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PRODUCTION OF SILK FIBERS

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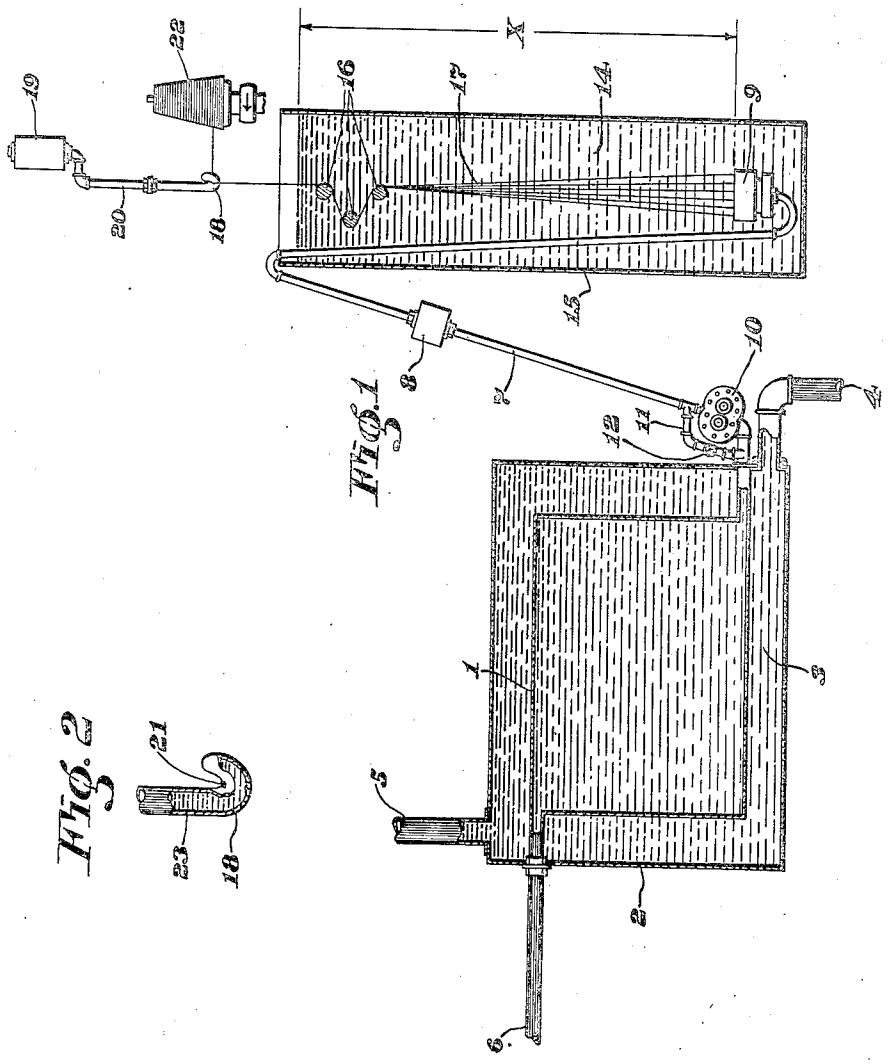



FIG. 1




FIG. 2

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## PRODUCTION OF SILK FIBERS

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7 Claims. (Cl. 18—54)

My invention relates to the production of silk fibers, and more particularly it relates to new and useful improvements in processes for producing such fibers.

Filaments or threads of artificial silk are commonly formed by dissolving cellulosic materials in suitable solvents, and extruding the cellulose solution thus formed through a spinneret or draw plate into a precipitating bath. On the other hand, the formation of filaments of real silk, or fibroin, presents difficulties not encountered when dealing with cellulose. Solutions of fibroin are much more delicate and unstable than cellulose solutions. Solvent materials which are satisfactory for cellulose, or for mixtures of cellulose and fibroin, are in general unsuitable as solvents for fibroin alone, and the factors influencing the solubility of fibroin and the characteristics of fibroin solutions have been little understood or even known.

Successful operation requires that the solution when extruded through the spinneret be in a relatively viscous condition. Even after the fibroin is dissolved it is difficult to maintain the viscosity of the solution up to the point of precipitation, and the precipitation itself presents problems peculiar to fibroin.

After extended study and practice, I have discovered certain factors to have an important bearing on the successful formation of filaments or threads of fibroin, and I have developed a process for the preparation of such fibers in which the above and other difficulties are overcome, as herein set forth.

