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[54] **PVA-PVC FIBERS AND PROCESS FOR THEIR PRODUCTION**

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[63] Continuation-in-part of Ser. No. 340,040, March 12, 1973, now abandoned.

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[58] **Field of Search** 260/899

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[57] **ABSTRACT**

Synthetic fibers having superior fire retardancy, light resistance and tenacity, said fibers consisting of a polyvinyl alcohol having an average degree of polymerization of 500 to 3000 and a degree of saponification of at least 99.5 mol percent, polyvinyl chloride and boric acid, the weight ratio of polyvinyl alcohol to polyvinyl chloride being 90:10 to 55:45, the content of boric acid being 0.02 to 0.5 percent by weight based on the weight of the polyvinyl alcohol, said fibers being molecularly oriented to a sufficient degree in the direction of the fiber axis and having a hot water resistance of at least 110° C. even when not acetalized.

Where it is desired to obtain fibers of higher fire retardancy, a certain amount of stannic oxide or stannic acid is incorporated in the fibers. These fibers can be produced by the gel spinning method.

4 Claims, No Drawings

PVA-PVC FIBERS AND PROCESS FOR THEIR PRODUCTION

This is a continuation of Appl. Ser. No. 340,040, filed March 12, 1973, now abandoned.

This invention has for its object the provision of synthetic fibers having superior fire retardancy as well as superior tenacity and light resistance.

Many methods have previously been proposed to adhere or react a fire-retarding agent to and with synthetic fibers in order to render them fire-retardant. Some of these methods have been in commercial use. However, in order to obtain sufficient fire retardancy by post processing techniques, it is necessary to use the fire-retarding agent in a great quantity. Accordingly, the application of the fire retarding agent hampers the inherent properties of the fibers, or the fire retardancy is reduced on washing. On the other hand, a method of spinning a spinning dope containing a fire retardant to render the as-spun fibers themselves fire-retardant has recently been investigated considerably, but not satisfactory result has ever emerged from such effort.

Polyvinyl chloride (PVC) is known to have good fire retardancy. However, fibers produced from this polymer prove unsatisfactory for practical uses because of the poor tenacity and thermal stability of this polymer. With a view to removing this defect, fibers from a mixture of polyvinyl chloride and polyvinyl alcohol (PVA) have been proposed. Since, however, the polyvinyl alcohol is combustible, the resulting fibers have reduced fire retardancy, and unless the polyvinyl alcohol is acetalized after formation of the fibers, the water resistance of the fibers is insufficient. Another defect of the fibers from a mixture of polyvinyl chloride and polyvinyl alcohol is that they have poor resistance to light in spite of good resistance to light of the both of these polymers when taken individually. The conventional polyvinyl chloride/polyvinyl alcohol fibers still prove unsatisfactory.

In recent years, the fire retardancy requirements for fibers have become increasingly rigorous, and fibers for use in producing industrial material such as tent are required to have a high level of fire retardancy in addition to sufficient tenacity and resistance to light. However, there have been almost no fibers which prove satisfactory in all of these properties. If any, such fibers would be very expensive because of derivation from a very special polymer, and would not be able to gain wide acceptance.

It is an object of this invention to provide synthetic fibers having superior fire retardancy, tenacity and light resistance which can be manufactured at low cost.

Another object of this invention is to provide novel modified polyvinyl chloride/polyvinyl alcohol fibers of superior properties which do not suffer from the defects of the conventional polyvinyl alcohol/polyvinyl chloride fibers.

According to the present invention there is provided synthetic fibers having superior fire retardancy, light resistance and tenacity, said fibers consisting of a polyvinyl alcohol having an average degree of polymerization of 500–3000 and a degree of saponification of at least 99.5 mol%, polyvinyl chloride and boric acid, the weight ratio of polyvinyl alcohol to polyvinyl chloride being 90:10 to 55:45, the content of boric acid being 0.02 to 0.5% by weight based on the weight of the polyvinyl alcohol, said fibers being molecularly oriented to a sufficient degree in the direction of the fiber axis and having a hot water resistance of at least 110°C. even when not acetalized.

The synthetic fibers described above can be produced by dissolving a partially saponified polyvinyl alcohol having an average degree of polymerization of 500–3000 and a degree of saponification of 88.5 to 99.5 mol% and 0.5 to 4 % by weight, based on the weight of polyvinyl alcohol, of boric acid in water, mixing the resulting aqueous solution with an emulsion of polyvinyl chloride having an average particle diameter of not more than 1000 Å in a polyvinyl alcohol to polyvinyl chloride weight ratio of 90:10 to 55:45 to form a spinning solution, spinning the solution into an alkaline coagulation bath to form gelled filaments, drawing the gelled filaments between rollers, neutralizing the filaments in an acidic bath, then drawing the filaments in wet heat, washing the filaments with water until the content of the residual boric acid reaches 0.02 to 0.5 % by weight, drying the filaments, then drawing the filaments in dry heat at a total draw ratio of at least 10, and further subjecting the drawn filaments to a shrinking treatment.

Alternatively, in the above-mentioned method, the gelled filaments which have been neutralized with an acid bath may be immediately washed with water to a residual boric acid content of 0.02 to 0.5 % by weight, followed by drawing in wet heat, drying, drawing in dry heat at a total draw ratio of at least 10, and further subjecting the filaments to a shrinking treatment.

