Patented Jan. 29, 1935 1,989,098

UNITED STATES PATENT OFFICE

1,989,098

MANUFACTURE OF ARTIFICIAL THREADS

Leon Lilienfeld, Vienna, Austria

No Drawing. Application April 25, 1927, Serial No. 186,575. In Austria June 12, 1926

9 Claims. (Cl. 8—20)

In my U. S. Patents Nos. 1,683,199 and 1,683,200 and Reissue 18,170 I have described the manufacture from viscose of artificial threads of high dry tenacity, exceeding 2 grammes, and in many cases exceeding 3, 4 or 5 grammes per denier, by a process comprising coagulation of the viscose formed into threads by means of strong mineral acid, particularly strong sulphuric acid of at least 50 to 55 per cent., preferably of at least 60 to 65 per cent. strength. Artificial silk, of this high tenacity, is known in the art as "Lilienfeld silk".

This invention is a method for effecting an improvement in or modification of the products described in the aforesaid patents.

It is desirable in many cases to increase the extensibility of the artificial threads which are obtainable according to the processes of the aforesaid patents (such as artificial silk, staple fibre, or artificial wool), without influencing (or at least without considerably lowering) the strength or lustre of the threads.

This result may be attained according to the invention by treating the artificial threads with an agent adapted to cause the threads to shrink, under conditions which permit shrinkage of the thread to occur.

As agents for the purpose in question, mercerizing agents have proved particularly suitable, especially basic mercerizing agents and among them such compounds of alkali metals as contain at least one element of the oxygen group. Thus, good results are obtained with solutions of alkali hydroxides, and more particularly solutions of alkali hydroxides containing not less than 15, preferably not less than 18 per cent. of alkali hydroxide (calculated as NaOH). Useful results are, however, obtained with other mercerizing agents also, for instance, with a strong solution of an alkali sulphide (e. g. a solution of sodium sulphide of at least 15, for example 30 to 58 per cent. strength), or with a solution of an alkali hydroxide that contains an alkali sulphide, or with a strong mineral acid (e. g. sulphuric acid of 46–60° Baumé specific gravity, or phosphoric acid of specific gravity 1.5–1.8, or nitric acid of 50–60 per cent. strength, or hydrochloric acid of 26–32 per cent. strength), or with a solution of zinc chloride, or with a solution of a thiocyanate, for example calcium thiocyanate, or the like. Substances as set forth in this paragraph will hereinafter be included in the term "mercerizing agents".

The artificial threads may be treated in various ways with the shrinking agent. For example, they may be immersed in, or impregnated with a solution of the agent, or passed through the solution, or passed over rollers which are in contact with the solution; or they may be sprayed with an atomized solution of the agent, or treated with a solution of the agent in a foulard, or by calendering, or coating; in short, by any known method of application, impregnation, immersion or coating.

The invention is applicable not only to the treatment of artificial threads as such (e. g. artificial silk), in the form of spun threads, yarn in hanks or cops or in the form of warp or twisted yarn or the like, but also to artificial threads (e. g. artificial silk or staple fibre) in the form of woven fabrics. It is also applicable to threads or fabrics consisting wholly of artificial fibre (e. g. artificial silk, artificial wool, or staple fibre), and to mixed threads or fabrics, that is, to fibres or fabrics containing in addition to the artificial threads another fibrous material, for instance natural cotton, silk, wool or the like. The expression "artificial threads" throughout the application is intended to include, wherever the context permits, artificial threads such as artificial silk, cotton, wool, hair, and so on, in any of the forms hereinbefore mentioned.

The success of the process depends upon the fact that the artificial threads, or the materials consisting of, or containing them, are treated with the shrinking agent in such a manner that the shrinkage remains either at its full extent, this extent depending on the nature and concentration of the shrinkage agent used, or that at least a part of the shrinkage remains. That is to say, either the material under treatment may be subjected to no tension during or after the treatment or, if tension is applied, it must be subsequently discontinued or reduced.

