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METHOD OF MANUFACTURING FLAT VISCOSE FIBERS

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The present invention relates to a method of manufacturing tubular and flat viscose fibers having lusters and excellent self-bonding properties. The method is characterized in that a viscous containing water swelling high molecular weight substance of 2 to 50% based on the viscose and about 0.05 to 2% of viscose modifier (hereinafter shown by example) based on the viscose and having a great number of fine bubbles dispersed therein is spun into a spinning bath containing sulfuric acid alone or sulfuric acid and sulfates.

Viscose fibers have recently been used in large quantity for the purpose of paper making and non-woven fabrics, however, ordinary viscose fibers being different from wooden fibers and bast fiber, are difficult to fibrillate by beating. Also, the adhesivity between fibers can not be developed by the action of heat and water as the soluble vinylon binder fiber so that it is difficult to produce papers using only the viscose fibers, and it has been necessary to add some other binder.

In order to solve the above difficulties it has recently been found that hollow flattened viscose fibers, manufactured by adding a suitable foaming agent and by a special manufacturing condition, can be used for making paper without adding any binder. It is believed that the reason for this capability lies in the fibers being tightly bonded with each other by flattening the configuration when they are wetted and formed into a thin layer, the thin layers being subsequently dried from the water existing between fibers. It is also believed that by bringing each fiber together more intimately causes "Van der Waals" bond or hydrogen bond between the cellulose molecules constituting the fiber, thereby providing papers of sufficient strength by the intermolecular bonding force. The hollow flat viscose fibers obtained by known processes require very restrictive manufacturing conditions such that sufficiently flat viscose fibers are difficult to obtain and, consequently a paper of sufficient strength can not be obtained. Moreover, when the monofilament denier becomes large, the flatness becomes gradually reduced, and even sufficiently flat, though the bonding property of fibers with each other becomes insufficient for paper making because each fiber cannot come near enough to adjacent fibers to allow the intermolecular bonding force of cellulose to act between the fibers. Accordingly, such fibers alone fail to make papers or non-woven fabrics of good properties.

In heretofore known hollow flat viscose fibers, if the monofilament denier is more than 3 denier, the average thickness of the flat part usually becomes more than 4μ and the self bonding property between such fibers is almost or completely lost. Paper formed solely of such heretofore known hollow flat viscose fibers, when once wetted, loses the inert-fibrous binding force and the fiber is dispersed into the water.

In comparison, the method of the present invention not only produces, comparatively easily, tubular and flat viscose fibers but also a fiber of excellent flatness. When the tubular flat viscose fiber made by the method of the invention is used as the raw material for making paper it enables the production of paper which has excellent wetproof properties and luster and also has sufficient tensile

strength, even with a thick monofilament denier, without adding any other binder and it enables to perfectly prevent the reduction of self-bonding property and paper making ability of large denier fibers which had been basic disadvantages of conventional hollow flat viscose fibers.

The "water swelling high molecular weight substances" referred to above for the present invention include, for instance, polyvinyl alcohol (abridged as PVA hereafter) which is swelled by water at room temperature but soluble in warm water or hot water and PVA derivatives, or cellulose derivatives which swell in water and dissolve in alkali, such as hemi cellulose, methyl cellulose, ethyl cellulose, cyanoethyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose and the like.

The "tubular flat viscose fiber" of the invention refers to viscose fiber having at least 60% of its total length in a condition of tightly adhered inner surfaces almost without hollow portion and the width of the cross section of the fiber is at least 5 times the thickness. The content of the water swelling high molecular weight substance in the fiber depend upon the kind, object and fineness etc. of the fiber, but it is usually desirable to have an amount from 2 to 50% of the amount by weight of the regenerated cellulose in the fiber, and preferably, 5 to 30%.

The flat viscose fibers obtained by mixed spinning of the water swelling high molecular weight substance have a greater flatness, and in case of large fiber denier, excellent flatness and good self-adhesivity is obtainable so that it is unnecessary to add any other adhesive agent or binding fibers for making paper or non-woven fabrics.

