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PRODUCTION OF ARTIFICIAL THREADS,
FILAMENTS, BANDS, FILMS, OR THE LIKE
CONTAINING PROTEINSTheodoor Koch, Oosterbeek, Netherlands, assign-
or to American Enka Corporation, Enka, N. C.,
a firmNo Drawing. Application July 27, 1937, Serial
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This invention relates to the production of artificial threads, filaments, bands, films or the like containing proteins. It is known to spin into threads alkaline spinning solutions containing casein or other proteins by employing spinning baths containing acid. The artificial threads made in this way have, however, little value as substitutes for textile fibres since they possess only very low strength.

Attempts have been made to increase the strength of filaments prepared as described above by applying tension to the freshly formed thread by a process similar to that employed in the case of viscose silk or cuprammonium silk, but this method has not led to satisfactory results since even the application of slight tension is apt to break the threads.

Attempts have also been made to harden the threads during the spinning operation by the addition to the spinning bath of formaldehyde but threads made in this way have too little stretch and furthermore spinning baths containing formaldehyde are unpleasant to work with.

Now it was found that improved threads, filaments, bands, films or the like may be obtained from a solution containing protein by employing a glue precipitating bath containing aromatic or hydroaromatic sulfonic acids and/or condensation products of these aromatic or hydroaromatic sulfonic acids with aldehydes which substances have the property of tanning proteins.

The present invention accordingly comprises a process for the production of artificial threads, filaments, bands, films or the like containing proteins from solutions of alkali salts of protein by bringing the said solution into contact with an acid precipitating bath which process consists in incorporating in the precipitating bath a proportion of a substance which has a precipitating action on glue solutions and a tanning action on the freshly produced artificial product and thereafter subjecting the said artificial product to hardening with formaldehyde or the like.

The thread, filament, band, film or the like may be subjected to tension while still in the acid bath.

The tanning substances added to the precipitating bath may consist of condensation products of aromatic and hydroaromatic sulfonic acids and aldehydes and include in particular the water soluble methylene compounds resulting from the condensation of aromatic and hydroaromatic sulfonic acids or their hydroxy, amino

or chlorine derivatives and the like with aldehydes for example formaldehyde.

After formation in the presence of the above mentioned compounds the artificial products must be subjected to the action of free aldehydes in order to bring about the hardening of the protein.

Among the tanning substances which may be employed in the precipitating bath, the following specific compounds may be mentioned, dihydroxydiphenyl-methane-disulphonic acid (produced by the action of formaldehyde on phenol-sulphonic acid), condensation products of tetrahydronaphthalenesulphonic acid with formaldehyde or other aldehyde or condensation products of amino-sulphonic acids or hydroxy-amino-sulphonic acids of the naphthalene or anthracene series with formaldehyde or the like. The tanning substance may also consist of an aromatic sulphonic acid including the mono- or polysulphonic acids of aromatic or hydroaromatic hydrocarbons or of mono- or polysulphonic acids of oxygen-containing derivatives of aromatic or hydroaromatic hydrocarbons. The mono- or polysulphonic acids may further be employed in the form of their compounds with aliphatic alcohols. There may also be employed sulphonic acids of aromatic or hydroaromatic mono- or polyhydroxy compounds, of keto-compounds, or of carboxylic acids. Examples of the above substances are naphthalene-sulphonic acid, tetraline-sulphonic acid, toluene-isopropyl-sulphonic acid, phenol-sulphonic acid, cyclohexanone-sulphonic acid, benzoic-sulphonic acid and so forth. Such substances have a different action in the precipitating bath from that of free aldehydes since they do not attack the amino groups of the protein.

In practice it is not generally essential to employ the pure condensation product or the pure aromatic sulphonic acid, but the unpurified reaction product forms an effective tanning agent when added to the precipitating bath.

In addition to the tanning compounds the spinning bath may also contain a soluble salt or a mixture of soluble salts and these salts may include for example the sulphates of sodium, ammonium or zinc.

The acid concentration of the precipitating bath may vary between wide limits and this concentration may be controlled either by neutralising to a greater or smaller extent the acid condensation products added to the bath or by the addition of acid to the bath.

There may also be added to the spinning bath

carbo-hydrates such as glycerol, sugar and the like, or mineral or organic acids.