I have referred to the fact that the shrinkage (or at least some of it) remains or persists after the end of the treatment. I accordingly refer to the process as producing "permanent" shrinkage, to distinguish from any treatment in which the threads would leave the treatment in a stretched condition, as such a treatment would not accomplish the result of increasing the extensibility.

It is to be noted that in the treatment according to the invention, it is not necessary to impregnate or coat the artificial threads with any protective agent before they are subjected to the action of the shrinking agent, since the threads which are treated by the invention differ from threads of artificial silk hitherto known in that they withstand the action of shrinking agents without being materially damaged. However, preliminary treatment with a protective agent is not excluded from the invention for it does not prevent the production of the desired effect.

The treatment according to the invention may be combined into a single operation with a treatment for desulphurizing the threads. Thus, a suitable quantity of the shrinking agent, such as alkali hydroxide, may be added to the desulphuriz-

ing bath. If, however, the desulphurizing bath is a strong solution of an alkali sulphide, it may be unnecessary to add a further shrinking agent.

To the shrinking agent, for example a caustic alkali solution there may be added a suitable quantity of a neutral or alkaline salt, such as sodium chloride or sodium sulphate or sodium silicate or sodium aluminate or sodium zincate or borax or a sodium phosphate or sodium acetate or a mono- or polyvalent alcohol, such as ethyl alcohol or glycerine.

By this invention it is possible to increase the extensibility of the artificial threads by 30–200 per cent. or more, so that threads of even very low extensibility can be improved so as to attain an extensibility of at least 8 per cent. In addition to this, the present process has, in most cases, a favorable, i. e. increasing effect on the elasticity of the threads also.

The following examples illustrate the invention, the parts being by weight:—

1. Viscose silk made according to the process described in U. S. Patent No. 1,683,199 is introduced, in the finished, dried, but preferably unbleached state, in the form of hanks, without stretching, into a caustic soda solution of 18–25 per cent. strength at a temperature of 15–18° C. After a period of 1–5 minutes, it is removed and then introduced, if desired, after removal of the excess caustic soda by centrifuging or pressing, and/or, if desired, after a short washing, into sulphuric acid of 5–10 per cent. strength at room temperature for about 5 minutes, or into a hot or cold solution of ammonium sulphate of 5–25 per cent. strength, or into hydrochloric acid of 4 per cent. strength. It is then washed, if desired, bleached and dried without stretching, or under moderate tension.

2. The mode of operation is as in Example 1, with the difference that a solution of 200 parts of sodium chloride in 1500 parts of a caustic soda solution of 20 per cent. strength is employed as shrinking agent.

3. The procedure is as in Example 1, with the difference that a solution of 88 parts of sodium sulphate in 1500 parts of a caustic soda solution of 20 per cent. strength is used as shrinking agent.

4. The mode of operation is as in Example 1, except that a mixture of 1500 parts of a caustic soda solution of 22.5 per cent. strength with 150 parts of water-glass of 39° Baumé is employed as shrinking agent.

5. The procedure is as in Example 1, with the exception that a 20 per cent. caustic soda solution containing 8–10 per cent. of glycerine is used as shrinking agent.

6. The mode of operation is as in Example 1, with the difference that a solution of 270 parts of caustic soda and 450 parts of sodium sulphide in 1050 parts of water is employed as shrinking agent.

7. The procedure is as in Example 1, with the difference that a sodium sulphide solution of 50–58 per cent. strength is used as shrinking agent.

8. The procedure is as in Example 1, except that a 30–50 per cent. sodium sulphide solution containing 1–5 per cent. of caustic soda is used as shrinking agent.

As the strong sodium sulphide solutions act as desulphurizing agents, in Examples 6, 7, and 8 the dry silk need not be desulphurized prior to the treatment according to these examples.

9. The mode of operation is as in Example 1, with the difference that an 18–22 per cent. solution of caustic soda containing 8–10 per cent. of sodium sulphide is used as shrinking agent.

