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MANUFACTURE AND PRODUCTION OF ARTIFICIAL THREADS, FILAMENTS, AND THE LIKE

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This invention relates to the manufacture and production of filaments, threads and the like hereinafter referred to as threads, from casein or the like protein substance. It is known that such threads may be produced by the extrusion of a solution of, for example, casein through a jet provided with a number of holes into a coagulating bath and that after washing the resulting threads it is desirable to harden them by treatment in a bath containing one or more hardening agents such, for example, as an aluminium salt, formaldehyde or natural or synthetic tanning agents in order to render them more insoluble in water.

The object of the present invention is to treat threads obtained from casein and the like protein substances in such known manner in order to improve their properties particularly their resistance to the action of water or dilute acid at a high temperature.

According to the present invention the process for the treatment of threads which have been formed by the extrusion of a solution of casein or the like protein substance into a coagulant and have been thereafter treated with a hardening agent comprises treating the said threads with a solution of a salt, to which acid has been added which brings the pH of the threads to a value at or about the iso-electric point of the said protein then removing excess solution from the threads and heating them in the presence of moisture.

Salts which are suitable for use according to the present invention are those which have a buffering action in solution over a pH range in the region of the iso-electric point of the protein, that is in the case of casein about pH 4.6. Examples of such solutions are those containing sodium phosphate, sodium phthalate, sodium lactate, sodium borate, sodium acetate, aluminium acetate or substances forming aluminium acetate, for example aluminium sulphate and sodium or calcium acetate. If acetic acid is liberated in such solutions it can be neutralised by the addition of sodium carbonate. If an aluminium sulphate solution has already been used in the previous hardening treatment sufficient aluminium salt will have been absorbed by the threads to ensure that on the addition of sodium acetate solution the desired action will take place.

The treating solution may contain formaldehyde or its polymers such as paraformaldehyde. The threads, after treatment in the previous hardening bath, may be deprived of excess liquid and immediately treated according to the present invention, or they may be washed free from salts and then treated with or without an intermediate drying operation.

After treatment the excess liquid may be re-

moved by pressing off; draining or centrifuging.

Heating in the presence of moisture may be effected in a closed container or other apparatus capable of preventing undue loss of moisture. The temperature used should be at least 50° centigrade but not so high as to cause damage to the threads.

The following examples illustrate methods of carrying out the present invention although the invention is not restricted to these examples.

Example 1

A solution of casein in dilute caustic soda is extruded into a solution containing salt and acid and the fibres hardened at room temperature in the following bath for 10 hours:

Aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)	50
per cent solution	kilogrammes
Water	litres
Soda ash (Na_2CO_3)	3.6
Sodium acetate	4.4
40 per cent formaldehyde solution	21

The fibres are then washed in water, dried and immersed in an aluminium acetate solution made up as follows:

38 kilogrammes of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ solution of 50 per cent strength are added to 2 kilogrammes of lime ($\text{Ca}(\text{OH})_2$) and 3 kilogrammes of acetic acid in 12 litres of water. The white precipitate of calcium sulphate is filtered off leaving the aluminium acetate solution. 40 grammes per litre of soda ash are then added to neutralise excess acetic acid formed in the reaction, due to the free sulphuric acid liberated by hydrolysis of the aluminium acetate solution. After immersion for 2 hours in the aluminium acetate solution prepared as above, the fibres are whizzed free from excess liquor and heated in a closed vessel for 5 hours at 70° centigrade. They are then cooled, washed with water and dried. On being boiled in water for 30 minutes they are much less damaged and swollen than the unheated material.

Example 2

A solution of casein in dilute caustic soda is extruded into acid and salt, and then taken under tension for about a minute over a series of godets rotating in a bath of aluminium sulphate solution at 55° centigrade. The tow is then cut into staple lengths and placed in a bath of sodium acetate of 30 per cent strength, previously brought to a pH of 5.5 by means of acetic acid. This bath also contains 50 grammes per litre of formaldehyde. The mass of fibres are left in the bath for four hours, whizzed free of liquor and again placed in a bath of the same composition. After four hours the procedure is repeated, and after a further four hours the fibres are finally whizzed, and heated in a churn for four

hours at 90° centigrade. The fibres are then cooled, washed in water and dried. The material so treated has acquired a good resistance to boiling water and boiling dilute solutions of mineral acid.

Example 3

The tow after being cut into staple lengths is treated exactly as in Example 2, but instead of being heated in a churn it is placed in a closed stoppered bottle in an autoclave and heated for 2 hours at 124° centigrade under steam pressure. The resulting product has a good resistance to boiling dilute acid. If there is any slight discoloration of the material after heating in the autoclave this can be substantially removed by bleaching with sodium hydrosulphite.

