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MANUFACTURE OF TEXTILE FIBERS COMPOSED OF CASEIN

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This invention relates to the manufacture of textile fibres composed of casein or partly of casein and partly of cellulose.

It is known to treat artificial fibres composed of cellulose (rayon) first with a solution of urea and then, after the fibre has absorbed a sufficient quantity of urea, with formaldehyde, so as to form on the fibre an insoluble product of condensation which partially waterproofs the fibre and renders it more highly resistant to the effects of moisture, and at the same time to obtain a fibre which is creaseless.

Attempts have been made also to treat casein fibres in the same way, that is first with urea and then with formaldehyde. It has been found, however, that such treatment fails to produce any appreciable effect on the casein fibre. This is due to the fact that a casein fibre, that is, as ordinarily produced, with the use of formaldehyde in the insolubilising treatment, contains formaldehyde and for the reason is prevented from absorbing the necessary quantity of urea, which instead of coming into contact with the formaldehyde already present in the fibres, condenses on the exterior surface thereof and there forms a pulverulent deposit of condensed urea effective to prevent the passage of urea into the interior of the fibre.

It is further known that casein dissolves in aqueous solutions of urea and it is known also to use a solution of casein in an aqueous solution of urea as the spinning solution in the manufacture of wet-spun fibres, that is, fibres produced by spinning a solution of the basic substance of which the fibre is to be composed in a coagulation bath operative to coagulate the thin stream of solution entering the bath into a filament. Successful results are, however, not obtainable by this process. Thus, it is difficult to obtain perfect coagulation. In addition, a spongy load tends to form inside the fibre during the step of insolubilising the fibre with formaldehyde. This is due to the more rapid reaction of the formaldehyde with the urea contained in the fibre than with the casein of which the fibres is composed, the urea in the fibre hardening in consequence before the casein substance of the fibre and forming in the result an amorphous or spongy load inside the fibre. Owing to the presence of this load in the fibre, the latter is less resistant to dryness and moisture.

According to the present invention, a process for the manufacture of wet-spun textile fibres composed of casein or partly of casein and partly of cellulose, comprises spinning a solution, more

especially an aqueous solution, of casein or of a mixture of casein and cellulosic viscose in a formaldehyde-free coagulation bath and treating the coagulated filament in a succession of baths including or comprising in the order named: (*a*) a bath or baths consisting of urea dissolved in a solution, more especially an aqueous solution, of a neutral or acid salt of a mineral or organic acid and (*b*) a urea-free saline bath or baths containing formaldehyde, more especially an aqueous bath or baths of this description.

It is to be understood that the succession of baths through which the coagulated filament is passed in order to produce finished fibre may include other baths additional to the baths (*a*) and (*b*) mentioned above, for example deacidifying and partially hardening baths, as in the specific examples of the invention hereinafter set forth.

The baths or baths (*a*) is or are concentrated and possessed of an astringent action towards the filament. It or they may, for example, be of a composition similar to the baths that are used in the processes forming the subject matter of U. S. patent applications dated August 17, 1936, Ser. No. 96,470, now Patent No. 2,450,889; April 4, 1939, Ser. No. 270,919, now abandoned; February 17, 1938, Ser. No. 330,725 now abandoned; July 31, 1940, Ser. No. 348,992 now abandoned; and U. S. Patents No. 2,338,915; No. 2,297,397; No. 2,338,917.

It is found that casein fibres and mixed casein and cellulose fibres produced in accordance with the present invention as outlined above are considerably improved as compared with casein fibres and mixed casein and cellulose fibres as ordinarily produced, in respect of resistance to moisture, resistance to the boiling acid baths that are used for dyeing and resistance to soap and water in the machine of fast colors.

Further improvement in respect of the foregoing properties and a higher order of strength with dryness and moisture of the fibre are obtainable if the filament is drawn out and maintained in tension during its passage as a continuous thread through at least the bath or baths containing formaldehyde or after the filament has left that bath or those baths, until it is out, it being convenient to treat in this manner a large number of filaments simultaneously spun in the coagulating bath and then gathered together in a ribbon for the subsequent (post-coagulation) treatments as in the process forming the subject matter of U. S. patent applications, dated February 17, 1938, Ser. No.

