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ARTIFICIAL FIBROIN THREAD

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9 Claims. (Class 18—54)

Our present invention relates to a new process of manufacturing in a continuous manner long, practically endless, fine threads from the wastes of natural silk by dissolving them and subsequently reprecipitating them in a coagulating bath.

Another object of our invention is to provide a solution of natural silk waste in which the fibroin molecule is practically not decomposed and from which fine threads are obtainable which are equivalent to cultivated natural silk fibers. Additional objects of our invention are the new threads, further objects of our invention relating, for instance, to the precipitating bath and to the method of spinning, will be seen from the detailed specification following hereafter.

The whole crux of our invention can well be exemplified by brief discussion of the prior art. Efforts have been made to dissolve natural silk in organic acids or in hydrochloric acid. By spinning, however, threads from these solutions, hard and brittle products were obtained. The fibroin molecule is decomposed by these solvents, so that these methods did not lead to a satisfactory result.

Considerably better results were obtained by dissolving silk at a raised temperature in neutral, strongly water-soluble salts and by drawing out the viscous mass in threads when the pre-coagulation is complete. Spinning on a factory scale according to the said process is, however, scarcely possible, because the pre-coagulation requires a very long time, viz. ¼ hour and more, and a difficultly perceptible coagulation optimum lies within narrow ranges. Furthermore, the solutions easily separate into their component parts, whereby an extremely viscous mass is produced; in spite of exact observation of the required spinning conditions, often threads of inferior quality or no threads at all are obtained.

By our present invention, all these disadvantages are remedied; one may dissolve natural silk wastes at ordinary temperature with the formation of a viscous mass which is stable for a sufficiently long time and which can be spun without difficulties.

We have found that ortho-phosphoric acid is very well suited as a solvent for natural silk. A solution of wastes of silk in phosphoric acid prepared at room temperature is stable for several hours even at ordinary temperature; at 0° C. its ability of being regenerated is not affected for one day and even more.

In order to obtain a silk thread from this viscous solution, we use a precipitating bath containing an aqueous solution of alkali metal salts of strong acids, for instance a halogen acid, sulfuric acid, phosphoric acid, nitric acid, preferably in the presence of alkali metal salts of weak acids, such as acetic acid or formic acid. Instead of alkali metal salts we may use the corresponding ammonium salts. The salts of a weak acid have the advantage of accelerating the coagulation of the fibroin solution by reacting with the phosphoric acid used as a solvent.

The solidity and softness of the threads may be enhanced when coagulating the fibroin solution in two stages by the action of two subsequent precipitating baths from which the first has a weaker precipitating action on the fibroin solution than the second. The first bath preferably consists in the main of a concentrated solution of an alkali metal salt of a mineral acid. The best result is not obtained if a sodium salt or a potassium salt is individually used, but rather when a mixture of potassium and sodium salts is used. To enhance the coagulating velocity of the precipitating bath a saturated aqueous solution of alkali formate or acetate is added to it in a quantity corresponding to ⅙ to ⅓ of its volume.

Furthermore, formaldehyde may be added to the salt solution forming the first precipitating bath to improve the tenacity of the thread and to increase the spinning velocity. A bath of this composition permits one to spin without difficulty even when the thread to be formed is immersed in the first bath in a length of only 10 to 20 cm.

After having passed the first bath the thread formed is guided immediately in a second bath consisting in the main of a saturated solution of an alkali metal salt of formic acid, acetic acid or other fatty acids, or of a mixture of these salts. We may add a salt of an aliphatic hydroxy acid or an aliphatic acid containing a carbonyl group, for instance lactic acid or pyro-racemic acid. A salt of lactic acid, for instance, prevents recrystallization of the salts contained in the precipitating solution on the threads after having left the bath. Because of this, said salts may likewise be added to the first precipitating bath.

Even after having passed the second precipitating bath, the thread is still water-soluble or at least swellable in water. It becomes water-insoluble after having run a longer space in the air and after having been stretched five- to eightfold of its original length. Then it may be collected on a spool, freed from salt and acid by washing and soaping.

When spinning threads of our fibroin solution through a nozzle provided with a plurality of fine holes, it may occur that the individual fibers stick together. To avoid this disadvantage, we add to the acid fibroin solution a small quantity of an ethereal oil, for instance, turpentine. 0.02 to 0.1 per cent of oil calculated on the quantity of the fibroin solution are sufficient. By addition of the oil the fibroin solution is colored weakly brown, this coloration, however, has no influence on the finished thread. This addition has certain advantages. The individual threads are set free more easily on the spinning nozzle and the capacity of being spun and the uniformity of the threads is enhanced. Furthermore, as mentioned above, the single threads do not stick together and are separated from each other completely by an after-treatment with wetting agents or soap.

The following example serves to illustrate our invention:

1 part of natural silk wastes is dissolved while stirring or kneading in 10 parts of phosphoric acid of 85 per cent strength. Then 0.04 per cent of turpentine, calculated on the quantity of the solution, are added. The viscous, weakly yellowish-brown solution is filtered and freed from air bubbles by centrifuging. This solution is pressed from a cooled storing vessel with or without the use of a spinning pump in the first precipitating bath through a glass nozzle provided for instance with 120 holes of 0.08 mm. diameter. This first precipitating bath contains per liter

	Grams
Sodium chloride	132
Potassium chloride	122
Sodium lactate	21
Potassium lactate	25
Sodium formate	22
Potassium formate	28
Anhydrous formaldehyde	15

This precipitating solution thus contains

	Grams
Hydrochloric acid	142
Lactic acid	34
Formic acid	30

bound by about equal parts of potassium and sodium.