Example 4

The tow is treated in the bath of sodium acetate and formaldehyde described in Example 2, but instead of changing the bath a number of times, the whole is allowed to stand for 24 hours at room temperature. The mass is then washed free from salt and formaldehyde by means of water. It is then whizzed, and again placed in a bath of 30 per cent sodium acetate of pH 5. After leaving to stand for 24 hours, the fibres are again whizzed, placed in a churn and heated for 4 hours at 90° centigrade. The product has acquired a good resistance to boiling water.

Example 5

A solution of casein in dilute caustic soda is extruded into acid and salt solution. The tow is then dropped continuously onto a conveyor system whereon it is hardened for 45 minutes in a bath containing aluminum and sodium sulphates and formaldehyde. The thread is then taken off the belt and continuously stretched about 200 per cent in an aqueous solution containing 30 per cent of sodium acetate and 2 per cent of acetic acid at 60° centigrade. The tow is then kept under tension for about a minute on rollers rotating in the aforementioned stretching bath and wound up on an aluminium reel rotating in an enclosed bath of:

3 parts of sodium acetate 30 per cent solution to which acetic acid has been added to give an acidity of pH 5 and 1 part of 40 per cent formaldehyde solution. The pH of this solution should be about 5. The reel of tow after winding up continuously for an hour is placed in an earthenware pot, with several other reels if desired, and the pot is carefully closed with a tight fitting lid. The whole is then left at room temperature for 24 hours to ensure completion of the hardening process. The pot is then heated to 80° centigrade and left at that temperature for four hours. The reel and threads are then placed in cold water for a short time in order to soften the filaments and remove as much salt and formaldehyde as possible. Finally the tow is either unwound continuously into a large skein and further washed and dried, or cut off the reel and processed in staple form. The final product has not only lost its tendency to shrink thereby increasing in denier and losing strength, but has also acquired a good resistance to boiling water.

What I claim is:

1. A process for the treatment of threads which have been formed by the extrusion of a solution of casein into a coagulant and have been thereafter treated with a hardening agent which comprises treating the said threads with an aqueous

solution of a salt, to which solution acid has been added which brings the pH of the threads to a value at about the iso-electric point of the casein, then removing excess solution from the threads and heating them in the moist condition without allowing the moisture to evaporate and thereafter drying them.

2. A process for the treatment of threads which have been formed by the extrusion of a solution of casein into a coagulant and thereafter treated with a hardening agent which comprises treating the said threads with an aqueous solution of sodium acetate to which solution acid has been added which brings the pH of the threads to a value at about the iso-electric point of the casein, then removing excess solution from the threads and heating them in the moist condition without allowing the moisture to evaporate and thereafter drying them.

3. A process for the treatment of threads which have been formed by the extrusion of a solution of casein into a coagulant and thereafter treated with a hardening agent, which comprises treating the said threads with an aqueous solution of aluminum acetate to which solution acid has been added which brings the pH of the threads to a value at about the iso-electric point of the casein, then removing excess solution from the threads and heating them in the moist condition without allowing the moisture to evaporate and thereafter drying them.

4. A process for the treatment of threads which have been formed by the extrusion of a solution of casein into a coagulant and thereafter treated with a hardening agent which comprises treating the said threads with a concentrated aqueous solution of a salt of acetic acid to which solution acid has been added which brings the pH of the threads to a value at about the iso-electric point of the casein, then removing the excess solution from the threads and heating them in a closed chamber in the presence of moisture and thereafter drying them.

5. A process for the treatment of threads which have been formed by the extrusion of a solution of casein into a coagulant and thereafter treated with a hardening agent which comprises treating the said threads with an aqueous solution of sodium acetate and formaldehyde to which solution acid has been added which brings the pH of the threads to a value at about the iso-electric point of the casein, then removing the excess solution from the threads and heating them in the moist condition without allowing the moisture to evaporate and thereafter drying them.

6. Process for the manufacture and production of filaments, threads and the like, which comprises extruding a solution of casein through a jet into a coagulating bath, washing the so formed threads, hardening the washed threads by treatment in a bath containing a hardening agent to render them more insoluble in water, cutting the threads into staple lengths, and thereafter treating the staple fibres with an aqueous solution of sodium acetate to which solution acid has been added which brings the pH of the staple fibres to a value at about the iso-electric point of the casein, whizzing the staple fibres free of excess solution, and then heating them for more than an hour in the moist condition without allowing the moisture to evaporate and thereafter drying them.

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