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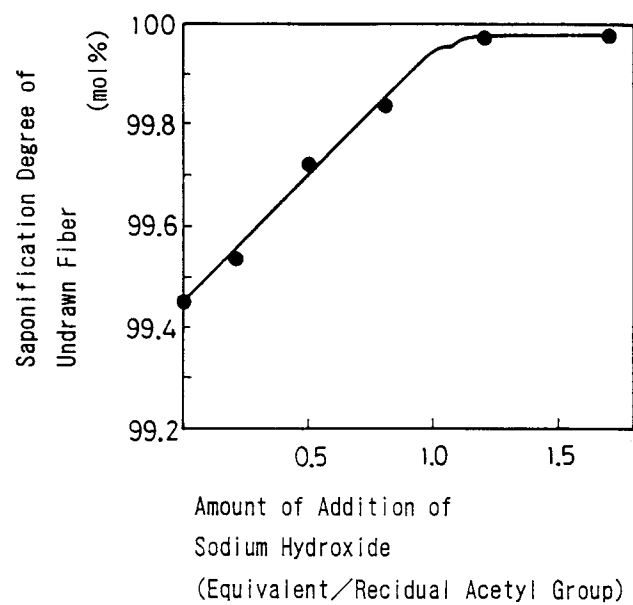
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(54) **Method for preparation of a polyvinyl alcohol-based spinning solution.**

(57) Methods for the preparation of a polyvinyl alcohol-based spinning solution. One method comprises dissolving polyvinyl alcohol in a solvent, and adding an alkaline ingredient to, and causing the same to be dissolved in the solvent and/or polyvinyl alcohol. Another method comprises dissolving polyvinyl alcohol under heating in a solvent, adding an alkaline ingredient to the solvent and/or polyvinyl alcohol to form a polyvinyl alcohol/solvent/alkali mixture, thereby saponifying a residual acetyl group of the polyvinyl alcohol, then adding an acid ingredient to the mixture, and effecting heating.

EP 0 661 392 A1

FIG. 1



FIELD OF THE INVENTION

The present invention relates to a method for preparing a polyvinyl alcohol-based spinning solution for use in producing polyvinyl alcohol (hereinafter referred to as PVA) fibers. More particularly, the invention relates to a method for the preparation of a polyvinyl alcohol-based spinning solution which makes it possible to obtain in a simple and efficient manner a PVA spinning solution having a high saponification degree effective to provide improved hot water resistance from commercially available PVA's having a commercial saponification degree.

BACKGROUND OF THE INVENTION

In the past, a detailed review was made of the relationship between the hot water resistance of PVA fibers and the saponification degree of material PVA's; and as result, it has been known that the lower the saponification degree, the higher the boil-off shrinkage ratio is. PVA fibers are mainly used in the area of industrial materials in which fiber materials are generally required to have a low boil-off shrinkage ratio.

For the purpose of producing a PVA, commercially it is general practice that vinyl acetate is polymerized in a methanol solvent into a methanol solution of polyvinyl acetate, which in turn is saponified through catalytic action of acid or alkali, being thereby converted into PVA.

However, this saponification reaction is an ester exchange reaction. If the degree of saponification is more than 99 mol %, the reaction is reversible and it is impossible to obtain the degree of saponification more than 99 mol %. Therefore, the degree of saponification of commercially available PVA is about 99 mol %. When the degree of saponification is required more than 99 mol %, resaponification reaction is needed.

PVA fibers have hitherto been produced under general name of vinylon, and in the process of producing vinylon there is employed a coagulating bath containing alkaline ingredients of high concentration. Therefore, even where the material PVA is not so highly saponified, a saponification reaction progresses in the coagulating bath so that the final product has a high degree of saponification on the order of 99.9 mol % or more. For this reason, in any known process for producing PVA fibers, no special care has been taken with respect to the saponification degree of the material PVA. No particular problem has been posed as long as the material PVA has a saponification degree of a commercially acceptable level, i. e., 99 mol % or more.

In recent years, various attempts have been made to improve the strength and initial modulus of PVA fibers. For example, USP 4,599,267 discloses a spinning method wherein a glycerin solution of a PVA with a weight-average molecular weight of 500,000 or more is spun into a methanol bath. USP 4,603,083 and USP 4,698,194 disclose a spinning method wherein a dimethyl sulfoxide solution of PVA is spun into a methanol bath. According to these spinning methods, all steps involved in the process of spinning, such as preparation of spinning solution, coagulating, and washing, are carried out using organic solvents. Therefore, no saponification reaction will progress in the spinning process as in the earlier mentioned process for vinylon production.

Therefore, in order to obtain fibers made of a PVA with a high saponification degree which have improved hot-water resistance, it is necessary to increase the saponification degree of PVA at the material stage thereof. Several methods have been known which are intended to increase the saponification degree of material PVA. For example, one method comprises dispersing a powdery or granular mass of PVA in water to prepare a suspension, adding to the suspension an alkaline ingredient in such an amount as is more than required for effecting a saponification reaction, and, if necessary, effecting heating for a saponification reaction. There is also known a method in which a similar process is carried out using alcohol.

With these methods, however, although it may be possible to increase the degree of saponification, the problem is that such method involves a complex operation procedure and troublesome subsequent polymer handling. The problem will be discussed in detail. Usually, PVA polymers are commercially available in the form of dry polymer. Such a polymer must be first suspended in water or alcohol. Then, an excessive amount of an alkaline ingredient is added to the suspension for saponification reaction, and thereafter the excess alkaline ingredient must be neutralized with acid. Subsequently, the liquid and the polymer therein are separated from each other by dehydration or otherwise. This separating step must be followed by washing, and after the washing step a drying step is required for restoring the polymer to its original state of dry polymer.

In this way, in order that the saponification degree of PVA may be rendered higher at the stage of material polymer, the PVA must be passed through a number of processing stages, which will naturally result in an increase in the material cost.

As such, for purposes of producing PVA fibers by using a process in which an organic solvent is used, it has been desired that a method be developed which enables the preparation of a spinning solution having a high degree of saponification from commercially available PVA having a commercial saponification degree. To date, however, no such method has been proposed.