10. Artificial silk is spun on a bobbin according to the process of U. S. Patents Nos. 1,683,199 or 1,683,200, whereupon, preferably after being washed with water for a shorter or longer time, it is twisted and converted into a skein. This skein is then in the wet state desulphurized in a known manner by means of a warm, weak solution of sodium sulphide and, if desired, after being washed again, introduced without tension into a solution of 200 parts of sodium chloride or of 88 parts of sodium sulphate in 1500 parts of a caustic soda solution of 20 per cent. strength where it remains for 1–5 minutes. From this bath the hank is, optionally after being washed with water, introduced for about 5 minutes into sulphuric acid of 5–10 per cent. strength at room temperature or in a solution of ammonium sulphate of 25 per cent. strength at room temperature or at 50° C. The skein is then washed, if desired, bleached and dried without stretching or under moderate tension only.

11. The procedure is as in Example 10, with the exception that a mixture of 1500 parts of a caustic soda solution of 22.5 per cent. strength with 150 parts of water-glass of 39° Baumé is used as shrinking medium.

12. The mode of operation is as in Example 10, except that the skein is not desulphurized, but only washed, and that a solution of 270 parts of caustic soda and 450 parts of sodium sulphide in 1050 parts of water is used as shrinking bath, which, at the same time, acts as desulphurizing agent also.

13. The mode of operation is as in Example 10, with the difference that the skein is not desulphurized, but only washed, and that a sodium sulphide solution of 58 per cent. strength is employed as shrinking agent, which, at the same time, acts as desulphurizing agent also.

14. The procedure is as in Example 10, with the exception that a 30–50 per cent. sodium sulphide solution containing 1–5 per cent. of caustic soda is used as shrinking agent, which, at the same time, acts as desulphurizing agent also.

15. The procedure is as in Example 13, with the difference that an 18–22 per cent. caustic soda solution that contains 8–10 per cent. of sodium sulphide, is used as shrinking agent.

16. The procedure is as in any of the preceding examples, with the exception that the artificial silk is stretched during a part of the process, the stretching being discontinued, or considerably reduced, towards the end of, or after the treatment with the shrinking agent.

17. A fabric consisting of, or containing viscose silk (made according to the process described in U. S. Patent No. 1,683,199, is passed through one of the shrinking baths given in the preceding examples. It is allowed to shrink during or after the treatment with the shrinking agent, and is, if desired, after removal of the excess of the shrinking medium by pressing or centrifuging and/or, if desired, after a short washing, then introduced into dilute sulphuric acid (for example of 5–10 per cent. strength), washed, and dried without stretching, or whilst stretching only moderately.

18. The procedure is as in Example 17, with the exception that the fabric contains cotton in addition to the artificial silk or staple fibre.

19. The procedure is as in any of the preceding examples, with the exception that the artificial silk is in the form of warps.

20. The procedure is as in any of the preceding examples, with the exception that the thread or fabric is impregnated or sized with a solution of gelatine or albumen of 2–3 per cent. strength, or with a solution of starch of 3–4 per cent. strength, before it is treated with the shrinking medium.

In the examples other shrinking agents may be used, for instance, instead of caustic soda solution, a solution of another alkali hydroxide, for example caustic potash of equivalent strength, or instead of the sodium sulphide another alkali sulphide, for instance potassium sulphide, or sulphuric acid of 47 to 50° Baumé specific gravity, or hydrochloric acid of 27 to 30 per cent. strength, or nitric acid of 50 to 60 per cent. strength, or a 40 to 80 per cent. solution of calcium thiocyanate.

The artificial threads or fabrics may be keired or treated at room, or at a raised temperature under atmospheric or increased pressure in any known manner with an alkaline agent, for instance with sodium carbonate or lime, or with a very dilute caustic alkali solution, or with a solution of sodium carbonate and a dilute caustic alkali solution, or with a solution of soap or Turkey red oil or the like.

The expression "mercerizing agents" means in the description and claims all chemicals known as mercerizing agents in the mercerization art.

The expression "oxygen group" is intended to include the following elements: O, S, Se and Te.

The expression "strong. mineral acid"' means in the description and in the claims: Sulphuric acid of at least 50 per cent. of H_2SO_4 and the other mineral acids equivalent in strength, i. e. hydrochloric acid of at least 35 per cent. strength, nitric acid of at least 60 per cent. strength, phosphoric acid of at least 1.5 specific gravity and arsenic acid of at least 75 per cent. of H_3AsO_4.