330,725 now abandoned; July 31, 1940, Ser. No. 348,992 now abandoned; and U. S. Patent No. 2,338,917.

In order to obtain a higher resistance of the fibres that are produced in accordance with this invention to acid boiling than is obtainable with the use of normal temperature in the baths (*a*) and (*b*) a temperature above 28° C. may be employed in those baths or at least in the bath or one or more of the baths (*b*) containing formaldehyde, as in the process forming the subject matter of the aforesaid U. S. patent applications No. 330,725, 348,992, both now abandoned and U. S. Patent No. 2,338,917, for example, if a temperature not above 25° C. has been used in the bath or baths (*a*) and also in one or more of the insolubilising, formaldehyde containing baths (*b*), a temperature above 25° C., preferably a temperature of 70–75° C., may be employed in another or other of the baths (*b*) subsequent in the succession of baths to the first-mentioned of the baths (*b*). In this way, the fibre obtained will be much softer and larger after acid boiling than a urea-free fibre and from this point of view, can be compared with a fibre treated with a chromium salt, but with the advantage, however, that the fibre retain a perfectly white appearance.

It should be remarked that casein filaments already coagulated but not yet insolubilized by formaldehyde, cannot be treated with a simple solution of urea, as a simple solution of urea dissolves casein and in consequence the filament would at once dissolve in the solution. On the other hand, by using a saline solution of urea, preferably concentrated and astringent, no dissolving of the filament occurs, but only a slight swelling of the filament, which can be adjusted at will by varying the degree of concentration and/or the astringent capacity of the solution according to the amount of urea that has to be absorbed by the filament and to the degree of penetration of the urea that has to be obtained.

Urea may in some cases be present in the formaldehyde-free acid salt coagulating bath, but in general, coagulation of the filament is hindered and there tends to be a large loss of urea in the first de-acidifying bath following the coagulating bath.

Examples

I. 100 kgs. of washed and dried casein are swelled in water and then dissolved in an aqueous solution of caustic alkali, equivalent, for instance, to 20 litres of sodium hydrate at 5° Bé. The volume of the resulting solution of casein is then increased to 500 liters, after which the solution is filtered one or more times. After maturation it is spun in the form of filaments in a formaldehyde-free coagulating bath containing, for instance, 90 gms. of 66° Baumé sulphuric acid and 350 grs. of sodium sulphate per litre of the bath. The filaments emerging from the coagulating bath are gathered together in a continuous ribbon and passed on, preferably under more or less tension through the following baths in succession:

(*a*) An aqueous saline bath containing 200 gms. of sodium chloride per litre.

(*b*) An aqueous saline bath containing 150 gms. of sodium chloride, 200 gms. of aluminium sulphate and 150 gms. of alumina paste containing 10% of Al_2O_3 per litre.

(*c*) An aqueous saline bath having the composition of the bath (*b*) but containing in addition 100 gms. of urea crystals per litre of the bath and more sodium chloride until the bath is saturated.

(*d*) An aqueous saline bath having the composition of the bath (*b*) but containing in addition 30–40 gms. of 100% formaldehyde per litre of the bath.

The fibres are now cut to the required length after which they are treated, preferably in an autoclave, in an aqueous bath (*e*) containing 150 gms. of aluminium sulphate, 200 gms. of sodium chloride and 40 gms. of 100% formaldehyde per litre, for 5–6 hours.

The insolubilized fibres are now washed and treated in an aqueous bath or baths (*f*) of soluble phosphates, for instance such a bath containing 4 gms. of monosodium phosphate per litre, after which the fibres are washed again and dried.