In general, the sulphonic acids of the mono- or polyhydroxy compounds have the advantage of a higher solubility when salts are present. These added substances also possess the advantage that they are simple and cheap to manufacture, and even at low concentrations they have a tanning action which is even superior to that of the condensation products mentioned above. The freshly spun thread has an appreciably increased strength and the rate of drawing off may thus be increased.

Threads, filaments, bands, films or like artificial products obtained in accordance with the present invention are firmer than those prepared in the normal precipitating baths so that a higher degree of stretching may be applied thereto, this stretching resulting in a more pronounced orientation of the micells and in the production of products possessing greater strength.

Following is a description by way of example of two methods of carrying the present invention into effect:

Example I

A 17.5% solution of sodium caseinate is spun into a spinning bath consisting of 20% zinc sulphate, 1% sulphuric acid and 5% of the neutralised condensation product obtained by the action of half a molecule of formaldehyde on one molecule of cresyl sulphonic acid.

The casein solution is spun with a total titre of 250 denier from a spinning nozzle having 50 holes each of a diameter of 80 mu. After the thread has travelled through a distance of about 60 centimetres in the spinning bath a tension of for example 25 grams is allowed to act upon it and a considerable increase in strength is thereby obtained. On spinning a solution of sodium caseinate under similar conditions but without the addition of the condensation product of formaldehyde and cresyl sulphonic acid to the spinning bath it is impossible to apply a tension of this magnitude without breaking the thread.

The thread is subsequently hardened with a 10% solution of formaldehyde and is then washed and dried at a moderate temperature. Hardening may take place immediately after spinning or at a later stage. The product is flexible and has a strength which even exceeds that of sheep's wool.

Example II

Casein obtained from skim milk is dissolved in 14% ammonia water to form a 16% casein solution. This solution is spun at 45° C. in a spinning bath containing 10% by weight of sodium sulphate, 10% by weight of zinc sulphate, 3% by weight of sulphuric acid and 3% by weight of cresol sulphonic acid.

The initial tension which may be applied to the thread in the spinning process if the above-mentioned sulphonic acid is employed in the spinning bath is greater than that which can be used if the sulphonic acid is not present. This increased tension results in an increased rate of spinning.

What I claim is:

1. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing at least one substance selected from the group consisting of aromatic and hydroaromatic acids and the conden-

sation products of aromatic and hydroaromatic sulphonic acids with aldehydes, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally treating the product with a hardening agent.

2. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing at least one substance selected from the group consisting of aromatic and hydroaromatic acids and the condensation products of aromatic and hydroaromatic sulphonic acids with aldehydes, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with an aldehyde.

3. The process as defined in claim 2 wherein the substances contained in the precipitating bath are in an unpurified state.

4. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of casein into an acid precipitating bath containing at least one substance selected from the group consisting of aromatic and hydroaromatic acids and the condensation products of aromatic and hydroaromatic sulphonic acids with aldehydes, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with an aldehyde.

5. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing a condensation product of an aromatic sulphonic acid and an aldehyde, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

6. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing a condensation product of an hydroxy aromatic sulphonic acid and an aldehyde, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

7. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing the condensation product of cresyl sulphonic acid and formaldehyde, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

8. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing a hydroaromatic sulphonic acid, for exerting a glue precipitating action and for tanning the formed product, tensioning said

product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

5 9. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing an oxyhydroaromatic sulphonic acid, for exerting a glue precipitating
10 action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

15 10. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing cyclohexanone-sulphonic acid, for exerting a glue precipitating
20 action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

25 11. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid

precipitating bath containing an aromatic sulphonic acid, for exerting a glue precipitating action and for tanning the formed product, tensioning said product while in said bath and finally
5 hardening the product by treatment with formaldehyde and the like.

12. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing an aromatic monosulphonic acid, for exerting a glue precipitating
10 action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

15 13. A process for the production of protein-containing artificial threads, filaments, bands and the like, which comprises extruding a solution of an alkali salt of a protein into an acid precipitating bath containing cresyl sulphonic acid, for exerting a glue precipitating
20 action and for tanning the formed product, tensioning said product while in said bath and finally hardening the product by treatment with formaldehyde and the like.

THEODOOR KOCH.