The expression "strong sulphuric acid" or "sulphuric acid containing at least 50 per cent, of sulphuric acid monohydrate" means in the description and claims: Sulphuric acid of 50 to 98 or 100 per cent. strength.

The statements in the description and claims regarding percentages relate to percentages by weight.

I claim:

1. Process for increasing the extensibility of artificial threads of high dry tenacity, exceeding 2 grammes per denier, of the kind produced from viscose by means of a coagulating bath consisting of a strong mineral acid, which process comprises treating the threads with at least one mercerizing reagent of a concentration capable of mercerizing cotton, and allowing permanent shrinking of the said threads to occur during said treatment.

2. Process for increasing the extensibility of artificial threads of high dry tenacity, exceeding 2 grammes per denier, of the kind produced from viscose by means of a coagulating bath containing not less than about 55 per cent. of H_2SO_4, which process comprises treating the threads with a liquid containing a caustic alkali of not substantially below 15% concentration, calculated as NaOH, and allowing permanent shrinking of said threads to occur during said treatment.

3. Process for increasing the extensibility of artificial threads of high dry tenacity, exceeding 2 grammes per denier, of the kind produced from viscose by means of a coagulating bath consisting of a strong mineral acid, which process comprises treating the threads with a liquid containing an alkali sulphide of at least 15 per cent strength (calculated as Na_2S), and allowing permanent shrinking of said threads to occur during said treatment.

4. Process for increasing the extensibility of artificial threads of high dry tenacity, exceeding 2 grammes per denier, of the kind produced from viscose by means of a coagulating bath containing a strong mineral acid, which process comprises treating the threads with a liquid containing not substantially less than 15% (figured as NaOH and Na_2S) of a caustic alkali and an alkali sulphide, and allowing permanent shrinking of said threads to occur during said treatment.

5. As new products, artificial threads produced from viscose, which threads in the dry state have both a tenacity exceeding 2 grammes per denier and an extensibility of at least 8 per cent, which material has been produced by treating artificial threads produced from viscose and having a dry tenacity exceeding 2 grammes per denier, with a mercerizing reagent having a shrinking action on said threads not substantially less than the shrinking action of a 15% aqueous caustic soda, and allowing permanent shrinkage of the said threads to occur during said treatment.

6. As new products, artificial threads produced from viscose, which threads in the dry state have both a tenacity exceeding 4 grammes per denier and an extensibility of at least 8 per cent., which products have been produced by treating artificial threads produced from viscose and having a dry tenacity exceeding 4 grammes per denier, with a mercerizing reagent having a shrinking action on said threads not substantially less than the shrinking action of a 15% solution of caustic soda, and allowing permanent shrinkage of said threads during said treatment.

7. The process of increasing the extensibility of regenerated cellulose threads having a dry tenacity exceeding 2 grammes per denier produced from viscose by means of a setting bath consisting of a strong mineral acid, which comprises treating such threads with at least one shrinking agent having a shrinking action equivalent to that of an aqueous caustic soda solution of at least about 15% strength continued for about 1 to 5 minutes, and allowing permanent shrinking of the said threads to occur during the said treatment.

8. The process of increasing the extensibility of regenerated cellulose threads having a dry tenacity exceeding 2 grammes per denier, which comprises treating such threads with at least one shrinking agent having a shrinking action equivalent to that of an aqueous caustic soda solution of about 15 to 22% strength continued for about 1 to 5 minutes, and allowing a permanent shrinking of the said threads to occur during the said treatment.

9. The process of increasing the extensibility of Lilienfeld silk, which is characterized by having a dry tenacity exceeding 2 grammes per denier, which comprises treating such threads with at least one shrinking agent, said shrinking agent being a basic compound of an alkali metal which contains at least one element of the oxygen group, said shrinking agent having a shrinking action equivalent to that of an aqueous caustic soda solution of at least about 15% strength continued for about 1 to 5 minutes, and allowing a permanent shrinking of said threads to occur during the said treatment.

LEON LILIENFELD.