The synthetic fibers have sufficiently high fire retardancy as compared with the conventional ordinary fibers. According to one preferred embodiment of this invention, there are provided synthetic fibers having a higher level of fire retardancy, and superior light resistance and tenacity, which consist of a polyvinyl alcohol having an average degree of polymerization of 500–3000 and a degree of saponification of at least 99.5 mol%, polyvinyl chloride, boric acid and a tin compound selected from stannic oxide and stannic acid, the weight ratio of polyvinyl alcohol to polyvinyl chloride being 90:10 to 55:45, the content of boric acid being 0.02 to 0.5 % by weight based on the weight of polyvinyl alcohol and the content of the tin compound being 0.1 to 5 % by weight based on the total weight of the polymers, said fibers being molecularly oriented to a sufficient degree in the direction of the fiber axis and having a water resistance of at least 110°C. even when not acetalized.

The above fibers having a higher degree of fire retardancy can be produced by a process comprising dissolving a partially saponified polyvinyl alcohol having an average degree of polymerization of 500–3000 and a degree of saponification of 88.5 to 99.5 mol% and 0.5 to 4 % by weight based on the weight of the polyvinyl alcohol, of boric acid in an aqueous dispersion of a tin compound having an average particle size of not more than 20 microns and selected from stannic oxide and stannic acid, mixing the resulting aqueous dispersion with an emulsion of

polyvinyl chloride having an average particle diameter of not more than 1000 Å to form a spinning solution, the weight ratio of the polyvinyl alcohol to polyvinyl chloride being 90:10 to 55:45 and the content of the tin compound being 0.1 to 5 % by weight based on the total weight of the polymers, spinning the resulting spinning solution into an alkaline coagulation to form gelled filaments, drawing the gelled filaments between rollers, neutralizing them in an acidic bath, drawing the filaments in wet heat, washing the filaments with water until the content of residual boric acid reaches 0.02 to 0.5 % by weight, drying the filaments, drawing them in dry heat at a total draw ratio of at least 10, and then subjecting the filaments to a shrinking treatment.

Alternatively, the gelled filaments which have been neutralized in an acidic bath may be directly washed with water to a residual boric acid content of 0.02 to 0.5 % by weight, followed by drawing in wet heat, drying, drawing in dry heat to a total draw ratio of at least 10, and shrinking treatment.

The invention will be described below in greater detail.

The most novel and marked feature of the fibers of this invention is that the polyvinyl alcohol/polyvinyl chloride fibers contain boric acid. When boric acid is present in the polyvinyl alcohol/polyvinyl chloride fibers, the drawability of the fibers is greatly improved. This enables the fibers to be drawn at a high ratio hitherto impracticable, for example, at a total draw ratio of at least 10, and more than 12 under preferred conditions, and to attain a high tenacity that cannot be expected of the conventional polyvinyl alcohol/polyvinyl chloride fibers, for example, a tenacity of at least 6 g/denier. Furthermore, while the conventional polyvinyl alcohol/polyvinyl chloride fibers have poor water resistance unless acetalized, and cannot endure practical use, we have unexpectedly found that the fibers of the present invention which have been drawn at a high ratio because of the boric acid contained therein have sufficient water resistance without acetalization. We assume that such a surprising result may be ascribed to the fact that when the polyvinyl alcohol/polyvinyl chloride spinning solution containing boric acid is spun into an alkaline coagulation bath, gellation of the filaments first occurs and consequently, freshly spun gel filaments having a homogeneous sectional area are obtained, and that by the subsequent dehydration of the gel filaments, the filaments can be drawn at a high ratio to form filaments of a homogeneous structure having a substantially circular cross section.

Since the fibers of this invention need not to be acetalized, the reduction in fire retardancy and light resistance which inevitably occurs in acetalization can be avoided, and these properties can also be greatly improved.

A second feature of the invention is based on the inventors' discovery that stannic oxide and stannic acid act as effective fire retardants for polyvinyl alcohol/polyvinyl chloride fibers.

Antimony trioxide (Sb_2O_3) has previously been known well as a fire retardant having synergism with polyvinyl chloride, and is being used in great quantities. On the other hand, it is also well known that stannic oxide (SnO_2) has synergism with polyvinyl chloride. But the latter has hardly been used since it is inferior in fire retarding effect to antimony oxide or is at best similar thereto, and is very expensive.

It was attempted to render polyvinyl alcohol/polyvinyl chloride fibers fire retardant by adding a tin salt of a strong acid to an acetalization bath for the fibers thereby to incorporate stannic acid in the fibers (German OLS 2029734). As will be mentioned in detail later on, the fire retardancy of the fibers is improved, but their tenacity and especially light resistance are very poor. We have produced films from a mixture of a polyvinyl alcohol/polyvinyl chloride polymer composition with stannic oxide, stannic acid or antimony trioxide, and the fire retardancy of each of the films was evaluated in terms of LOI (limiting oxygen index determined in accordance with ASTM D-2863-70). The results are shown in Table 1.