Objects of my invention are to provide a process whereby it is possible and practicable to produce from waste fibroin-containing materials, for example from waste silk, fibers having the appearance, and the chemical and physical properties of the natural product; to provide for fibroin a solvent material of high solvent power, capable of furnishing fibroin solutions of high and stable viscosity; to provide a process wherein the precipitation of the fibroin is accomplished with maximum effectiveness; and to provide improvements in the treatment of the precipitated fibers.

Still further objects reside in the provision of methods of operation adapted to effect these and other desirable results.

Wild silk, waste silk from cocoons or from a silk mill, silk fabric, fiber or yarn (provided it is not weighted with mineral material), when formed and treated in accordance with my invention, will yield a silk fiber of the general appearance and with the chemical and substantially the physical properties of natural silk. For purposes of illustration, I shall describe my process in connection with its application to silk waste.

In practising my improved process, I first remove the sericin coating from the silk fibers, if this has not already been done, preferably maintaining the temperature between 75° and 80° C. during this step. I then dissolve the fibroin in a cuprammonium solvent material (as hereinafter more fully described) free from sulfate and other acid radicals, and containing glycerine or sugar,—preferably a non-reducing sugar.

During preparation and before precipitation of the fibroin, the fibroin solution is preferably maintained at around 0 to 3° C. After careful filtering, this solution is extruded in fine streams through a spinneret into a bath containing sodium acid sulfate and preferably also aluminum sulfate, whereby the fibroin is precipitated in the form of continuous filaments. These filaments or fibers are subjected to a stretching operation, treated to prevent their adherence together, and wound on a bobbin.

In the accompanying drawing, Fig. 1 illustrates apparatus suitable for carrying out my improved process, and

Fig. 2 is an enlarged detail view of the hook 18, partially in section.

Referring to the drawing, 1 is a tank adapted to contain the fibroin solution. Any suitable means for cooling this tank and its contents may be employed. I have shown it within a larger container 2, arranged so that cold brine 3 may be circulated around the tank 1 by means of the inlet pipe 4 and the outlet 5 of the container 2. The pipe 6, which communicates with the tank 1, is connected to a pump or other suitable means (not shown) for exerting pressure on the fibroin-containing solution in the tank, whereby this solution is forced through the outlet pipe 7, filter 8, and spinneret 9, into the precipitating bath.

In the line 7 is inserted the gear pump 10, around which is provided the by-pass 11 with valve 12. 9 is a spinneret such as shown and described in a co-pending application of Furman, Ser. No. 346,881, through which the fibroin-containing solution is extruded into the precipitating bath 14 in the container 15. Horizontal bars or rods are shown at 16, around which the precipitated threads 17 are passed in the manner shown in Fig. 1.

18 is a hollow hook, supplied from the tank 19 by the pipe 20 with a material which exudes from the orifice 21 and coats the fibers as they

pass over the hook, so as to prevent their adherence together when they are wound on the bobbin 22.

As an example of the application of my process to the treatment of silk waste, I may proceed as follows:

Preparatory to putting the fibroin in solution, the waste material is subjected to a "boiling-off" operation which removes the sericin coating from the silk fibers. This operation consists of agitating the material in a solution of a soap in warm water. After the removal of the sericin, the silk is ready to be put into the "spinning solution".

As stated above, the customary cellulose solvents are not satisfactory as solvents for fibroin alone. One factor in the unsuitability of typical cellulose solvents, when dealing with fibroin, is the presence therein of the sulfate ion or other acid radicals. I have found that when the sulfate radical is present in fibroin solutions, the viscosity of the solution falls off rapidly. For best results it is therefore important to employ a solvent free from such radicals. My solutions, when subjected to the well-known barium chloride test for the presence of the sulfate ion, must give a negative test for the presence of such ions.

In the preparation of my solution, I have found it advisable to first mix all the ingredients except the fibroin. The resulting preferred fibroin solvent is, as stated above, not a solvent for cellulose, and my solutions are characterized by the fact that they contain such concentrations of ingredients as will not dissolve cellulose. This characteristic furnishes a means by which any cellulose, etc., which may be mixed with the fibroin material may be eliminated from the finished product,—i. e., such constituents do not dissolve in the solvent, and they may be strained out of the fibroin solution.

A preferred fibroin solvent solution comprises the following ingredients in substantially the proportions set forth:

| | |
|---|---|
| Blue copper hydroxide (dry basis) | 700 g. |
| Ammonia (approx. 29% $NH_3$) | 750 c. c. |
| Sodium hydroxide solution (30.4% NaOH) | 1500 c. c. |
| C. P. glycerine | 1600 c. c. |

The blue copper hydroxide is ordinarily used in the form of a paste containing about 90% of water, the exact amount to use being determined by analysis. However prepared, the solution must give a negative test for the presence of the sulfate ion when tested with barium chloride.