The length of immersion of the thread may be varied between 10 to 80 cm. The bath is kept at room temperature. After having passed the first bath, the thread is guided, suitably over an easily movable roll, in the second bath consisting of a saturated aqueous solution of ammonium formate to which ⅛ of its volume of a concentrated sodium lactate solution has been added. The temperature of this second bath is also room temperature. The length of immersion in this bath is chosen as long as possible, preferably longer than 50 cm. After having left this bath, the thread runs through a space of air of about one or more meters. The drawing speed is so regulated that the thread is at most weakly stretched on its way from the spinning nozzle through the precipitating baths and through the air space. Only after having passed the air space, is the thread stretched, by means of a stretching device, five- to eightfold of its original length by guiding it, for instance, over a plurality of rolls rotating with increased circumferential speed. Then it is collected on a spool, washed, soaped and dried.

In this manner, soft and lustrous threads with an individual titer of one denier and with a dry tenacity up to 2 grams per denier and a wet tenacity more than 1 gram per denier and of an extensibility of about 12 per cent are obtainable.

Our threads show no decomposition of fibroin, they yield all chemical reactions of the genuine fibroin of natural silk and have the same optical behavior in polarized light as natural silk. The X-ray diagram of our threads is not different from that of natural silk. They differ, however, from natural silk by being digested by proteases.

Various modifications and changes in details of the conditions given in the foregoing example are considered to be within the spirit of the invention and the scope of the following claims. The composition of the precipitating baths may be varied within certain limits. As mentioned above, ammonium salts are equivalents of the alkali metal salts and may substitute them in the coagulating liquids. The first precipitating bath may be used for a long time, even after it has dissolved an essential quantity of phosphoric acid.

What we claim is:—

1. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, causing the viscous solution to pass through suitably formed openings to come into contact with a precipitating liquid, and imparting a stretch to the pre-coagulated thread after it leaves the coagulating bath.

2. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, causing the viscous solution to pass through suitably formed openings to come into contact with a liquid comprising a concentrated aqueous solution of an alkali metal salt of a strong mineral acid, and imparting a stretch to the pre-coagulated thread after it leaves the coagulating bath.

3. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, adding an ethereal oil, causing the viscous solution to pass through suitably formed openings to come into contact with a liquid comprising a concentrated aqueous solution of an alkali metal salt of a strong mineral acid, and imparting a stretch to the pre-coagulated thread after it leaves the coagulating bath.

4. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, adding an ethereal oil, causing the viscous solution to pass through suitably formed openings to come into contact with a liquid comprising a concentrated aqueous solution of an alkali metal salt of a strong mineral acid, passing the thread through a second liquid comprising a concentrated aqueous solution of an alkali metal salt of a lower fatty acid, and imparting a stretch to the thread after it leaves the second precipitating bath.

5. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, adding an ethereal oil, causing the viscous solution to pass through suitably formed openings to come into contact with a liquid comprising a concentrated solution of a potassium and a sodium salt of a strong mineral acid and containing formaldehyde, passing the thread through a second liquid comprising a concentrated aqueous solution of an alkali metal salt of a lower fatty acid, and imparting

a stretch to the thread after it leaves the second precipitating bath.

6. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, adding an ethereal oil, causing the viscous solution to pass through suitably formed openings to come into contact with a liquid comprising a concentrated solution of a potassium and a sodium salt of a strong mineral acid and containing formaldehyde and an alkali metal salt of an aliphatic acid of the group consisting of hydroxy acids and acids containing the carbonyl group, passing the thread through a second liquid comprising a concentrated aqueous solution of an alkali metal salt of a lower fatty acid, and imparting a stretch to the thread after it leaves the second precipitating bath.

7. The process of manufacturing artificial fibroin threads which comprises dissolving natural silk in phosphoric acid, adding an ethereal oil, causing the viscous solution to pass through suitably formed openings to come into contact with a liquid comprising a concentrated solution of a potassium and a sodium salt of a strong mineral acid and containing formaldehyde and an alkali metal salt of an aliphatic acid of the group consisting of hydroxy acids and acids containing the carbonyl group, passing the thread through a second liquid comprising a concentrated aqueous solution of an alkali metal salt of the lower fatty acids with addition of an alkali metal salt of an aliphatic acid of the group consisting of hydroxy acids and acids containing a carbonyl group, and imparting a stretch to the thread after it leaves the second precipitating bath.

8. The process which comprises dissolving 1 part of natural silk wastes in 10 parts of phosphoric acid of 85 per cent strength, adding 0.04 per cent of turpentine, centrifuging the filtered solution and causing it to pass through a nozzle provided with holes of 0.08 mm. diameter in a bath containing per liter 142 grams of hydrochloric acid, 34 grams of lactic acid, 30 grams of formic acid, partly bound by potassium and partly by sodium, and 15 grams of formaldehyde, passing the thread through a second liquid comprising a saturated solution of ammonium formate and sodium lactate, allowing the thread to run freely a long space of air, and then imparting a stretch to the thread to form individual fibers of a titer of 1 denier.

9. As a new product, artificial threads consisting substantially of fibroin and having a dry tenacity up to 2 grams per denier and a wet tenacity up to 1 gram per denier, showing the chemical reactions and the X-ray diagram of natural silk but being digestable by proteases.

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