5

DISCLOSURE OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method for the preparation of a PVA-based spinning solution which makes it possible to obtain in a simple and efficient manner a PVA spinning
10 solution having a high saponification degree effective to provide improved hot water resistance from commercially available PVA having a commercial saponification degree. It is another object of the invention to provide a method of producing PVA fibers having such high saponification degree in a simple and efficient manner from such commercially available PVA.

The present inventors have made an extensive research in order to solve the above discussed problem
15 and, as a result, the present invention has been developed.

According to one aspect of the invention, a first method for the preparation of a polyvinyl alcohol-based spinning solution is provided which comprises dissolving polyvinyl alcohol in a solvent, and adding an alkaline ingredient to, and causing the same to be dissolved in the solvent and/or polyvinyl alcohol.

According to other aspect of the invention, a method of spinning a polyvinyl alcohol fiber is provided
20 which comprises dissolving polyvinyl alcohol in a solvent thereby to prepare a spinning solution, adding an alkali solution to the spinning solution, and spinning fibers from the alkali-mixed spinning solution.

According to still other aspect of the invention, a second method for the preparation of a polyvinyl alcohol-based spinning solution is provided which comprises dissolving polyvinyl alcohol under heating in a solvent, adding an alkaline ingredient to the solvent and/or polyvinyl alcohol to form a polyvinyl alcohol /
25 solvent / alkali mixture, thereby saponifying a residual acetyl group of the polyvinyl alcohol, then adding an acid ingredient to the mixture, and effecting heating.

The invention will now be described in detail.

In the present invention, measurements for polymerization degree and for saponification degree are in accordance with JIS K 6726.

In the description to follow, it is understood that unless specified otherwise, particulars stated are
30 common to all of the first and second preparation methods and spinning method of the invention.

PVA's useful for the purpose of the invention are not particularly limited, but in order to insure production of a final fiber product having high strength and high modulus, the PVA should preferably have a polymerization degree of 1500 or higher, more preferably a polymerization degree of 3000 or higher. In the
35 present invention, the saponification degree of the PVA may be of a commercially acceptable level, because the PVA is brought in contact with an alkaline ingredient for improvement in the saponification degree thereof prior to the stage of PVA dissolution. The saponification degree is preferably 99 mol % or higher.

In the present invention, such PVA is dissolved in a solvent to provide a spinning solution. Useful
40 solvents include, for example, water, ethylene glycol, dimethyl sulfoxide, glycerin, and mixtures of these. Above all, dimethyl sulfoxide is most preferred.

The concentration of PVA in the preparation of a spinning solution is preferably determined within a concentration range of from 3 to 35 wt. % in order to ensure production of a final fiber product having good physical properties. If the concentration is less than 3 wt. %, the spinnability of the PVA is bad. If the
45 concentration is more than 35 wt. %, the viscosity of the PVA is excessively high so that the drawability of the resulting fiber tends to be lower.

According to the first preparation method, the PVA is dissolved in a solvent to provide a spinning solution. In this case, it is very important that an alkaline ingredient be added to the solvent and/or PVA before the PVA is dissolved. As already stated, the hot water resistance of a PVA fiber is substantially
50 influenced by the saponification degree of a fiber. If the saponification degree is relatively low or, more specifically, 99.4 mol % or lower, the PVA fiber will be dissolved in boiling water at 100 °C. According to the first preparation method, however, an alkaline ingredient is added to the solvent and/or PVA in conjunction with the dissolving of the PVA. Therefore, a saponification reaction proceeds simultaneously with the dissolving of the PVA or step by step as the PVA is dissolved, and this enables saponification
55 degree to be enhanced to 99.8 mol % or more.

The manner of adding the alkaline ingredient to the solvent and/or PVA is not particularly limited. For example, the alkaline ingredient may be added directly to the solvent; or the alkaline ingredient as prepared in the form of a solution may be added to the solvent; or such a solution of alkaline ingredient may be

added by being impregnated into a powdery or granular mass of the PVA. In a further alternative, these methods may be used in combination. Of these methods, the one in which a solution of the alkaline ingredient is added to the solvent, or the one in which addition is made by impregnating the PVA with such a solution, is easy in operation and is most preferred.

5 In the first preparation method, the amount of the alkaline ingredient added is preferably at least 0.1 equivalent but at most 2.0 equivalents of the amount of a residual acetyl group of the PVA. If the addition of the alkaline ingredient is less than 0.1 equivalent, the saponification degree can not be higher. If the addition is more than 2.0 equivalents, a residual alkaline ingredient is present in an excessive amount in the spinning solution. In particular, it is more preferable that the amount of the alkaline ingredient added is at least 0.8
10 and at most 1.3 equivalents, in which case the saponification degree can be sufficiently enhanced and, in addition, the residual amount of alkaline ingredient can be minimized.

In the present invention, where the alkaline ingredient is added in the form of a solution to the solvent and/or PVA, the solvent used in preparing the solution may be one having good capability of dissolving the alkaline ingredient used. For example, it is convenient and is therefore preferable to use water, alcohol, or a
15 mixture of these. In this case, it is preferable that the amount of water and/or alcohol is regulated so as to be at least 0.1 wt. % but at most 10 wt. % relative to the total weight of the spinning solution, whereby the alkaline ingredient can be sufficiently dissolved and there is no problem of the spinnability of the spinning solution.

Alkaline ingredients useful for the purpose of the invention are not particularly limited insofar as they are effective to permit smooth progressing of a saponification reaction. Specifically, alkaline ingredients, such as sodium hydroxide, potassium hydroxide, and lithium hydroxide, are preferred because they are inexpensive and easily available. These ingredients may be used alone or in combination.

In the present invention, for the purpose of preparing a spinning solution in this way, various additives, such as heat resisting agents, crosslinking agents, pigments, and other additives, may be added as far as
25 the saponification reaction is not hindered.

In this way, according to the invention, a spinning solution comprised of a PVA having increased saponification degree can be obtained. The increase in the saponification degree of the PVA can be determined by measuring the saponification degree of an undrawn fiber as spun from the spinning solution.