In place of the glycerine as above set forth, I may substitute a sugar,—preferably a non-reducing sugar such as sucrose, and I have obtained satisfactory results with a smaller proportionate amount of sucrose,—as little as one-fourth of the amount of glycerine called for by the above example. The glycerine or sugar performs an important function in maintaining the solvent power of the cuprammonium solution and the viscosity of the fibroin solution.

The fibroin solvent mixture should be cooled down to around 2° C., or a little lower, if convenient. To the above mixture 3430 grams (dry basis) of fibroin is added.

The fibroin is preferably added in a moist form containing approximately an equal weight of water. I have found that it dissolves more readily in this condition, probably because it is more permeable to the solvent, and because the solvent will spread more rapidly over a wet surface.

The solution is now made up to 25 liters.

It is possible to obtain a cuprammonium solution free from sulfate or other acid radicals by various methods and to depart from the precise formula and method of preparation given in the above illustration. The important considerations are the absence from the solution of sulfate or other acid radicals, and the presence of the glycerine or sugar.

It is desirable to keep the solution cold while it is being prepared and before use. For this purpose, it is convenient to make it up in a container which is provided with a stirrer inside, and which itself may be surrounded with ice and salt. It usually requires between one and two hours for the fibroin to dissolve completely.

The solution is then filtered very carefully to remove even the finest particles of dirt and is transferred to the tank 1 which supplies the so-called spinning machine. It is allowed to remain here until air bubbles are removed which can be facilitated by applying a vacuum to the tank. It is then ready to be "spun"; all this while it is maintained at around 2° C., or lower.

The spinning operation is performed by extruding the fibroin solution in fine streams through a spinneret into a precipitating bath in which the threads are hardened into continuous filaments. I preferably employ the method and apparatus disclosed in the before-mentioned co-pending application, whereby difficulty in starting the operation, and subsequent troublesome clogging of the apparatus, are avoided.

According to this method, I prefer to supply the fibroin solution from the tank 1 at a considerable head of pressure, and simply employ the gear pump 10 as a metering device to regulate the normal flow of the liquid. In starting the spinning operation, a cap (not shown) is placed over the head of the spinneret 9, and the spinneret with its supply pipe filled with air is immersed in the precipitating bath 14. Then the valve 12 in the by-pass 11 is opened, so that the full force of the liquid under the high pressure applied through the pipe 6, for example 40 or 50 pounds, is allowed to rush around the metering pump 10 and into the line 7, thereby rapidly building up a considerable pressure in the line to the spinneret 9. This pressure tends to lift the cap from the spinneret head, and keeps the spinneret holes free and clear of the precipitating bath until the fibroin solution following, itself fills the holes. Upon this solution passing through the spinneret holes into the bath, it is precipitated and hardened into filament form, as shown in Fig. 1. Upon the spinning operation being well started, the speed of the pump 10 may be regulated so as to provide the proper rate of flow for the desired spinning speed, and the by-pass valve 12 is then closed. Though I prefer to employ the by-pass device to start the spinning operation, it will be clear that a similar result may be obtained by a temporary speeding up of the pump 10.

In combination with my fibroin solution, a preferred precipitating bath is an aqueous solution of sodium acid sulfate ($NaHSO_4$), made up in the proportion of 350 grams of sodium acid sulfate to 1000 c. c. of water. I have found that the efficiency of this bath is increased by the presence therein of a relatively small amount of aluminum sulfate. Accordingly, I preferably add to each liter of the precipitating solution, 100 grams of crystallized aluminum sulfate.

Whereas a cellulose solution, extruded through a spinneret into a precipitating bath, will pre-

cipitate practically simultaneously throughout the cross-section of the filament, a solution of fibroin so extruded first forms a skin or coating of precipitated fibroin which retards the contact of the precipitant with the central portion of the filament. I have found that in order to effect complete precipitation and the formation of a satisfactory filament, it is necessary that the fibroin filament remain in the precipitating bath for a considerably longer period of time than is required in the case of a cellulose filament. Whereas a shallow precipitating bath, for example, six or eight inches deep, is commonly used in precipitating filaments from a cellulose solution, in my improved process I employ a bath of a much greater depth for precipitating my fibroin solution. The distance from the spinneret head to the surface of the precipitating bath, designated "x" in Fig. 1, is preferably about three to four feet. Since the time relation involved is the controlling factor, it will be evident that the exact depth of the precipitating bath will depend somewhat upon the rate at which the filaments are drawn therethrough, but with the above described depth of precipitating bath, a precipitating rate of 2½ feet per second is found satisfactory.