Table 1

Polymer	Polyvinyl chloride	Polyvinyl alcohol	Ratio of PVS/PVC 75/25	Ratio of PVS/PVC 67/33
Amount (%) of additives	2	2	–	–
Sb_2O_3	36	19.5	27	29
SnO_2	35.5	19.5	31	34
Stannic acid	36.5	19.5	32.5	36

As is clear from Table 1, SnO_2 or stannic acid has a far greater fire-retarding effect on the polyvinyl alcohol/polyvinyl chloride system than Sb_2O_3. This was an unexpected result. It is not entirely clear why such a result was obtained, but we assume that it will probably be ascribable to the following cause. When fibers consisting only of polyvinyl alcohol/polyvinyl chloride or those consisting of polyvinyl alcohol/polyvinyl chloride containing antimony trioxide as a fire-retardant are burned, they heat decompose while being melted. On the other hand, when fibers of polyvinyl alcohol/polyvinyl chloride containing SnO_2 or stannic acid are burned, they have a reduced tendency to melt, but immediately before melting, the polymer becomes cured and infusible at a high temperature and its carbonization will be promoted. It seems that polyvinyl alcohol plays an important role in the curing reaction of the polymer. In addition, it is assumed that polyvinyl chloride evolves hydrogen chloride gas at the time of burning, and the hydrogen chloride gas reacts with SnO_2 or stannic acid to form a chloride of tin which will be effective for preventing the burning of the fibers. Accordingly, the polyvinyl alcohol/polyvinyl chloride/SnO_2 or stannic acid composition could have an especially good fire retardancy.

In order to obtain fibers of high tenacity, the polyvinyl alcohol should have an average degree of polymerization of 500-3000, and in order to obtain high water resistance, the polyvinyl alcohol should have a degree of saponification of at least 99.5 mol%. Inclusion of polyvinyl chloride is essential for obtaining fire retardant fibers. The weight ratio of polyvinyl alcohol to polyvinyl chloride should be 90:10 to 55:45. The amount of polyvinyl chloride outside this specified range is not preferred because

smaller amounts cause insufficient fire retardancy, and larger amounts reduce both the tenacity and light resistance of the resulting fibers.

The polyvinyl chloride that can be used in this invention is not only a homopolymer of vinyl chloride, but may also be a copolymer of at least 75 mol% of vinyl chloride with another comonomer and a grafted vinyl chloride copolymer to which polyvinyl alcohol has been grafted (the ratio of grafting polyvinyl alcohol is usually not more than 5 mol%). When the polyvinyl alcohol grafted vinyl chloride copolymer is used, the amount of the polyvinyl alcohol in the graft copolymer is added to the amount of polyvinyl alcohol in calculating the polyvinyl alcohol/polyvinyl chloride ratio.

In order to increase tenacity and water resistance, boric acid should be contained in an amount of 0.02 to 0.5 % by weight based on the polyvinyl alcohol of the fibers. If the amount of boric acid is outside this range, it cannot be expected to increase the drawability of the spun filaments, and the desired results cannot be obtained. A boric acid salt or boron oxide may also be used as the boric acid to be incorporated.

In order to increase the fire-retardancy of the fibers to a greater degree, SnO_2 or stannic acid should be uniformly dispersed in an amount of 0.1 to 5 % by weight based on the polymer in the fibers. The stannic acid is preferably β-stannic acid. If the amount of the tin compound is less than 0.1 % by weight, the fire-retardancy of the fibers is not satisfactorily improved, and if the amount exceeds 5 % by weight, the properties of the fibers such as tenacity are deteriorated. Accordingly, the amounts outside the specified range are economically disadvantageous and undesirable.

As previously stated, in order to obtain a high degree of tenacity and sufficient water resistance, the fibers should be fully drawn both in wet heat and in dry heat and subjected to a shrinking treatment thereby to orient the fibers molecularly and also crystallize them so as to provide a tenacity of preferably at least 3.5 g/denier and a water resistance of at least 110°C.

The method of producing the fibers of this invention will be described below, first with reference to the production of synthetic fibers of polyvinyl alcohol/polyvinyl chloride/boric acid.

Boric acid is added to partially saponified polyvinyl alcohol, and the mixture is dissolved in water at 90 to 130°C. The solution is cooled to 40 to 75°C., and mixed with an aqueous emulsion of polyvinyl chloride, followed by defoaming at 40 to 75°C. to afford a spinning solution. The spinning solution held at 40 to 75°C. is spun into a bath containing alkaline dehydrated salts. After various treatments including roller drawing, neutralization, wet heat drawing and water washing, the filaments are dried, drawn in dry heat and shrunken. If desired, the filaments may be treated, after the rinsing step, with an aqueous solution of salts.