According to the second preparation method, PVA is dissolved in a solvent to form a spinning solution
30 and, in this conjunction, an alkaline ingredient is added to the solvent and/or PVA to provide a mixture of the PVA/solvent and the alkaline ingredient. As a result, a residual acetyl group of the PVA is saponified. Then, an acid ingredient is added before dissolution takes place. As already stated, the hot water resistance of PVA fibers is substantially influenced by the saponification degree of a final fiber product; if the saponification degree is relatively low, or more specifically lower than 99.4 mol %, the PVA fiber will be
35 dissolved in boiling water at 100 °C. According to this second preparation method, however, the alkaline ingredient added to the solvent and/or PVA is brought into contact with the PVA before the dissolution of the PVA takes place. Thus, a saponification reaction is enhanced by the alkaline ingredient so that the saponification degree can be increased to the order of 99.8 % or more.

The addition of the acid ingredient is important. Without such addition, the presence of an alkaline
40 residue results in the formation of other chemical bond in PVA molecular chains. This in turn may result in some coloration and, in some extreme case, a molecular chain breakage, thus resulting in a lower polymerization degree, which would not be preferable to the objective of the invention.

In the second preparation method, a mixture comprising such alkaline add acid additions is heated and dissolved, whereby a spinning solution is prepared. The temperature for the process of heating and
45 dissolving is not particularly limited. However, a temperature of 80 °C or more is preferred, since heating and dissolving at such temperature will result in uniform dissolution.

In this second preparation method, the amount of the alkaline addition is preferably at least 0.3 equivalent but at most 5.0 equivalents of the amount of a residual acetyl group of the PVA. If the amount of the alkaline addition is less than 0.3 equivalent, it is difficult to obtain a reasonably high saponification
50 degree. If the amount is greater than 5.0 equivalents, the alkaline concentration of the mixture is excessively high, which may easily lead to decreased polymerization degree, other chemical bond formation, and/or coloration. In particular, an alkaline addition of at least 0.8 equivalent but at most 1.3 equivalents is more preferable, because such troubles as above noted can be made more unlikely to occur.

In the second preparation method, the condition for adding the acid ingredient is preferably such that
55 the mixture of the PVA and the solvent with the alkaline ingredient has been kept at a temperature of 40 °C or more but less than 80 °C for at least 5 minutes but at most 4 hours. If the temperature is less than 40 °C and the time period for holding the mixture as such is less than 5 minutes, an insufficient saponification reaction will take place. If the temperature is more than 80 °C. and the holding time is more than 4 hours,

there will occur formation of other chemical bonds and molecular chain breakage.

The amount of acid ingredient addition is not particularly limited. However, if the amount of acid addition is greater than the amount of alkaline addition, the resulting spinning solution may be unstable, or there may occur some coloration. Therefore, it is preferable that the amount of acid addition be less than the number of equivalents of the alkaline addition.

Useful acids for such addition include inorganic acids, such as hydrochloric acid, sulfuric acid, and phosphoric acid; organic acids, such as acetic acid, paratoluene, sulfonic acid; and mixtures of these.

Nextly, the spinning method in accordance of the invention will be described.

A number of spinning processes are applicable to the spinning method of the invention, including the dry/wet spinning process wherein a spinning solution using an organic solvent as such is discharged through an inert atmosphere zone into a coagulating bath comprised of an organic solvent or a cooling bath; the wet spinning process wherein a spinning solution in which water is used as the solvent is discharged into a coagulating bath; and the dry spinning process wherein a spinning solution is discharged into a heated air. Of these processes, the dry/wet spinning method in which an organic solvent is used is preferred.

In the above described first and second preparation methods, during the stage of preparing a spinning solution by dissolving polyvinyl alcohol in a solvent, an alkaline ingredient is added. In contrast to this, according to the spinning method of the invention, a spinning solution is first prepared without addition of an alkaline solution, and subsequently an alkaline solution is added thereto. The resulting spinning solution is used as such in the stage of spinning. This provides same benefits as those described earlier.

Where an alkaline solution is added to a previously prepared spinning solution in this way before spinning is carried out, even if the saponification degree of the material PVA is low, a saponification reaction is carried out at the stage of spinning solution, so that the saponification degree of a final product can be increased to as high as 99.8 mol % or more.

The period for addition of the alkaline solution to the spinning solution is not particularly limited. For example, in case that a spinning solution is prepared by dissolving the PVA in a tank, the alkaline solution may be introduced into the tank after the PVA has been dissolved. In case that the PVA is dissolved in a continuous dissolver, the alkaline solution may be added at a location adjacent an outlet port of the dissolver. More preferably, such addition is made in a pipe line provided for transferring the spinning solution to a spinneret, which provides greater simplicity. In this case, it is preferable that a static agitator is provided on the pipeline at a location downward of a position set for such addition, because the alkaline solution added is allowed to be more uniformly mixed throughout the entire spinning solution.

Above mentioned additives, such as heat resisting agent, crosslinking agent, pigment, and other additives, may be added to the spinning solution simultaneously upon addition of the alkaline solution.

As stated above, according to the present invention, during the stage of preparing a spinning solution, an alkaline ingredient is added to the solvent and/or PVA for dissolving the PVA, so that the alkaline ingredient reacts with a residual acetyl group of the PVA. This makes it possible to obtain in a simple and efficient manner a spinning solution having a high saponification degree, from a commercially available PVA having a commercial saponification degree. This points to the usefulness of the invention.

Also, according to the invention, during the stage of preparing a spinning solution, an alkaline ingredient is added to the solvent and/or PVA and then an acid ingredient is added, the PVA being then heated and dissolved. Thus, the alkaline ingredient is caused to react with a residual acetyl group of the PVA thereby to improve the saponification degree of the PVA. Subsequently, dissolution of the PVA takes place when a residual alkaline ingredient has reacted with the acid ingredient to form a salt. Therefore, in this case, too, it is possible to obtain a spinning solution for producing a PVA fiber having a high saponification degree, from a commercially available PVA having a commercial saponification degree.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing by way of example the relationship between the amount of addition of an alkaline ingredient and the saponification degree of an undrawn fiber obtained as a final product.