In order for the fiber to have good luster and self-bonding properties, the internal surfaces of the tubular flattened portion should be almost perfectly adhered, without gap, and the upper and rear surfaces should be smooth and substantially parallel. Also, the width of the cross section of the fiber should have at least 5 times the thickness, preferably more than 10 times to several times 10, and the tubular flattened portion should be at least 60% of the total length of fiber. As the percentage increases the luster and self-bonding properties improve, making it possible to obtain a thin paper having a large breaking length with luster-like cellophane. However, according to the purpose for the fiber, it is sometimes preferable to mix in 20 to 30% solid fiber. For instance, if it is desired to obtain a paper having high tear strength, it is better to use fiber having 20 to 30% of its total length unflattened or to mix in 20 to 30% of regular unflattened fiber to fiber which is 100% flattened portions. The fiber of the invention can be obtained by spinning a viscose containing a water swelling high molecular weight substance of 2 to 50% based on the cellulose in the viscose and a viscose modifier of 0.05 to 2% based on the viscose and having many fine bubbles dispersed therein, into a bath containing sulfuric acid only or containing sulfuric acid and sulfate.

With less than 2% of the content of water swelling high molecular weight substance in the viscose, substantially no improvement of flatness is recognized; and when the content is more than 50%, the tenacity of the fiber is reduced and the effect of improving the flatness reaches substantially its maximum so that adding more than 50% water swelling high molecular substance produces almost no further improvement in the flatness over 50%.

With less than 0.05% of the viscose modifier based on the viscose, flatness cannot substantially be developed; and in the case of more than 20%, the coagulation and regeneration of the cellulose are delayed excessively and the tenacity of the fiber is reduced. Also, the spinning operation becomes difficult and without fine bubbles are not dispersed in the fiber, it is impossible to produce tubular flat fibers. Similarly, with fine bubbles only, and without inclusion of the water swelling high molecular weight substance and viscose modifier, the excellent tubular flat

viscose fibers produced in accordance with the invention can never be obtained.

The term "viscose modifier" refers to a substance to be added in a small quantity to the viscose or spinning bath in order to manufacture strong viscose fibers having so-called all skin structure. Typical viscose modifiers are the following:

(1) Polyoxyalkylene derivatives.—Example: polyethylene glycol, tetraethylene glycol, dimethyl ether.

(2) Aliphatic amines.—Example: cyclohexyl amine, triethanol amine.

(3) Quaternary ammonium salts.—Example: benzyl trimethyl ammonium hydroxide, tetraethyl ammonium bromide.

(4) Polyhydroxypolyamine.—Example: tetrahydroxyethyl, 1,3-diamino-2-phenol.

(5) Dithiocarbamates.—Example: cyclohexyl dithiocarbamate, sodium amyl dithiocarbamate.

Such viscose modifiers are preferably added by dissolving sodium xanthogenate in caustic soda, but it may be added to the viscose after dissolved. Adding 0.05 to 2.0% of the viscose modifier based on the viscose is effective and usually 0.1 to 1% is preferable. The optimum quantity to be added should be determined by the kind of viscose modifier, quantity of dispersed bubbles, composition of viscose and other conditions. The reason why viscose modifiers, which are in the manufacture of strong viscose fibers, are also effective in the manufacture of excellent flat viscose fibers is not yet clear. There are several methods for dispersing a great number of fine bubbles in viscose, the viscose obtained by dissolving sodium xanthogenate contains quite a large number of fine bubbles dispersed therein so that it can be used for this purpose. Furthermore, air or nitrogen gas can be injected into the viscose, and the gas may be dispersed as fine bubbles by using a suitable agitator or colloid mill. The total quantity of the fine bubbles to be dispersed is preferably of 1 to 10% by volume of viscose and the size of bubbles is preferably smaller than the diameter of the spinneret for the spinning.