The greatest feature of the method of producing the fibers of this invention is that the spun gel filaments are drawn to a high extent. However, in order to produce fibers of superior properties without any trouble, various contrivances are required. First, the polyvinyl alcohol used preferably has an average degree of polymerization of 500 to 3000. If the average degree of polymerization is less than 500, it is impossible to obtain fibers of high tenacity, and if it is above 3000, the viscosity of the spinning solution is too high with ordinary concentrations of the polymer and the spinning cannot be performed in good condition. If the concentration of the polymer is reduced to lower the viscosity of the spinning solution, fibers of superior properties cannot be obtained. The degree of saponification of polyvinyl alcohol is preferably 88.5 to 99.5 mol%. Even if polyvinyl alcohol to be used for preparing the spinning solution has a low degree of saponification, fibers of high water resistance can be obtained because its saponification occurs during spinning because of the alkaline coagulating bath employed. Although depending upon the concentration of the alkali, polyvinyl alcohols having a saponification degree of less than 88% will not become completely saponified with a saponification degree of at least 99.5%, and sufficient hot water resistance cannot be obtained. As will be described below, the spinning in accordance with the present invention needs to be carried out at a relatively low temperature of 40 to 75°C. from the standpoint of stability of the emulsion. Completely saponified polyvinyl alcohols having a degree of saponification of 99.5 % or more have poor dispersion stability at low temperatures and become gelled by a shearing force, which in turn causes the blockage of the candle filter material used and shortens the life of the filter material. Accordingly, the method of this invention is based on the principle that a partially saponified polyvinyl alcohol which has good dispersion stability at low temperatures but gives polyvinyl alcohol/polyvinyl chloride fibers of poor hot water resistance is used and completely saponified during spinning by the use of an alkaline coagulating bath, and that this new procedure, coupled with high ratio drawing, contributes to the production of polyvinyl alcohol/polyvinyl chloride fibers of excellent hot water resistance.

The boric acid (H_3BO_3) may be any water-soluble boric acid salt, and its amount is preferably 0.5 to 4 % by weight calculated as boric acid based on the weight of the polyvinyl alcohol. If the content is less than 0.5 %, sufficient gellation does not occur, and if it is above 4 %, gellation is too vigorous to form brittle gel filaments, leading to manufacturing troubles.

The spinning condition may be improved by adding a small amount of an organic acid or inorganic acid to the polyvinyl alcohol/boric acid aqueous solution to adjust its pH to 3–6 for prevention of excessive gellation, or by adding a dispersing agent in order to disperse the emulsion of polyvinyl chloride to be added subsequently.

The polyvinyl chloride emulsion may be produced by any known method. As previously stated, the polyvinyl chloride may be a homopolymer of vinyl chloride, a copolymer containing at least 75 mol% of vinyl chloride units, or a polyvinyl alcohol-grafted vinyl chloride copolymer. Copolymers containing less than 75 mol% of vinyl chloride units are not preferred because of their poor dyeability. The polyvinyl chloride particles in the emulsion should have a particle size of not more than 1000 Å. If the particle

size is larger, the spinning condition becomes poor and the tenacity of the resulting fibers is low.

Since the polyvinyl chloride emulsion coagulates at a temperature of 75°C. or above and polyvinyl alcohol gells at a temperature of 30°C. or below, the polyvinyl alcohol/boric acid aqueous solution is first cooled to 30 to 75°C. and then mixed with the polyvinyl chloride emulsion so as to provide a polyvinyl alcohol/polyvinyl chloride weight ratio of 55:45 to 90:10. If the amount of polyvinyl chloride is less than 10 % by weight, the dyeability of the resulting fibers is poor, and if it is above 45 %, the tenacity of the fibers is reduced. Since according to the process of the present invention, drawing of the filaments can be performed at a high ratio, the resulting fibers have a high tenacity even if polyvinyl chloride is contained in a larger amount than in the case of producing polyvinyl chloride/polyvinyl alcohol fibers by the conventional dehydrating-coagulating method using a bath of Glauber's salt.

The resulting spinning solution consisting of the polyvinyl alcohol/polyvinyl chloride emulsion and boric acid is defoamed by allowing it to stand at 30 to 75°C. The polyvinyl alcohol gells at a temperature below 30°C., and at a temperature above 75°C., the polyvinyl chloride emulsion coagulates. In both cases, spinning solutions of good spinnability cannot be obtained.

The total polymer concentration of the spinning solution is not particularly critical, but usually from 8 to 20 % by weight.

The spinning solution so formed is then spun into an alkaline coagulation bath. The bath first gives rise to gelled filaments almost instantaneously, and then gradually dehydrates the gelled filaments. For example, sodium carbonate alone or a mixture of an alkali hydroxide or sodium carbonate with Glauber's salt is suitable. It is desirable that the coagulating bath should be such that it causes complete saponification of the partially saponified polyvinyl alcohol and has sufficient coagulating ability. The typical bath contains sodium hydroxide and Glauber's salt. The concentration of the sodium hydroxide should be adjusted to 5–200 g/liter although differing according to the degree of saponification of the polyvinyl alcohol used. If it is below 5 g/liter, the saponification of polyvinyl alcohol does not proceed sufficiently and the gellation of the filaments by boric acid neither proceeds fully. If it is above 200 g/liter, polyvinyl chloride decomposes because of strong alkalinity. The concentration of Glauber's salt is preferably a to $(a-200)$g/liter (exclusive of values less than O), wherein a is the saturated concentration at each sodium hydroxide concentration.

Where sodium carbonate is used, its concentration should be at least 30 g/liter, because it is weakly alkaline and does not cause sufficient saponification of polyvinyl alcohol.