DESCRIPTION OF EMBODIMENTS

Next, embodiments of the invention will be described in detail.

It is understood that in the following examples and comparative examples, values for boil-off shrinkage ratio and thermal shrinkage ratio were determined with respect to 90 cm samples in accordance with JIS L 1013.

First, Examples 1 to 15 which correspond to the first preparation method and spinning method of the invention, together with Comparative Examples 1 to 4, will be explained.

(Example 1; Comparative Example 1)

In Example 1, a PVA having a polymerization degree of 4000 and a saponification degree of 99.45 mol % (with a residual acetyl group of 0.55 mol %) was dissolved in dimethyl sulfoxide to a concentration of 15 wt %. In that case, a solution prepared by dissolving in water 1.0 equivalent of sodium hydroxide relative to the weight of the residual acetyl group was added to the dimethyl sulfoxide, and the PVA was introduced into the mixed solution, which was heated up to 115 °C with stirring so that the PVA was dissolved therein, a spinning solution being thus prepared. In that conjunction, the quantity of water was so adjusted as to be 4 wt. % relative to the total quantity of the spinning solution.

By way of Comparative Example 1, a spinning solution was prepared in the same way as Example 1, except that no addition was made of sodium hydroxide. In this case, too, the quantity of water was so adjusted as to be 4 wt. % relative to the total quantity of the spinning solution.

Each of these spinning solutions was discharged at 100 °C through a spinneret having 300 holes of 0.3 mm each in hole diameter into a methanol coagulating bath at room temperature according to the dry/wet spinning process. Then, coagulated filaments were washed with methanol while being taken up, the dimethyl sulfoxide present in the filaments being thus removed. Subsequently, a lubricant was applied and drying was effected. Thus, an undrawn fiber was obtained.

Measurements were made with the undrawn fiber obtained in respect of their respective saponification degrees and polymerization degrees. The undrawn fiber of Example 1 had a saponification degree of 99.97 mol % and a polymerization degree of 3970, whereas the undrawn fiber of Comparative Example 1 had a saponification degree of 99.45 mol % and a polymerization degree of 3980. This witnessed that the undrawn fiber of Example 1 had a sufficiently high saponification degree in contrast to the undrawn fiber of Comparative Example 1.

These undrawn fibers were hot-drawn to a drawing ratio of 17.7 by using a supply roll and a take-up roll, with their surface temperatures set at 80 °C and 170 °C respectively, and a hot air oven disposed between the rolls and having an inlet temperature of 160 °C. and an outlet temperature of 220 °C. As a result, PVA fibers were obtained.

The PVA fiber of Example 1, as obtained from the spinning solution incorporating sodium hydroxide, exhibited good hot water resistance, with a boil-off shrinkage ratio registered at 1.42 %. In contrast to this, the PVA fiber of Comparative Example 1, as obtained from the spinning solution prepared without addition of sodium hydroxide, was found very unsatisfactory in hot water resistance, with a boil-off shrinkage ratio registered only at 68.2 %.

(Example 2; Comparative Example 2)

In Example 2, a PVA having a polymerization degree of 3300 and a saponification degree of 99.21 mol % (with a residual acetyl group of 0.79 mol %) was dissolved in dimethyl sulfoxide to a concentration of 17 wt %. In that case, a solution prepared by dissolving in methanol 1.25 equivalents of potassium hydroxide relative to the weight of the residual acetyl group was added to the dimethyl sulfoxide, and the PVA was introduced into the mixed solution, which was heated up to 115 °C with stirring so that the PVA was dissolved therein, a spinning solution being thus prepared. In that conjunction, the quantity of methanol was so adjusted as to be 2 wt. % relative to the total quantity of the spinning solution.

By way of Comparative Example 2, a spinning solution was prepared in the same way as Example 2, except that no addition was made of potassium hydroxide. In this case, too, the quantity of methanol was so adjusted as to be 2 wt. % relative to the total quantity of the spinning solution.

Each of these spinning solutions was discharged at 100 °C through a spinneret having 172 holes of 0.4 mm each in hole diameter into a methanol coagulating bath at room temperature according to the dry/wet spinning process. Then, coagulated filaments were washed with methanol while being taken up, the dimethyl sulfoxide present in the filaments being thus removed. Subsequently, a lubricant was applied and drying was effected. Thus, an undrawn fiber was obtained.

Measurements were made with the undrawn fibers obtained in respect of their respective saponification degrees and polymerization degrees. The undrawn fiber of Example 2 had a saponification degree of 99.98 mol % and a polymerization degree of 3280, whereas the undrawn fiber of Comparative Example 2 had a saponification degree of 99.20 mol % and a polymerisation degree of 3270. This witnessed that the undrawn fiber of Example 2 had a sufficiently high saponification degree in contrast to the undrawn fiber of

Comparative Example 1.

Then, these undrawn fibers were hot-drawn to a drawing ratio of 18.3 by using a supply roll and a take-up roll, with their surface temperatures set at 80 °C and 170 °C respectively, and a hot air oven disposed between the rolls and having an inlet temperature of 160 °C and an outlet temperature of 220 °C. As a result, PVA fibers were obtained.

The PVA fiber of Example 2, as obtained from the spinning solution incorporating potassium hydroxide, exhibited good hot water resistance, with a boil-off shrinkage ratio of 1.22 %. Whilst, with the PVA fiber of Comparative Example 2, as obtained from the spinning solution prepared without addition of potassium hydroxide, measurement of its boil-off shrinkage ratio was tried, but fiber fusion occurred and the measurement could not be made.

(Examples 3 to 7)

For the preparation of a spinning solution by dissolving the PVA as used in Example 1 in dimethyl sulfoxide to a concentration of 15 wt. %, a solution prepared by dissolving in water 0.2 equivalent (Example 3); 0.5 equivalent (Example 4); 0.8 equivalent (Example 5); 1.2 equivalents (Example 6); 1.7 equivalents (Example 7) of sodium hydroxide relative to the weight of the residual acetyl group of the PVA, was respectively added to the dimethyl sulfoxide. The PVA was introduced into respective mixed solution, which was heated up to 115 °C with stirring so that the PVA was dissolved therein, a spinning solution being thus prepared. In that conjunction, the quantity of water was so adjusted as to be 5 wt. % relative to the total quantity of the spinning solution.

