space, from about 1 to 10 weight percent, based on the total weight of the fiber, of a second acrylonitrile copolymer incompatible with said first polymer and containing from 50 to 95 weight percent acrylonitrile and from 5 to 50 weight percent of a monomer of the formula



wherein R₁ is hydrogen or methyl and R₂ is selected from hydrogen, hydroxyalkyl of 2 to 4 carbon atoms and $\text{-(CH}_2\text{CH}_2\text{O)}_n\text{R}_3$ wherein n is an integer of about 1 to 50 and R₃ is selected from hydrogen, alkyl of 1 to 4 carbon atoms, and aryl of monocyclic structure having less than about 10 carbon atoms.

2. The fiber of Claim 1 wherein said second acrylonitrile copolymer contains an acrylic acid comonomer.

3. The fiber of Claim 1 wherein said first acrylonitrile polymer contains a halogen-containing comonomer in the amount of 5 to 30 weight percent used on the weight of the copolymer.

4. The fiber of Claim 1 wherein said fiber contains dispersed therein an insoluble, solid additive in an amount of 0.1 to 30 weight percent based on the weight of the fiber.

5. The fiber of Claim 4 wherein said insoluble, solid additive is hexabromobenzene.

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