After being subjected to roller drawing, neutralization and drawing in wet heat, the filaments were washed with water until the residual boric acid content is 0.02 to 0.5 % by weight based on the weight of polyvinyl alcohol. After applying salt solution to the fiber, the filaments are dried. If the remaining boric acid content is less than 0.02 %, the drawability of the filaments becomes poor, and it is impossible to give good tenacity and hot water resistance. If it is above 0.5 %, the resulting fibers lack hot water resistance and become brittle.

Since after drawing in wet heat, the filaments are in the oriented state to some extent, the filaments are not swollen during the subsequent water-washing step, and injuries ascribable to swelling can be reduced. The length of a washing bath to remove boric acid should be large. On the other hand, when the filaments are drawn in wet heat after roller drawing, neutralization, water washing and applying a salt solution to the fiber, the fibers are washed with water in the loosened state, and therefore the fibers are well swollen. In this case, the length of the washing bath can be short, but because of swelling injuries, the properties of the resulting filaments are somewhat poor. The choice of these procedures can be freely made according to the desired purpose.

Then, the filaments are drawn in dry heat at a total draw ratio of at least 10, and subjected to a shrinking treatment to molecularly orient and crystallize the filaments fully. Shrinking is generally performed by about 2–25%, preferably about 5–15 %. With the conventional method using a bath of Glauber's salt, it is difficult to increase the total draw ratio to more than 10 unless some special conditions are employed. According to the present invention, it is possible to increase the total draw ratio to more than 10, and by employing such a high draw ratio, the polyvinyl alcohol/polyvinyl chloride fibers can possess fire retardancy, high tenacity and superior hot water resistance.

Now, another embodiment of the method of this invention in which the spinning solution consists of polyvinyl alcohol, polyvinyl chloride, boric acid and either stannic oxide or stannic acid will be described.

Partially saponified polyvinyl alcohol and H_3BO_3 are dissolved under heating in an aqueous dispersion of powdery SnO_2, and the solution is cooled to 30–80°C. The solution is then mixed with an aqueous emulsion of polyvinyl chloride, and the mixture is defoamed to afford a spinning solution. The spinning solution is spun into an alkaline coagulation bath, and then in the same way as described above with reference to the method of producing fibers consisting of polyvinyl alcohol, polyvinyl chloride and boric acid, the filaments are subjected to various treatments including roller drawing, neutralization, drawing in wet heat, washing with water, drying, drawing in dry heat, and shrinking.

The powdery SnO_2 or stannic acid is well dispersible, and the average particle size of the dispersed particles should be not more than 20 microns. If the size is above 20 microns, the particles may be precipitated at the time of defoaming or block the candle filter material. Even if the particles are dispersed in the fibers, the area of their contact with the polymers becomes small and the fire-retarding effect is reduced.

The stannic acid used in this invention is a monohydrate of SnO_2. The preferred stannic acid is metastannic acid (or also called β-stannic acid) produced by treating metallic tin with nitric acid. If desired, another fire-retarding agent such as Sb_2O_3 may be used in addition to SnO_2 or stannic acid.

As stated above, the polyvinyl alcohol/polyvinyl chloride fibers of this invention have novel features in the following two points.

(1) Since the fibers are spun by H_3BO_3 gel spinning, the drawability of the spun filaments is superior, and sufficient hot water resistance can be obtained without acetalizing the resulting filaments.

(2) The fine particles of SnO_2 or stannic acid which is very superior as a fire-retarding agent and is hardly soluble in water, acid or alkali are uniformly dispersed in the fibers.

Furthermore, the fibers possess fire retardancy, tenacity and light resistance.

The fibers of this invention retain the superior dyeability characteristic of polyvinyl alcohol/polyvinyl chloride fibers, and can be used also as interior decorating fibrous material such as carpets or curtains.

The fibers of this invention attain excellent tenacity and light resistance as well as excellent fire-retardancy only when all of the conditions such as the degree of polymerization and the degree of saponification of polyvinyl alcohol, the mixing ratio of polyvinyl alcohol and polyvinyl chloride, the content of boric acid, or the molecular orientation and crystallization of the fibers, and in the case of fibers of a higher level of fire retardancy, the content of SnO_2 or stannic acid are met. In order to clarify this matter, Table 2 shows how the properties of the fibers change with changes in the various conditions for producing them. The test methods used here and in the Examples are shown in the footnote.

Table 2

Run No.	Composition of the fibers: Degree of polymerization of polyvinyl alcohol	Degree of saponification (mol%)	PVA/PVC ratio	SnO_2 (percent based on polymers)	H_3BO_3 (percent based on PVA)	DEA[2]	Properties of the fibers: Total draw ratio[2]	Hot water resistance[3] (°C.)	Tenacity (g/denier)	Light resistance[4]	Fire retardancy[5] (Grade)
1	1750	99.9	60/40	–	0.10	–	12	116	5.7	70%	3
2	1750	99.9	75/25	1	0.15	–	12	116	8.0	90	3
3	400	99.9	75/25	1	0.18	–	10	112	3.1	87	3
4	1750	99.2	75/25	1	0.12	–	11	103	6.8	85	3
5	1750	99.9	50/50	1	0.11	–	10.5	114	2.1	45	3
6	1750	99.9	95/5	5	0.21	–	12	117	8.5	93	1
7	1750	99.9	65/35	0.08	0.01	–	9.3	108	3.8	70	3
8	1750	99.9	80/20	1.5	0.7	–	11	109	6.2	91	3
9	1750	99.9	75/25	1	0.15	–	9.2	108	4.2	88	3
10	1750	99.9	75/25	0.5	0.13	–	12	116	8.1	90	3
11	1750	99.9	75/25	0.5	0.13	–	7	101	3.4	90	3
12	1750	99.9	75/25	0.5	0.13	35	7	120	3.3	45	1
13	1750	99.9	59/41	0.5	0 [6]	–	8	103	3.8	60	3
14	1750	99.9	59/41	0.5	0 [6]	33	8	119	3.5	30	2
15	1750	99.9	59/41	(1.2)[7]	0 [6]	32	7	121	2.4	25	2