The respective spinning solution so prepared was dry/wet spun into an undrawn fiber in the same way as in Example 1. Then, the fiber was drawn in the same way as in Example 1. In Table 1 are shown saponification and polymerization degrees of the undrawn fibers obtained, as well as boil-off shrinkage and thermal shrinkage ratios of the drawn fibers. The relationships between alkaline additions and saponification degrees with respect to undrawn fibers are shown in Fig. 1 wherein the measurement results of Example 1 are also covered.

Table 1

	Example 3	Example 4	Example 5	Example 6	Example 7
Amount of Alkali (equivalent)	0.2	0.5	0.8	1.2	1.7
Saponification degree (mol %)	99.53	99.72	99.83	99.97	99.98
Polymerization degree	4000	4000	3990	4000	4000
Boil-off shrinkage ratio (%)	3.51	1.98	1.42	1.23	1.17
Thermal shrinkage ratio (%)	1.82	1.24	1.40	1.07	1.02

As is apparent from Fig. 1, against the amount of sodium hydroxide of up to 1.3 equivalents of the residual acetyl group of PVA, the saponification degree of the PVA increased in proportion as the amount of sodium hydroxide increased. However, as the amount of sodium hydroxide exceeded 1.3 equivalents, the saponification degree virtually levelled off.

As is clearly seen from Table 1, PVA fibers obtained in Examples 3 to 7 exhibited good hot water resistance without exception. In particular, PVA fibers obtained in Examples 4 to 7, wherein the amount of sodium hydroxide was at least 0.5 equivalent, showed very good heat resistance, with a boil-off shrinkage ratio of less than 2 %.

(Example 8)

A PVA having a polymerization degree of 3300 and a saponification degree of 99.64 mol % (with 0.36 mol % of a residual acetyl group) was impregnated by spraying with an aqueous solution in which was dissolved 1.1 equivalents of sodium hydroxide relative to the quantity of the residual acetyl group. The PVA was dissolved in dimethyl sulfoxide to a concentration of 17 wt. %, a spinning solution being thereby prepared. In this case, the quantity of water was so adjusted as to be 7 wt. % relative to the total weight of the spinning solution.

The spinning solution was dry/wet spun through a spinneret having 100 holes of 0.5 mm diameter each into a methanol coagulating bath, and thus an undrawn fiber was obtained. The undrawn fiber was drawn into a PVA fiber.

The undrawn fiber obtained had a saponification degree of as high as 99.99 mol %, and the drawn fiber had good boil-off shrinkage ratio of 1.12 %.

(Example 9; Comparative Example 3)

A PVA having a polymerization degree of 4000 and a saponification degree of 99.45 mol % (with 0.55 mol % of residual acetyl group) was dissolved in dimethyl sulfoxide to a concentration of 15 wt. %, a spinning solution being thereby prepared.

The spinning solution was spun into an undrawn fiber according to the dry/wet spinning process. In this case, spinning was carried out while an aqueous solution of sodium hydroxide as adjusted to a concentration of 2.4 wt. % was loaded into a transfer pipe for the spinning solution at the rate of 4.9 g/minute against the discharge rate of 160 g/minute of the spinning solution. Then, the coagulated filaments were washed with methanol while being taken up, whereby the dimethyl sulfoxide present in the filaments was removed. Subsequently, a lubricant was applied and drying was effected. Thus, an undrawn fiber was obtained.

In this case, the amount of sodium hydroxide was 1.0 equivalent relative to weight of the residual acetyl group of the PVA, and the quantity of water was 3 wt. % relative to the quantity of the spinning solution.

As Comparative Example 3, spinning was carried out while water, instead of the aqueous solution of sodium hydroxide, was added according to the same procedure as Example 9, and an undrawn fiber was thus obtained.

Measurements were made with the undrawn fibers obtained in respect of their respective saponification degrees and polymerization degrees. The undrawn fiber of Example 9 had a saponification degree of 99.91 mol % and a polymerization degree of 3990, whereas the undrawn fiber of Comparative Example 3 had a saponification degree of 99.45 mol % and a polymerization degree of 3980. This witnessed that the undrawn fiber of Example 9 had a sufficiently high saponification degree in contrast to the undrawn fiber of Comparative Example 3.

These undrawn fibers were hot-drawn to a drawing ratio of 17.7 by using a supply roll and a take-up roll, with their surface temperatures set at 80°C and 170°C respectively, and a hot air oven disposed between the rolls and having an inlet temperature of 160°C and an outlet temperature of 220°C. As a result, PVA fibers were obtained.

The PVA fiber of Example 9, as obtained from the spinning solution incorporating sodium hydroxide, exhibited good hot water resistance, with a boil-off shrinkage ratio registered at 1.49 %. In contrast to this, the PVA fiber of Comparative Example 3, as obtained from the spinning solution while water only was added thereto, was found very unsatisfactory with a boil-off shrinkage ratio of 68.2 % only.

(Example 10; Comparative Example 4)

A PVA having a polymerization degree of 3300 and a saponification degree of 99.21 mol % (with 0.79 mol % of residual acetyl group) was dissolved in dimethyl sulfoxide to a concentration of 17 wt. %, a spinning solution being thereby prepared.

The spinning solution was spun into an undrawn fiber according to the dry/wet spinning process. In this case, spinning was carried out while a methanol solution of potassium hydroxide as adjusted to a concentration of 3.0 wt. % was loaded into a transfer pipe for the spinning solution at the rate of 6.8 g/minute against the discharge rate of 120 g/minute of the spinning solution. Then, the coagulated fiber was washed with methanol while being taken up, whereby the dimethyl sulfoxide present in the thread was removed. Subsequently, a lubricant was applied and drying was effected. Thus, an undrawn fiber was obtained.

