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SPINNING PROCESS FOR ARTIFICIAL  
FILAMENTS

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## 1 Claim. (Cl. 18—54)

This invention relates to improvements in a process of producing films, filaments, threads, cords, bristles, ribbons, tubings, bands and similar shaped articles. More particularly it relates to an improvement in a process for forming such articles from polyvinyl alcohol.

By the term "polyvinyl alcohol" as used herein I mean to include in addition to unsubstituted polyvinyl alcohols those polymers wherein a portion of the hydroxyl groups are replaced by formal, butyral, formate, propionate, nitrile, ethylene or other groups, which groups, however, are not present in amounts sufficient to destroy the water-solubility or water-sensitivity of the polymer.

In U. S. Patent No. 2,236,061 (Izard and Kohn) there is disclosed a process of converting aqueous polyvinyl alcohol solution into shaped products which comprises shaping the polyvinyl alcohol into the desired form, thereafter immersing the shaped material in a coagulating bath consisting of an aqueous solution of an inorganic salt having substantially no oxidizing action such as ammonium sulfate, and finally washing the coagulated material with water to remove the inorganic salt therefrom. While this process results in clear, transparent flexible structures which are a marked improvement over the cloudy brittle products which are formed when the previous practice of coagulating the polyvinyl alcohol in a bath of organic water-miscible solvent, such as acetone or alcohol, is followed, still it is not entirely satisfactory from the commercial standpoint for the reason that it is difficult to completely remove the inorganic salts from structures formed by this method by washing with water unless prolonged washing is resorted to, and if the washing step is of a duration sufficient to accomplish the desired complete removal of salts it is generally found that the water also exerts an undesirable swelling action on the polyvinyl alcohol structures. Moreover, the concentration of inorganic salt in the wash water is so low that recovery of the salt for reuse is prohibitively expensive and the commercial attractiveness of the process further suffers as a consequence.

Therefore, an object of this invention is to provide an improved expedient for washing freshly precipitated polyvinyl alcohol structures.

A further object is to provide for the efficient and harmless removal of inorganic salts present in polyvinyl alcohol structures freshly precipitated in an aqueous solution of inorganic salt.

A still further object is to wash freshly precipitated polyvinyl alcohol structures containing

inorganic salt in such fashion that the salt may be easily and economically recovered from the wash liquid for reuse.

These and other objects will more clearly appear hereinafter.

Unexpectedly, I have found that if, in place of water, an aqueous solution of an organic oxy compound from the group consisting of ethyl alcohol, acetone and dioxane is employed to wash polyvinyl alcohol structures freshly precipitated from an aqueous inorganic salt solution such as aqueous ammonium sulfate, the complete removal of the salt is accomplished without injurious effect on the polyvinyl alcohol structure, and in addition, when the salt dissolved in the mixed solvent reaches a certain critical concentration the solvent separates into two layers, one containing mainly organic oxy compound and water which may be immediately reused in the preliminary stages of the washing step without further treatment, and the other being a concentrated solution of the salt in water from which the salt may be easily and economically separated for reuse in the coagulating bath. The small amount of organic oxy compound in this aqueous layer can be easily removed by volatilization and recovered by condensation for reuse.

Accordingly the objects hereinabove stated are realized by my invention which comprises washing precipitated polyvinyl alcohol structures containing residual inorganic salt from the coagulating bath with an aqueous solution of an organic oxy compound of the group consisting of acetone, ethyl alcohol and dioxane, the water and organic oxy compound being so proportioned that the solution exerts substantially no swelling action on the polyvinyl alcohol structures. The washing is continued until the polyvinyl alcohol structure is completely freed from the contaminating salt, and thereafter the structure is dried, e. g. in a current of warm air, and/or is further processed as desired.

A preferred wash solution suitable for the practice of this invention consists of a mixture of equal parts by volume of water and acetone. In its useful range the acetone content may vary between 30-80% by volume. If solutions containing less than 30% acetone are employed, such solutions have a tendency to cause swelling of the polyvinyl alcohol, while if the acetone content is over 80%, the coagulating salt, e. g. ammonium sulfate, is not completely removed. Other solutions which are satisfactory include ethyl alcohol and water, in which the alcohol content is at least 75%, and dioxane and water in the ratio

of three parts of dioxane to two of water. In using the mixed solvents of this invention, it is important to select such concentrations of acetone, ethyl alcohol or dioxane in water as will have no harmful swelling action on the coagulated structure as filaments, threads, films, etc., of polyvinyl alcohol which are slightly swollen tend to lose their strength and are therefore often rendered useless. This property of polyvinyl alcohol is in marked contrast to water-sensitive materials such as threads formed from regenerated cellulose or from cellulose acetate which may be caused to swell slightly without appreciable reduction in tensile strength.

When employing a wash solution consisting of a mixture of acetone and water, it is desirable to subject the polyvinyl alcohol structure, after the inorganic salt has been removed therefrom and before drying, to a final rinse with an acetone-water mixture comprising a high proportion, e. g. 95%, of acetone. The purpose of this step is to insure in the final stages of drying the presence of a relatively high percentage of acetone in the acetone-water mixture whereby the polyvinyl alcohol structure will not be exposed for any appreciable length of time to the action of water alone.

The following examples are given to illustrate specific applications of the invention, but they are in no wise to be considered limitative thereof. Parts and percentage compositions are by weight unless otherwise indicated.