[1] DFA: Degree of formalization of the fibers which were heat-treated and then acetalized with formaldehyde (mol % based on polyvinyl alcohol)

[2] Total draw ratio: except Runs Nos. 9, 11, 12 and 15, the total draw ratios indicated are 90 % of the maximum draw ratios at which the filaments could be drawn without breakage. Accordingly, these values substantially show the drawability of the filaments.

[3] Hot water resistance: The filaments were immersed in water while a weight of 1/500 g per denier was suspended from the filaments. The immersed filaments were heated at a rate of 2°C. per minute, and the temperature at which the filaments were dissolved and cut and the weight fell was measured. This temperature indicates the hot water resistance.

[4] Light resistance: The ratio of the remaining tenacity of the filaments after the filaments were exposed for 100 hours with a FA-I type Fade-O-meter (product of Toyo Rika Kabushiki Kaisha).

[5] Fire retardancy: Filaments of 1800 total denier were twisted at a rate of 90 turns per meter, and knitted into a fabric having a unit weight of 250 g/m² using a knitting machine. The knitted fabric was evaluated by the method described in JIS-L-1091 A-1. Grade 3 is passable, and grade 1 is not passable.

[6] The spinning solution did not contain H_3BO_3, and the spun filaments were dehydrated and coagulated using a Glauber's salt bath.

[7] The spinning solution did not contain H_3BO_3, and the spun filaments were dehydrated and coagulated using a Glauber's salt bath. The resulting filaments were heat-treated, and treated with an acetalization bath containing tin tetrachloride to acetalize the filaments and at the same time incorporate stannic acid thereinto.

The present invention will be illustrated in greater detail by the following Examples.

EXAMPLE 1

H_3BO_3 was added to polyvinyl alcohol having a degree of polymerization of 1700 and a degree of saponification of 97.8 mol%, and the mixture was dissolved in water at 100°C. to form an aqueous solution containing 16.2% of polyvinyl alcohol and 1.5 %, based on polyvinyl alcohol, of H_3BO_3. The solution was cooled to 60°C. A polyvinyl chloride emulsion having an average particle diameter of 200 Å and a pH of 7 obtained by the emulsion-polymerization of vinyl chloride using sodium laurylsulfate as an emulsifier was mixed with the above solution with the PVA/PVC weight ratio and the total polymer concentration varied as shown in Table 3. The mixture was allowed to stand for one day at 60°C. to defoam it.

The spinning solution was spun into a coagulating bath containing 50 g/liter of sodium hydroxide and 160 g/liter of sodium sulfate. The spun filaments were drawn to two times of the original length using rollers, then neutralized, and drawn in wet heat at a draw ratio of 2. The drawn filaments were washed with water to a residual H_3BO_3 content of 0.1 % based on the weight of polyvinyl alcohol. The filaments were passed through a bath containing 400 g/liter of Na_2SO_4 to apply Glauber's salt to the filaments, followed by drying. The dried filaments were drawn in dry heat at 228°C. at a draw ratio of 3, and shrunken 10 % at 231°C. in dry condition. There were obtained filaments having a monofilament denier of 2. The total draw ratio was 12. The properties of the filaments which were subsequently heat-treated were measured, and the results are shown in Table 3.

Table 3

Run No.	Production conditions		Degree of saponification (mol%)	Properties of the filaments			
	PVA/PVC	Polymer concentration (%)		Tenacity (g/d)	Water resistance (°C)	Light resistance	Fire retardancy (grade)
1	85:15	15.7	more than 99.9	9.2	118	96	3
2	75:25	16.5	more than 99.9	8.1	118	92	3
3	65:35	18.6	more than	6.8	117	83	3

It is seen from the results shown in Table 3 that according to the method of this invention, saponification proceeds completely and the fibers obtained possess excellent tenacity, hot water resistance, light resistance, and fire retardancy. The spinning condition was good for 5 days, and the method of this invention proved excellent in operability.

EXAMPLE 2

H_3BO_3 was added to polyvinyl alcohol having a degree of polymerization of 1700 and a degree of saponification of 97.5 %, and the mixture was dissolved in water at 100°C. to form an aqueous solution containing 16.2 % of polyvinyl alcohol and 2.5 %, based on the weight of polyvinyl alcohol, of H_3BO_3. The solution was cooled to 50°C. A polyvinyl chloride emulsion having an average particle diameter of 500 Å and obtained by the emulsion polymerization of vinyl chloride in the presence of polyvinyl alcohol was added to the above aqueous solution at 50°C. with the PVA/PVC weight ratio of 80:20 and the polymer concentration of 16.4 %. The mixture was allowed to stand at 50°C. for 1 day to defoam it.