In this case, the amount of potassium hydroxide was 1.0 equivalent relative to the weight of the residual acetyl group of the PVA, and the quantity of methanol was 5.5 wt. % relative to the quantity of the spinning solution.

5 As Comparative Example 4, spinning was carried out while methanol, instead of the methanol solution of potassium hydroxide, was added according to the same procedure as Example 10, and an undrawn fiber was obtained.

Measurements were made with the undrawn fibers obtained in respect of their respective saponification degrees and polymerization degrees. The undrawn fiber of Example 10 had a saponification degree of 99.96 mol % and a polymerization degree of 3270, whereas the undrawn fiber of Comparative Example 4
10 had a saponification degree of 99.20 mol % and a polymerization degree of 3270. This witnessed that the undrawn fiber of Example 10 had a sufficiently high saponification degree in contrast to the undrawn fiber of Comparative Example 4.

These undrawn fibers were hot-drawn to a drawing ratio of 18.1 by using a supply roll and a take-up roll, with their surface temperatures set at 80°C and 170°C respectively, and a hot air oven disposed
15 between the rolls and having an inlet temperature of 160°C and an outlet temperature of 220°C. As a result, PVA fibers were obtained.

The PVA fiber of Example 10, as obtained from the spinning solution while a methanol solution of potassium hydroxide was added thereto, exhibited good hot water resistance, with a boil-off shrinkage ratio of 1.29 %. Whilst, with the PVA fiber of Comparative Example 4, as obtained from the spinning solution
20 while only methanol was added thereto, measurement of its boil-off shrinkage ratio was tried, but fiber fusion occurred and the measurement could not be made.

(Examples 11 to 15)

25 The same PVA as used in Example 9 was dissolved in dimethyl sulfoxide to a concentration of 15 wt. % in a tank, whereby a spinning solution was prepared. Subsequently, a solution prepared by dissolving in water 0.2 equivalent (Example 11); 0.6 equivalent (Example 12); 0.9 equivalent (Example 13); 1.1 equivalents (Example 14); 1.9 equivalents (Example 15) of sodium hydroxide, relative to the weight of the residual acetyl group of the PVA within the tank, was respectively added to the spinning solution, followed
30 by stirring. In that case, the quantity of water was so adjusted as to be 5 wt. % relative to the quantity of the spinning solution.

The respective spinning solution was dry/wet spun into an undrawn fiber in the same way as in Example 9. Then, the fiber was drawn in the same way as in Example 9. In Table 2 are shown saponification and polymerization degrees of the undrawn fibers obtained, as well as boil-off shrinkage and
35 thermal shrinkage ratios of the drawn fibers.

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Table 2

	Example 11	Example 12	Example 13	Example 14	Example 15
Amount of Alkali (equivalent)	0.2	0.8	0.9	1.1	1.9
Saponification degree (mol %)	99.51	99.83	99.89	99.96	99.97
Polymerization degree	4000	4000	4000	4000	4000
Boil-off shrinkage ratio (%)	3.51	1.97	1.32	1.21	1.18
Thermal shrinkage ratio (%)	1.71	1.54	1.44	1.03	1.04

As is clearly seen from Table 2, PVA fibers obtained in Examples 11 to 15 exhibited good hot water resistance without exception. In particular, PVA fibers obtained in Examples 12 to 15, wherein the amount of sodium hydroxide was not less than 0.8 equivalent, showed very good heat resistance, with a boil-off shrinkage ratio as low as less than 2 %.

Next, Examples 16 to 24, which correspond to the second preparation method of the invention, will be explained, together with Comparative Examples 5 and 6 given for comparison purposes.

(Example 16; Comparative Examples 5 and 6)

A spinning solution was prepared by dissolving a PVA having a polymerization degree of 4000 and a saponification degree of 99.45 mol % (with 0.55 mol % of residual acetyl group) in dimethyl sulfoxide to a concentration of 15 wt. %. During this stage, a solution prepared by dissolving in water 2.0 equivalents of sodium hydroxide relative to the weight of the residual acetyl group was added to the dimethyl sulfoxide, and the PVA was introduced into the mixed solution, which was heated up to 60 °C under agitation. The PVA-introduced solution was kept intact for one hour, to which was then added 1.0 equivalent of acetic acid relative to the weight of the residual acetyl group of the PVA. This solution was again heated up to 115 °C, at which the PVA was dissolved, a spinning solution being thus prepared.

This spinning solution was discharged at 100 °C through a spinneret having 172 holes of 0.4 mm each in hole diameter into a methanol coagulating bath at room temperature according to the dry/wet spinning process. Then, coagulated filaments were washed with methanol while being taken up, the dimethyl sulfoxide present in the filaments being thus removed. Subsequently, a lubricant was applied and drying was effected. Thus, an undrawn fiber of Example 16 was obtained.

For purposes of comparison, dry/wet spinning was similarly carried out using a spinning solution which was prepared in the same way as in Example 16 except that no addition was made of sodium hydroxide and acetic acid (Comparative Example 5), and a spinning solution which was prepared in the same way as in Example 16 except that no addition was made of acetic acid (Comparative Example 6), and thus undrawn fibers were obtained.

Measurements were made with these undrawn fibers in respect of their respective saponification degrees and polymerization degrees. The undrawn fiber of Example 16 had a saponification degree of 99.96 mol % and a polymerization degree of 4000, showing good improvement in saponification degree.

Whilst, the undrawn fiber of Comparative Example 5 had a saponification degree of 99.45 mol % and a polymerization degree of 3990, showing that the saponification degree remained low. The undrawn fiber of Comparative Example 6 had a saponification degree of 99.97 mol % and a polymerization degree of 3560, showing good improvement in saponification degree but considerable decrease in polymerization degree. It was also observed that the undrawn fiber of Comparative Example 6 was colored dark brown.

These undrawn fibers were hot-drawn to a drawing ratio of 17.5 by using a supply roll and a take-up roll, with their surface temperatures set at 80 °C and 170 °C respectively, and a hot air oven disposed between the rolls and having an inlet temperature of 160 °C and an outlet temperature of 220 °C. As a result, PVA fibers were obtained.