In carrying out the method of the invention is has been found that by adding a small quantity of a surface active agent to the viscose, splendid tubular flat viscose fibers can be more easily produced, and the precise amount surface active agent to be added depends on its kind and the quantity of viscose modifier added, etc. However, 0.01 to 1% is generally suitable, preferably, 0.05 to 0.5%. In any event, the quantity of surface active agent is usually less than the quantity viscose modifier.

For spinning a viscose containing the water swelling high molecular weight substance and the viscose modifier, with or without a small quantity of surface active agent in addition, and having a great number of fine bubbles dispersed therein, the composition and viscosity of the viscose and spinning bath may be same as in the case of a conventional viscose fiber. And also those conditions which produce high tenacity and high elongation fibers by spinning a viscose with modifier into a high zinc sulfate bath may be used, or those conditions which produce high tenacity, low elongation fiber by spinning a viscose of high polymerization degree into a coagulating bath containing sulfuric acid only may be used.

The fibers obtainable by the method of the invention are not only for use in making papers but also, in general, for non-woven fabrics, cloths, domestic decoration, wall paper and other fibers for building construction.

Example 1

PVA of degree having a polymerization 1,000 was dissolved in hot water and added to caustic soda and carbon disulfide and stirred at 20° C. for 90 minutes to xanthogenize PVA. A PVA-xanthate solution formed in this manner and having a composition 8.5% PVA and 5.0% of alkali and a viscose having a composition of 5.0% alkali and 8.5% cellulose were mixed at a ratio of 30:70 and at the same time polyethylene glycol having a molecular weight of 600 was added to the mixed viscose to a concentration of 1% based on the mixed viscose. While injecting compressed air, the mixture was stirred for 1 hour and a viscose having a great number of fine bubbles dispersed therein was obtained. This viscose at an aging degree of 14 Hottenroth value was spun through a nozzle having 3,000 holes, 0.065 mm. dia. into a coagulation bath consisting of 10% sulfuric acid, 4% zinc sulfate and 21% sodium sulfate at 60° C. and the fiber thus spun was stretched for 40% in a second bath of saturated Glauber's salt solution at 95° C. and wound up at a spinning speed of 50 m./min. The fiber of 1.5 monofilament denier thus obtained consisted of a tubular flat part for about 80% of the total length of the fiber with its inner surfaces substantially perfectly adhered together, and without hollow cavity. The thickness of the cross section of the fiber was 3μ and the width 63μ. The tubular flat fiber obtained from a similar viscose without addition of PVA had a ratio of tubular flat portion to total length of fiber of about 70% and the thickness of the cross section was 3μ in an average and the width 49μ.

Example 2

To the solution of sodium xanthogenate obtained by a conventional process in caustic soda, 6% (based on the cellulose in viscose) of carboxy methyl cellulose and 0.2% (based on the produced viscose) of Turkey red oil were added and agitated at 18° C. for 4 hours to dissolve. The viscose thus obtained and having 8% cellulose and 6% alkali with a great number of small bubbles dispersed therein was spun, without deaerating, at aging degree of 13 salt index into the same coagulation bath as in Example 1, stretched 60% in the second bath, and then wound up at a spinning speed of 40 m./min. a fiber of 1.5 monofilament denier was produced. This fiber consisted of a tubular flat portion having smooth surface and 90% of its total length were perfectly adhered at the inner surfaces and had no hollow cavity and the thickness of its cross section was 3μ, while the width was 90μ.