The spinning solution was spun into a coagulating bath containing 10 g/liter of sodium hydroxide and 350 g/liter of sodium sulfate. The spun filaments were drawn to two times the original length by rollers, drawn in wet heat at a ratio of 2 in a saturated Glauber's salt bath at 65°C., and washed with water until the residual H_3BO_3 content reached 0.15 % based on polyvinyl alcohol. The filaments were then immersed in an aqueous solution containing 6 g/liter of Tire Cord Oil #2010 (product of Sanyo Chemical Co. Ltd., which contains more than 80% mineral oil), and dried. The filaments were drawn in dry heat at a draw ratio of 3 at 230°C. and then shrunken 10 % in dry heat at 235°C. The total draw ratio was 12, and the resulting fibers had a monofilament denier of 1.5, a degree of saponification of 99.9 %, a tenacity of 8.9 g/d and a hot water resistance of 118°C. The light resistance of the fibers was 93 %, and the grade of fire retardancy was 3. Thus, all of the tenacity, hot water resistance, light resistance and fire retardancy of the filaments were superior, and the spinning condition was good for 5 days. The properties were stable.

EXAMPLE 3

Polyvinyl alcohol having a degree of polymerization of 1750 and a degree of saponification of 98.5 % and H_3BO_3 were added to an aqueous dispersion of SnO_2 having an average particle size of 1.2 microns, and dissolved therein by heating. The solution was cooled to 60°C., and mixed with a polyvinyl chloride emulsion having an average particle diameter of 200 Å and a pH of 6.9 which was obtained by the emulsion polymerization of vinyl chloride using Emal-O (product of Kao Soap Co. Ltd. containing sodium laurylsulfate as its principal constituent) as an emulsifier. The weight ratio of polyvinyl alcohol to polyvinyl chloride was 75:25, the total polymer concentration was 16.5 %, the content of SnO_2 was 2 % by weight based on the polymers, and the content of H_3BO_3 was 1.8 % by weight based on polyvinyl alcohol. The resulting spinning solution was allowed to stand for one day at 60°C.

The spinning solution was spun into a coagulating bath containing 60 g/liter of sodium hydroxide and 160 g/liter of sodium sulfate. The spun filaments were drawn to two times the original length by rollers, neutralized, and drawn in wet heat at a draw ratio of 2. The filaments were washed with water to a residual H_3BO_3 content of 0.1 % by weight based on polyvinyl alcohol, passed through a bath containing 300 g/liter of sodium sulfate to apply the salt to the filaments, and dried. The filaments were then drawn at a draw ratio of 3 at 229°C. in dry condition, and shrunken 10 % in dry condition at 233°C. The resulting filaments had a degree of saponification of 99.95 mol%, a PVA/PVC ratio of 75/25, an SnO_2 content of 2 % based on polymer and an H_3BO_3 content of 0.1 % based on polyvinyl alcohol, and a monofilament denier of 2. The total draw ratio was 12.

The properties of the resulting filaments were measured in the same way as set forth below Table 2. The filaments were found to have a hot water resistance of 116°C., a tenacity of 7.8 g/d, a light resistance of 87 %, and a fire retardancy of grade 3. The spinning condition was quite good for 10 days showing superior operability.

EXAMPLE 4

Polyvinyl alcohol having a degree of polymerization of 1700 and a degree of saponification of 99.1 mol%, borax and nitric acid (to adjust the pH to 4.5) were added to an aqueous dispersion of stannic acid and Sb_2O_3 having an average particle size of 0.8 micron, and dissolved by heating. The solution was cooled to 50°C. A polyvinyl chloride emulsion having an average particle diameter of 500 Å and obtained by the emulsion polymerization of vinyl chloride in the presence of polyvinyl alcohol was mixed with the above solution with the PVA/PVC weight ratio of 65:35, the polymer concentration of 17.8 %, the stannic acid content of 0.3 % based on polymer (calculated as SnO_2), the Sb_2O_3 content of 1 % based

on polymer and the borax content of 2.5 % based on polyvinyl alcohol. The resulting spinning solution was allowed to stand for one day to defoam it.

The spinning solution was spun into a coagulating bath containing 15 g/liter of sodium hydroxide and 350 g/liter of sodium sulfate. The spun filaments were drawn to two times the original length by rollers, neutralized, and drawn in wet heat in a saturated Glauber's salt bath at 68°C. at a draw ratio of 2. The drawn filaments were washed with water to a residual H_3BO_3 content of 0.22 % based on polyvinyl alcohol, passed through a bath containing 0.05 g/liter of sodium hydroxide and 300 g/liter of sodium sulfate, and then dried. The filaments were then drawn in dry condition at 235°C. at a draw ratio of 3.1, and shrunken 10 % in dry condition at 235°C. There were obtained filaments having a monofilament denier of 2.5. These filaments had a PVA saponification degree of 99.96 mol%, a hot water resistance of 117°C., a tenacity of 7.1 g/denier, a light resistance of 75 %, and a fire retardancy of grade 3.