The preferred temperature for the various baths are: 35°–40° C. for bath (*a*):
50°–55° C. for bath (*b*):
35°–40° C. for bath (*c*):
50°–55° C. for bath (*d*):
70°–75° C. for bath (*e*):
35°–40° C. for bath or baths (*f*):

II. The procedure in this example is the same as in Example I, except that the filaments are cut after bath (*c*) instead of after bath (*d*), the cut fibres being gathered together in a vessel containing bath (*d*), in which they are treated for 3–4 hours at 35°–40° C., then treated in bath (*e*) at 70°–75° C. for 5–7 hours, then washed, then treated in the bath or baths (*f*) and finally, washed again and dried.

III. The procedure in this example is the same again as in Example I, except that the filaments are cut after the bath (*b*) instead of after bath (*d*), the cut filaments being gathered together in a vessel containing bath (*c*), in which they are treated for 2–3 hours at 35°–40° C., and then, after having been squeezed out, in conformity with Example II, omitting bath (*e*).

IV. The procedure in this example is the same again as in Example I, except that the aluminium sulphate in bath (*e*) is replaced with more sodium chloride until the bath is saturated.

V. The procedure in this example is the same as in Example I to IV with the use of the baths (*a*), (*b*), (*c*), (*d*), *and* (*e*) as specified therein, with the exception that the aluminium sulphate and/or sodium chloride are either partly or totally substituted in the baths with other soluble neutral or acid salts including, for example, sulphates, chlorides, formiates, acetates, lectates or nitrates, of the mineral or organic acids.

It is to be understood that the term "urea" as employed herein includes all soluble salts containing urea such for example as thio-urea.

It is also to be understood that the invention includes both the use of milk casein and also the use of vegetable casein for example soya bean casein, either being used alone or the two in admixture with one another.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is performed, I declare that what I claim is:

1. Process for manufacturing casein textile fibers comprising the wet spinning of the casein solution into a coagulating bath free of formaldehyde to form casein filaments; and, after removal from said bath, treating such filaments in at least one bath containing a substantial concentration of urea, but being free of formaldehyde, whereby uncondensed urea penetrates the

filaments and is absorbed therein, said urea bath containing at least one non-basic soluble salt rendering the bath substantially saline and thereby functioning to a degree sufficient for the protection of the filaments against dissolving into such bath; and thereafter removing such urea-containing filaments from said urea bath and treating the same in at least one urea-free formaldehyde bath of saline character for insolubilizing the same.

2. Process as in claim 1 and wherein the urea bath is rendered saline by incorporating therein to the saturation point non-basic soluble salt material.

3. The process as in claim 1 and wherein the urea bath is maintained at temperatures elevated above 25° C.

4. The process as in claim 1 and wherein the urea bath is maintained at an elevated temperature of about 35 to 40°.

5. Process as in claim 1 and wherein the coagulated filaments are kept under stretching tension during passage through the coagulating and urea and formaldehyde baths until the time when the hardened fibers are cut to length.

6. Process as in claim 1 and wherein the coagulated filaments are kept under stretching tension during passage through the saline washing bath and the saline bath containing sodium chloride and an aluminum salt and the saline bath containing urea and the saline bath containing formaldehyde.

7. Process as in claim 1 and wherein the aqueous urea bath is rendered saline by the addition of sodium chloride and an aluminum salt.

8. Process as in claim 7 and wherein the aluminum salt is aluminum sulphate.

9. Process as in claim 1 and wherein the aqueous urea bath is rendered saline by the addition of sodium chloride and aluminum sulphate.

10. Process as in claim 1 and wherein the aqueous urea bath is rendered saline by the addition of sodium chloride and aluminum sulphate in the proportions, per liter, of about 100 grams of urea crystals, about 150 grams initially of sodium chloride, and about 200 grams of aluminum sulphate; the sodium chloride content being then increased until substantial saturation is reached.

11. Process as in claim 10 and wherein the aqueous urea bath is added about 50 grams of aluminum paste containing about 10 percent of aluminum oxide.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,211,961	Meigs	Aug. 20, 1940
2,312,998	deKadt	Mar. 2, 1943

FOREIGN PATENTS

Number	Country	Date
467,812	Great Britain	June 22, 1937
508,781	Great Britain	June 26, 1939

OTHER REFERENCES

Ser. No. 327,734, diVasco (A. P. C.), published Apr. 27, 1943.