The PVA fiber of Example 16, as obtained from the spinning solution incorporating sodium hydroxide and acetic acid, exhibited good hot water resistance, with a boil-off shrinkage ratio registered at 1.45 %. Whilst, the PVA fiber of Comparative Example 5, as obtained from the spinning solution prepared without addition of sodium hydroxide and acetic acid, was found very unsatisfactory, with a boil-off shrinkage ratio of 51.7 %. The PVA fiber of Comparative Example 6, as obtained from the spinning solution prepared with addition of sodium hydroxide only, had good heat resistance, with a boil-off shrinkage ratio of 1.42 %, but was found as having become colored.

(Examples 17 to 19)

A spinning solution was prepared by dissolving a PVA having a polymerization degree of 3300 and a saponification degree of 99.21 mol % (with 0.79 mol % of residual acetyl group) in dimethyl sulfoxide to a concentration of 17 wt. %. During this stage, a solution prepared by dissolving in methanol 3.0 equivalents of potassium hydroxide relative to the weight of the residual acetyl group of the PVA was added to the dimethyl sulfoxide, and the PVA was introduced into the mixed solution, which was heated up to 70 °C under agitation. The PVA-introduced solution was kept intact for 40 minutes, to which was then added 2.9 equivalents of hydrochloric acid relative to the weight of the initial residual acetyl group of the PVA. This solution was again heated up to 105 °C to allow the PVA to be dissolved therein, whereby a spinning solution of Example 17 was prepared.

In Example 18, potassium hydroxide was added in the same quantity as in Example 17 and the solution was kept intact at 30 °C for 3 minutes. Then, hydrochloric acid of the same quantity as in Example 17 was added, which solution was heated up to allow the PVA to be dissolved therein. Thus, a spinning solution was prepared. In Example 19, potassium hydroxide was added in the same quantity as in Example 17, which was kept intact at 90 °C for 5 hours. Then, hydrochloric acid of the same quantity as in Example 17 was added, which solution was heated up to allow the PVA to be dissolved therein. A spinning solution was thus prepared.

Each of these spinning solutions was discharged at 105 °C through a spinneret having 300 holes of 0.3 mm each in hole diameter into a methanol coagulating bath at room temperature according to the dry/wet spinning process. Then, coagulated filaments were washed with methanol while being taken up, the dimethyl sulfoxide present in the filaments being thus removed. Subsequently, a lubricant was applied and drying was effected. Thus, an undrawn fiber was obtained.

Measurements were made with these undrawn fibers in respect of their respective saponification and polymerization degrees. The undrawn fiber of Example 17 had a saponification degree of 99.99 mol % and a polymerization degree of 3280, showing good improvement in saponification degree and virtually no decrease in polymerization degree. The undrawn fiber of Example 18 had a saponification degree of 99.54 mol % and a polymerization degree of 3290, showing only slight improvement in saponification degree. The undrawn fiber of Example 19 had a saponification degree of 99.99 mol %, showing good improvement, but showed a decrease in polymerization degree to 2940. It was also observed that this undrawn fiber of Example 19 had become slightly colored brown.

Then, these undrawn fibers were hot-drawn to a drawing ratio of 17.9 by using a supply roll and a take-tip roll, with their surface temperatures set at 85 °C and 180 °C respectively, and a hot air oven disposed between the rolls and having an inlet temperature of 170 °C and an outlet temperature of 230 °C. As a result, PVA fibers were obtained.

The PVA fiber obtained from the spinning solution of Example 17 exhibited good hot water resistance, with a boil-off shrinkage ratio registered at 1.48 %. The PVA fiber obtained from the spinning solution of Example 18 showed a boil-off shrinkage ratio of 9.85 % or a somewhat high value. The PVA fiber obtained from the spinning solution of Example 19 exhibited good boil-off shrinkage ratio of 1.44 %, but was found as having become slightly colored.

(Example 20)

A PVA having a polymerization degree of 3300 and a saponification degree of 99.64 mol % (with 0.36 mol % of the weight of a residual acetyl group) was impregnated by spraying with an aqueous solution in which was dissolved 1.5 equivalents of sodium hydroxide relative to the weight of the residual acetyl group. The PVA was introduced into dimethyl sulfoxide to a concentration of 17 wt. %, which was heated up to 50 °C under agitation and was then kept intact for 40 minutes.

Then, there was added 0.4 equivalent of phosphoric acid relative to the initial weight of the residual acetyl group of the PVA. Then, the PVA-introduced solution was heated up to 105 °C to allow the PVA to be dissolved therein. A spinning solution was thus prepared.

The spinning solution was discharged into a methanol coagulating bath through a spinneret having 100 holes of 0.5 mm hole diameter each, whereby an undrawn fiber was obtained. This undrawn fiber was then hot drawn to produce a PVA fiber.

The undrawn fiber obtained had a saponification degree of 99.99 mol %. The stretched fiber exhibited good hot water resistance, with a boil-off shrinkage ratio of 1.12 %.

(Examples 21 to 24)

For the preparation of a spinning solution by dissolving the PVA as used in Example 16, in dimethyl sulfoxide to a concentration of 15 wt. %, a solution prepared by dissolving in water 1.2 equivalents (Example 21); 2.5 equivalents (Example 22); 4.5 equivalents (Example 23); 6.0 equivalents (Example 24) of sodium hydroxide relative to the weight of the residual acetyl group of the PVA, was respectively added to the dimethyl sulfoxide. The PVA was introduced into respective mixed solution, followed by heating up to 60 °C with stirring. The respective PVA-introduced solution was kept intact for 1.5 hours, and then to the solution was added 0.2 equivalent (Example 21); 1.5 equivalents (Example 22); 3.5 equivalents (Example 23); 5.0 equivalents (Example 24) of acetic acid relative to the initial weight of the residual acetyl group of the PVA. Subsequently, the acetic acid-added solution was heated up to 120 °C. to allow the PVA to be dissolved therein. The spinning solution was thus prepared.