EXAMPLE 5

The same spinning solution as used in Example 3 was spun into a coagulating bath containing 40 g/liter of sodium hydroxide and 250 g/liter of sodium sulfate. The spun filaments were drawn to 2 times the original length using rollers, neutralized, and subsequently either (1) drawn in wet heat at a draw ratio of 2.2, washed with water and subjected to the application of a salt solution to the filaments, or (2) washed with water, subjected to the application of a salt solution to the filaments, and drawn in wet heat at a draw ratio of 2.2. Thereafter, the same drying, dry heat drawing (except drawing ratio) and shrinking treatment as in Example 3 were carried out. The properties of the resulting filaments, and the rate of washing off H_3BO_3 were measured. The results are shown in Table 4. The total draw ratio shows a maximum draw ratio of the filaments prepared by method (1) or (2).

Table 4

Method	Total draw ratio	Rate of washing of H_3BO_3 (m)*	Tenacity (g/de)	Hot water resistance (°C.)
(1)	12	40	8.0	115
(2)	13.5	22	7.4	114

* The length of a wash bath required to reduce the residual H_3BO_3 content to 0.11 % based on polyvinyl alcohol.

It is seen from the results obtained that in the case of employing the method (1), the length of the wash bath needs to be large, but the resulting filaments have high tenacity, whereas in the case of the method (2), the length of the wash bath can be short although the tenacity of the resulting filaments is somewhat low.

EXAMPLE 6

Polyvinyl alcohol having a degree of polymerization of 1750 and a degree of saponification of 98.5 mol% and H_3BO_3 were added to an aqueous dispersion of SnO_2 having an average particle diameter of 2 microns and Nannen 101 (a fire retardant agent produced by Nippon Kagaku Sangyo K, K., which contains Sb_2O_3 as a main component and Al and Ba compounds as minor components) and dissolved therein by heating. The solution was cooled to 60°C. A polyvinyl chloride emulsion having an average particle diameter of 250°C. and a pH of 6.9 and obtained by the emulsion-polymerization of vinyl chloride using Emal-O (product of Kao Soap Co., Ltd., which contains sodium lauryl sulfate) as an emulsifying agent was mixed with the above solution to form a spinning solution having a PVA/PVC weight ratio of 70/30, a total polymer concentration of 17.3 %, an SnO_2 content of 0.5 % based on polymer, a "Nannen" content of 1.3 % based on polymer and an H_3BO_3 content of 2.0 % based on polyvinyl alcohol. The spinning solution was allowed to stand for 12 hours to defoam it.

The spinning solution was spun into a coagulating bath containing 120 g/liter of sodium carbonate and 180 g/liter of sodium sulfate. The spun filaments were drawn to two times the original length using rollers, neutralized, drawn in wet heat at a draw ratio of 2 in a saturated Glauber's salt bath at 68°C., and washed with water to a residual H_3BO_3 content of 0.08 % based on polyvinyl alcohol. The filaments were then immersed in an aqueous solution containing 6 g/liter of Tire Cord Oil #2010 (product of Sanyo Chemical Co. Ltd.), dried, drawn in dry condition at 230°C. at a draw ratio of 3, and shrunken 10 % at 235°C. The total draw ratio was 12. The resulting filaments had a monofilament denier of 1.8, a PVA saponification degree of 99.95 mol%, a hot water resistance of 117°C., a tenacity of 7.6 g/denier, a light resistance of 82 %, and a fire retardancy of grade 3.

What we claim is:

1. Synthetic fibers having superior fire retardancy, light resistance and tenacity, said fibers consisting of a polyvinyl alcohol having an average degree of polymerization of 500 to 3000 and a degree of saponification of at least 99.5 mol%, polyvinyl chloride and boric acid, the weight ratio of polyvinyl alcohol to polyvinyl chloride being 90:10 to 55:45, the content of boric acid being 0.02 to 0.5 % by weight based on the weight of the polyvinyl alcohol, said fibers being molecularly oriented in the direction of the fiber axis and having a hot water resistance of at least 110°C. even when not acetalized.

2. The synthetic fibers of claim **1** wherein the polyvinyl alcohol has a degree of saponification of 99.5 mol% to substantially 100 %.

3. Synthetic fibers having a higher level of fire retardancy, and superior light resistance and tenacity, which consist of a polyvinyl alcohol having an average degree of polymerization of 500 to 3000 and a degree of saponification of at least 99.5 mol%, polyvinyl chloride, boric acid and a tin compound selected from stannic oxide and stannic acid, the weight ratio of polyvinyl alcohol to polyvinyl chloride being 90:10 to 55:45, the content of boric acid being 0.02 to 0.5 % by weight based on the weight of polyvinyl alcohol and the content of the tin compound being 0.1 to 5 % by weight based on the total weight of the polymers, said fibers being molecularly oriented in the direction of the fiber axis and having a hot water resistance of at least 110°C. even when not acetalized.

4. The synthetic fibers of claim **3** wherein said polyvinyl alcohol has a degree of saponification of 99.5 mol% to substantially 100 %.

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