The precipitating bath is provided with apparatus for picking up the fibers and maintaining them separate.

While the fibers are passing through the precipitating bath, it is advantageous to subject them to tension and to a stretching operation, which is particularly effective at this point because the fibers are in a semi-gelatinous condition. For accomplishing this, I provide a plurality of horizontal bars or rods beneath the surface of the precipitating bath, as shown at 16 in Fig. 1 of the accompanying drawing. The fibers are passed back and forth around and between these bars in the manner illustrated. For subjecting the fibers to additional tension, the upper guide may be so placed as to give to the thread a right angle turn just before it is wound on the bobbins.

In the manufacture of artificially-formed threads from fibroin, considerable difficulty is sometimes experienced in removing the thread from the bobbins on which it is wound as it comes from the precipitating bath. At this point, the thread has a tendency to shrink and then stick to the other threads. In order to avoid this I may apply to the thread, as it is being wound on the bobbin, a solution of a soap, either in water or in a mixture of water and alcohol. The thread being still wet with the acid constituents of the precipitating bath, these constituents set free the fatty acid of the soap, which has a tendency to form a film around the threads and prevent them from sticking together.

It is obvious that instead of using a soap, a solution of a fatty acid in alcohol, acetone or other suitable solvent may be used. Stearic acid is very good for this treatment, but any soap or fatty acid gives satisfactory results.

The treatment may be applied to the threads in the manner illustrated in the accompanying Figs. 1 and 2. Prior to winding on the bobbin 22, the fibroin threads coming from the precipitating bath pass over the hollow hook 18, which is shown in detail in Fig. 2. The solution of soap or fatty acid contained in the tank 19 may be supplied to the passage 23 inside the hook 18, by the pipe 20. This soap or fatty acid solution exudes from the orifice 21 and coats the threads as they pass across the orifice. This treatment may obviously be applied in any other suitable way, such as by spraying.

The subsequent treatment of the fibers may be in accordance with the disclosure of the copending Furman application, Serial No. 651,432.

In this specification and in the appended claims, I do not necessarily employ the words "solution" and "dissolve" in their strict chemical and technical sense, but I intend that they shall relate to other states as well,—for example, to the colloidal state.

I claim:

1. The process of making artificially-formed silk fiber which comprises dissolving fibroin in a cuprammonium solvent material containing an organic substance selected from the group consisting of sugars and glycerine, and free from acid radicals, filtering the resulting solution, forming fibers by extruding the filtered solution into a bath containing sodium acid sulfate and aluminum sulfate, collecting and winding the fibers thus formed on a bobbin, and treating the collected fibers to prevent their adherence together on the bobbin.

2. The steps in the process of making artificially-formed silk fiber which consist in dissolving fibroin in a cuprammonium solvent material free from acid radicals, while maintaining the temperature at about 5° C., forming fibers by extruding the resulting viscous solution through a spinneret into a precipitating bath containing sodium acid sulfate and aluminum sulfate, collecting the fibers thus formed, treating the collected fibers to prevent their adherence together, and winding the fibers on a bobbin.

3. The process of making artificially-formed silk fibers which comprises dissolving fibroin in a cuprammonium solvent material free from acid radicals, filtering the resulting solution, forming fibers by extruding the filtered solution into an acid precipitating bath, collecting the fibers thus formed, applying to the collected fibers while the same are wet with acid liquid a solution of a soap setting free fatty acid from the soap and coating the fibers therewith, and winding the fibers on a bobbin.

4. That step in a process for making artificially-formed silk fibers from a cuprammonium fibroin solution, which consists in precipitating said fibroin solution in an aqueous solution containing approximately 35% of the weight of the solvent of sodium acid sulfate and approximately 10% of the weight of the solvent of aluminum sulfate.

5. In a process for making artificially-formed silk fiber, the combination of a cuprammonium fibroin solution free from acid radicals and containing an organic substance selected from the group consisting of sugars and glycerine, with a precipitating bath, consisting of an aqueous solution containing approximately 35% of the weight of the aqueous solvent of sodium acid sulfate and approximately 10% of the weight of the aqueous solvent of aluminum sulfate.

6. In a process for making artificially-formed silk fibers, the step which comprises applying to the precipitated fibers, in the presence of an acid, a solution of a soap in a suitable solvent material, liberating fatty acid from the soap and coating the fibers with the fatty acid so liberated.

7. In a process for making artificially-formed silk fibers, the step of coating the fibers on the bobbins with a fatty acid by applying to the wet fibers a soap solution and liberating fatty acid therefrom by the action of acid on the soap.

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