The respective spinning solution so prepared was dry/wet spun into an undrawn fiber in the same way as in Example 16. Further, the undrawn fiber was hot-drawn in the same way as in Example 16. In Table 3 are shown saponification and polymerization degrees of the respective undrawn fibers obtained, as well as boil-off shrinkage and thermal shrinkage ratios of the respective drawn fibers.

Table 3

	Example 21	Example 22	Example 23	Example 24
Amount of Alkali (equivalent)	1.2	2.5	4.5	6.0
Saponification degree (mol %)	99.88	99.97	99.99	99.98
Polymerization degree	4000	4000	3990	3970
Boil-off shrinkage ratio (%)	2.41	1.38	1.41	1.27
Thermal shrinkage ratio (%)	1.63	1.25	1.29	1.12

As is apparent from Table 3, all the PVA fibers obtained in Examples 21 to 24 had good hot-water resistance, with their respective boil-off shrinkage ratios of lower than 3 %.

Claims

1. A method for the preparation of a polyvinyl alcohol-based spinning solution which comprises dissolving polyvinyl alcohol in a solvent, and adding an alkaline ingredient to, and causing the same to be dissolved in the solvent and/or polyvinyl alcohol.
2. A method for the preparation of a polyvinyl alcohol-based spinning solution as set forth in claim 1, wherein the amount of the alkaline ingredient is at least 0.1 equivalent but at most 2.0 equivalents of the amount of a residual acetyl group of the polyvinyl alcohol.

3. A method of spinning a polyvinyl alcohol fiber which comprises dissolving polyvinyl alcohol in a solvent thereby to prepare a spinning solution, adding an alkali solution to the spinning solution, and spinning fibers from the alkali-mixed spinning solution.
- 5 4. A method for spinning a polyvinyl alcohol fiber as set forth in claim 3, wherein the amount of the alkali solution added is at least 0.8 equivalent but at most 1.3 equivalents of the amount of a residual acetyl group of the polyvinyl alcohol.
- 10 5. A method for the preparation of a polyvinyl alcohol-based spinning solution which comprises dissolving polyvinyl alcohol under heating in a solvent, adding an alkaline ingredient to the solvent and/or polyvinyl alcohol to form a polyvinyl alcohol / solvent / alkali mixture, thereby saponifying a residual acetyl group of the polyvinyl alcohol, then adding an acid ingredient to the mixture, and effecting heating.
- 15 6. A method for the preparation of a polyvinyl alcohol-based spinning solution as set forth in claim 5, wherein the amount of the alkaline ingredient is at least 0.3 equivalent but at most 5.0 equivalents of the amount of a residual acetyl group of the polyvinyl alcohol.
- 20 7. A method for the preparation of a polyvinyl alcohol-based spinning solution as set forth in claim 5 or 6, wherein an acid ingredient is added in such a way that the amount of the acid ingredient is at most one equivalent of the alkaline ingredient.

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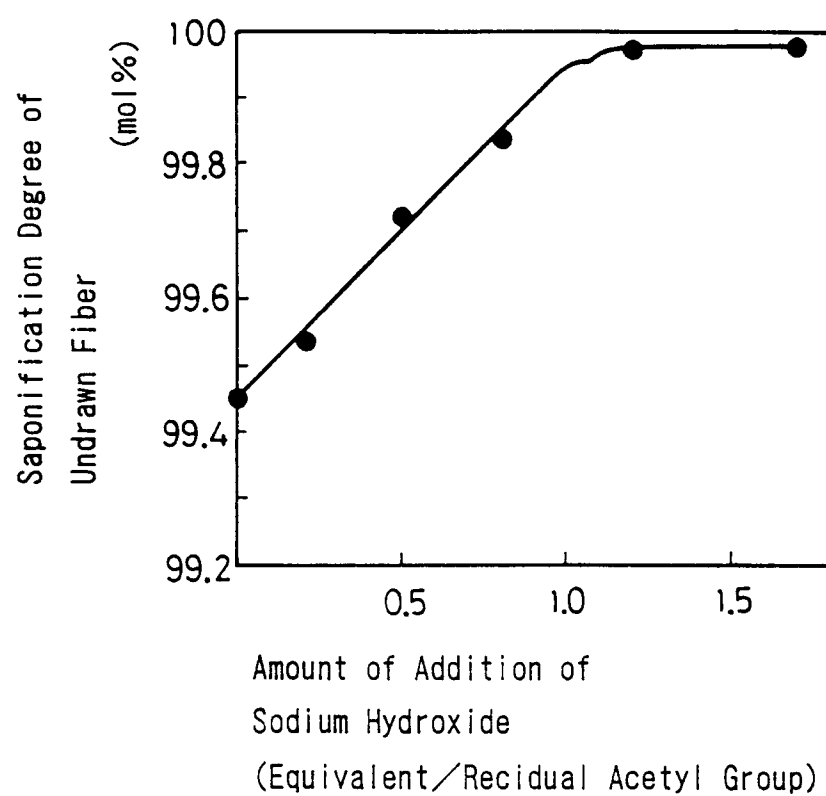
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FIG. 1





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EUROPEAN SEARCH REPORT

Application Number
EP 94 20 3761

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	PATENT ABSTRACTS OF JAPAN vol. 015 no. 173 (C-0828) ,2 May 1991 & JP-A-03 040808 (KURARAY CO LTD) 21 February 1991, * abstract *	
A	---	
A	PATENT ABSTRACTS OF JAPAN vol. 015 no. 173 (C-0828) ,2 May 1991 & JP-A-03 040807 (KURARAY CO LTD) 21 February 1991, * abstract *	
A	---	
A	EP-A-0 496 376 (UNITIKA LTD)	
A	---	
A	EP-A-0 338 534 (KURARAY CO)	
A	---	
A	EP-A-0 146 084 (TORAY INDUSTRIES)	
D	& US-A-4 698 194	
D	& US-A-4 603 083	
A	---	
A	EP-A-0 105 169 (ALLIED CORP)	
D	& US-A-4 599 267	

The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
THE HAGUE	10 April 1995	Tarrida Torrell, J
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