Example 3

A PVA-xanthate solution having 8.5% PVA and 5.5% alkali produced in a manner similar to Example 1, and a viscose having 8.5% cellulose and 5.5% alkali manufactured by a conventional process were mixed at a ratio of 25:75. At the same time 0.45% polyethylene glycol having molecular weight of 1,500 and 0.1% of non-ionic surface active agent, both based on the viscose, were added and violently agitated for two hours at 20° C. to provide a viscose having many fine bubbles dispersed therein. The viscose, without deaerating at an aging degree of 10 salt index was spun into a coagulation solution consisting of 8% sulfuric acid, 1% zinc sulfate and 24% sodium sulfate at 50° C. and then stretched 40% in a saturated Glauber's salt bath at 95° C. to provide a fiber having 5 monofilament denier, and 5 mm. long. This fiber had tubular flat structure and as a whole had luster. The thickness of the cross section was 7μ and the width 92μ. This fiber, without beating, was directly dispersed into water and without adding any binder, paper was formed by a manual operation and dried by a drier at 105° C. The paper thus obtained had a weight of 56.41 g./m.^{2} breaking length 4.25 km., wet breaking length 0.88 km., and tear factor 108. The tubular flat fibers spun under the same conditions from a viscose not mixed with PVA consisted as a whole of the flat portion having a cross-sectional thickness of 8μ and a width of 87μ, but paper could not be made under the same conditions.

Example 4

Instead of the polyethylene glycol in Example 3, 0.5% cyclohexyl amine was added to the PVA mixed viscose under the same conditions as Example 3. The viscose was spun under the same spinning conditions and produced a fiber having 8 monofilament denier and 5 mm. length.

This fiber had tubular flat structure and luster as a whole, with a cross-sectional thickness of 8μ and width of 104μ. The paper made of this fiber by the same process as in Example 3 had lusters and strength similar to those obtained in Example 3. On the other hand, the fiber obtained from the similar viscose without mixing PVA had completely tubular flat structure but paper could not be produced with this fiber alone.

Example 5

Sodium xanthogenate obtained by adding 50% carbon disulfide to a little aged alkali cellulose and sulfidized for 3 hours at 25° C. was dissolved in caustic soda and, at the same time, 0.8% (based on the produced viscose) Atlas G 3780 (Dendro-taroamine made by Atlas Company, U.S.A) was added and dissolved by stirring at 15° C. for 3 hours to provide a viscose having 5.3% cellulose and 4% alkali. PVA-xanthate solution containing 5.3% PVA and 4% alkali was prepared separately and mixed to the above viscose to make PVA 10% of cellulose and stirred for 1 hour at 15° C. The PVA mixed viscose, without deaerating, in an unripened state was spun into a coagulation bath consisting of 5% sulfuric acid at a temperature of 35° C. and stretched 40% in a second bath consisting of saturated Glauber's salt solution at 95° C. A monofilament of 1.5 denier thus obtained consisted of a tubular flat portion for 70% of its total length and papers having lusters was obtained by using this fiber alone.

What I claim is:

1. A method of manufacturing tubular flat viscose fiber which comprises extruding the viscose containing 2 to 50% by weight based on the cellulose in the viscose of a water swelling high molecular substance selected from the group consisting of polyvinyl alcohol, polyvinyl alcohol derivatives and cellulose derivatives and 0.05 to 2% by weight based on the viscose of a viscose modifier selected from the group consisting of polyoxyalkylene derivatives, aliphatic amines, quaternary ammonium salts, dithiocarbamates and hydroxypolyamines and having a large number of fine bubbles dispersed therein, into a coagulation bath containing sulfuric acid and sulfate.

2. In the method of manufacturing tubular flat viscose fiber which includes extruding the viscose containing a viscose modifier selected from the group consisting of polyoxyalkylene derivatives, aliphatic amines, quaternary ammonium salts, dithiocarbamates and hydroxypolyamines and having a large number of fine bubbles dispersed therein into a coagulation bath, the improvement which comprises adding to the viscose 2 to 50% by weight based on the cellulose in the viscose, of a water swelling high molecular weight substance selected from the group consisting of polyvinyl alcohol, polyvinyl alcohol derivatives and cellulose derivatives.

3. The improvement in accordance with claim **3** wherein said water swelling high molecular weight substance is selected from the group consisting of polyvinyl alcohol, hemi-cellulose, methyl cellulose, ethyl cellulose, cyanoethyl cellulose, carboxymethyl cellulose and hydroxyethyl cellulose.

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