#### Example I

A 20% solution of polyvinyl alcohol (substantially completely saponified polyvinyl acetate) was prepared at a temperature of 75° C. and maintained at this temperature by a surrounding water jacket. This solution was extruded through a spinneret (15 hole 0.006" in diameter) into a 40% solution of ammonium sulfate maintained at a temperature of 52° C. The filaments were led back and forth over free-running rollers for a total bath travel of 200", and were withdrawn from the bath at the rate of 1000" per minute. During coagulation a spinning tension of 52 grams was maintained. The wet filaments containing residual ammonium sulfate were collected on a spinning bobbin, which at the end of the operation was removed, and placed in a bath of 50% acetone and 50% water by volume, and left for a period of several hours. The bobbin was then removed from the bath and further washed by immersing several times in a fresh portion of the acetone-water mixture and was given a final rinse of 95% acetone solution in water, following which the filaments were dried on the bobbin at room temperature. The yarn was transferred to a twisting machine and given a twist of 3 turns per inch. The twisted yarn had a denier of 335, and the dried thread had a tenacity of 1.11 grams per denier. The elongation was 29.4%.

The solution used in the first wash had settled into a bottom layer containing mainly ammonium sulfate and water and a supernatant layer containing mainly acetone and water. These layers were easily separated, the aqueous ammonium sulfate solution being retained for use in the coagulating bath, and the acetone-water solution being retained for reuse in the washing of polyvinyl alcohol yarn.

When samples of this yarn were stretched 50% of their original length, they were found to have a tenacity of 1.19 grams per denier, and an elongation of 7.7%.

When samples of the threads were tested for the presence of water-soluble sulfates, a negative test was obtained showing that complete removal of the ammonium sulfate had been obtained in the washing steps.

#### Example II

A 15% solution of polyvinyl alcohol (fully saponified polyvinyl acetate) was prepared at a temperature of 60° C. This solution was extruded through a multiple-hole spinneret into a saturated solution of ammonium sulfate which was maintained at a temperature of 52° C. The filaments were led back and forth over a free-running roller for a total bath travel of 312" at a spinning tension of 0.11 gram per wind-up denier. The wet yarns containing residual ammonium sulfate were collected on spinning bobbins at the rate of 1000" per minute. After spinning the yarn was reeled into skeins from the wet bobbins, and the skeins were immersed in a tension-free condition in a bath of equal parts by volume of acetone and water. During the immersion period the skeins decreased in length by approximately 50%, and at the same time became finely crimped and wool-like in appearance. After several hours the skeins were removed from the bath, washed free of ammonium sulfate by using a fresh solution of acetone and water, and were given a final rinse of pure acetone. They were allowed to dry in the air at room temperature. The crimp was of a permanent nature and was not removed by processing the yarn through the usual textile operations or by stretching. The used wash solution was treated as in Example I.

When samples of these threads were tested for the presence of soluble sulfates a negative test was obtained.

#### Example III

Threads of polyvinyl alcohol were formed as in Example I. At the end of the spinning operation the spinning bobbin was removed and mounted on a pressure-feed washing chuck. The threads were pressure-washed with a solution of dioxane, 60%, and water, 40% by volume, for a period of 4 hours, and were then dried.

The threads were stretched twice the original length by passing over rolls heated at 150° C. A strong lustrous yarn was obtained which retained its water-soluble character.

A negative test was obtained when these threads were tested for the presence of soluble sulfates.

#### Example IV

A 50% solution of polyvinyl alcohol (fully saponified polyvinyl acetate) was prepared at a temperature of 75° C., and to this was added Aerosol OT (sodium dioctyl sulfosuccinate) in an amount equal to 0.01% of the solution. This solution was cast on a glass plate, and excess solution was removed by a doctor knife.

The plate and film were then immersed in a saturated solution of sodium sulfate maintained at a temperature of 40° C. After a coagulation period of approximately 5 minutes the plate and film were immersed in a 50% by volume of aqueous solution of acetone. After a period of several hours the film was removed from the plate and further washed with fresh portions of the solution. It was then given a final wash with pure acetone. A strong self-sustaining film of polyvinyl alcohol, 0.002" thick, was formed which retained its cast form, was not swollen by the

washing treatment, and was found to contain no coagulating bath salts.

While the invention has been illustrated specifically in connection with aqueous ammonium sulfate as the coagulating bath, it will be understood that other inorganic salts, e. g. sodium sulfate, zinc sulfate, etc., disclosed in U. S. Patent 2,236,061, may be removed from the polyvinyl alcohol structures in accordance with the principles of my invention.

By the term "inorganic salt" is meant the salt of an inorganic base with an inorganic or low molecular weight organic acid, such as those containing less than eight carbon atoms.

My invention enables the production, in continuous fashion, of many polyvinyl alcohol structures such as filaments, yarns, threads, film, tubes, etc., which are clear, transparent, flexible and relatively strong, and which retain their water-solubility unimpaired. Furthermore, the ready recovery of the coagulating salts and organic solvent from the wash liquid presents an

economic advantage which greatly adds to the commercial attractiveness of the particular process of preparing polyvinyl alcohol structures with which the present process is concerned.

All variations and modifications of the invention described hereinabove falling within the spirit thereof are intended to be included within the scope of this invention as defined in the appended claim.

10 I claim:

15 In the process for manufacturing filaments, yarns, threads, films and like structures of polyvinyl alcohol wherein an aqueous solution of polyvinyl alcohol is coagulated in an aqueous solution of ammonium sulfate to form a coagulated polyvinyl alcohol structure containing residual ammonium sulfate, the improved step which comprises washing said coagulated polyvinyl alcohol structure substantially free of said ammonium sulfate with a solution consisting of equal parts  
20 by volume of acetone and water.

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