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MANUFACTURE OF ARTIFICIAL TEXTILE FIBERS

Antonio Ferretti, Milan, Italy; vested in the Alien Property Custodian

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8 Claims. (Cl. 106—140)

This invention concerns improvements in or relating to the manufacture of artificial textile fibers.

A complete process is described in the prior application of this applicant, Serial No. 96,470 filed August 17, 1936, for the manufacture of artificial textile fibers derived from casein alone or from a mixture of casein and cellulose derivatives, with or without the addition of mineral substances.

The present invention concerns a process for improving the quality of such fibers and for reducing the costs of production. The present application is based upon and claims the filing date of applicant's corresponding Italian application filed March 2, 1937, subsequently issued on January 24, 1939, as Italian Patent No. 367,405.

In the production of artificial textile fibers according to the above numbered patent application, the manufacturing process is divided into four essential stages or main steps.

The first stage consists of the preparation of the basic substance from milk and is unchanged by the process according to the present invention.

In the second stage of the process the casein is dissolved, diluted, and matured. It has been found that the stability of the alkaline solution of casein can be increased, when substances which sterilise and prevent fermentation even in an alkaline medium are added to the solution. Thus, for example, phenol effects a powerful sterilising action when in a neutral or acid medium, but is quite ineffective, when it is in an alkaline medium, and therefore while it can readily be employed for the preparation of the casein in an acid medium, it is not suitable for use in an alkaline solution. Formaldehyde is a sterilising agent in both acid and alkaline media, but it has a hardening effect upon casein and therefore it could be employed only in combination with hydrosulphites (such as aldehydic hydrosulphite). According to the present invention efficient sterilisation is obtained by adding an aqueous solution of a hydrosulphite, preferably sodium hydrosulphite, to the alkaline solution of casein. By this addition, the stability of the casein solution is trebled, that is, the said solution is preserved in a state suitable for subsequent spinning over a period which is approximately three times that of an alkaline solution of casein to which sodium hydrosulphite has not been added. Other substances prevent fermentation in a similar manner and preferably those are employed which like sodium hydrosulphite, also have a reducing action, such as aldehyde hydrosulphite.

In addition to the solvents specified in said prior application for increasing the volume of the casein solution without a reduction of the viscosity, it has been found that the same object can be achieved by the use of very small quantities of formaldehyde. For example, 2,100 litres of an alkaline solution of casein, which has been prepared by the process indicated in the prior application referred to, to which sodium hydrosulphite has been added in the above manner, can be increased in volume to 3,150 litres, without a reduction of the viscosity, by diluting the solution with 1,050 litres of water which contain 2 kilogrammes of 100% formaldehyde. If the casein solution has been prepared without the addition of the hydrosulphite, it is preferable to reduce the quantity of formaldehyde to 1.70 kilogrammes.

The third stage in the process described and claimed in the said prior application concerns the spinning of the solution of casein and the coagulation of the fibers so formed.

In the factories which produce rayon by the viscose system (cellulose xanthogenate), a considerable quantity of residue from the coagulation bath, is wasted. According to the present invention, research has been conducted into the possibility of employing this residue for the coagulation of the casein fibers.

The residue is of a lower concentration than that in a normal coagulation bath, that is, it contains less acid and less sodium sulphate.

It has been found that this bath of residual matter can be utilised, provided that the density thereof is greater than 1.18 and the sulphuric acid content is greater than 25 grammes per litre of the bath. Uniform spinning of the alkaline solution of casein is effected with such a bath, but the fibers stick to one another, thus rendering the product unserviceable, unless immediately immersed in a sodium chloride solution, to which preferably aluminium salts and formaldehyde have been added. Instead of sodium chloride, solutions of alkaline metal salts or of alkaline earths could be applied, but the cost of the process would be increased, and the final product be of less value.

Other baths can be employed for the coagulation of the casein fibers, having a density greater than 1.18 and a sulphuric acid content greater than 25 grammes per litre of the bath, the sodium sulphate being replaced by other soluble sulphates or chlorides such as zinc sulphate, ammonium sulphate, ammonium chloride etc., separately or mixed with one another, but the cost of the coagulation process is correspondingly increased.

The fourth stage of the manufacturing process according to the prior application involves rendering the filaments or fibers insoluble, whether they be obtained from casein alone or from a mixture of casein and cellulosic viscose.

It is stated in the prior application that it is important in the production of tuft fibers to maintain the fibers in a stretched condition dur-

ing the first part of the process, that is during the passage through a weakly concentrated preparatory bath for rendering them insoluble, and to cut the fibers to the desired lengths before they are passed to the successive baths. In this manner fibers are obtained which are only slightly shrunk and which are uniformly twisted. The winding of the fibers upon bobbins, the immersion into the preparatory bath for rendering them insoluble, and the subsequent cutting of the fibers, involve three separate operations which are lengthy, difficult and costly to effect since the apparatus is complicated and requires the service of many operatives.

According to the present invention the process can be effected automatically and rapidly in the following manner.

The fiber bundles which emerge from the spinning nozzles are conveyed to the top of the spinning machine, thus forming a continuous band of fibers (for instance: one hundred spinning nozzles having one thousand holes each are equal to a band of one hundred thousand continuous fibers). This band is conveyed, under tension, first through a sodium chloride bath, and if it is desired to remove all or part of the acid and the salts which are carried from the preceding coagulation bath, the fibers are passed in the opposite direction to the flow of the sodium chloride; then the continuous band of fibers is conveyed, still under tension, through the preparatory bath for rendering the fibers insoluble, which is composed of sodium chloride and aluminium salts, either with or without the addition of formaldehyde, and when the fibers are sufficiently washed and subsequently hardened, the band is passed through an automatic cutter, which cuts the fibers to the desired length. The cut fibers, as stated above, must be collected in a bath of sodium chloride or of other alkaline metal salts or of alkaline earths, either with or without the addition of aluminium salts and formaldehyde, but preferably in a bath for rendering them insoluble which is composed of an aqueous solution of sodium chloride, aluminium salts and formaldehyde.

The sodium chloride in the initial immersion bath may be replaced by other soluble alkali metal salts or alkaline earths, but, in addition to the increased cost, the resultant product is not so good. Moreover, by the use of a sodium chloride bath, a quantity of sodium chloride is conveyed by the fiber into the subsequent baths for rendering the fibers insoluble, in which baths it is very useful and indeed almost indispensable.

The first immersion bath, which eliminates the acid and the sodium sulphate or other salts conveyed with the fibers from the coagulation bath, could also be omitted, when the said band is immediately immersed in the preparatory bath for rendering the fibers insoluble, or even directly into the complete highly concentrated bath.

The band, which passes through the bath at the same speed as it is spun (60 to 80 metres per minute) may be continuously immersed in the above described baths, but it is also possible to immerse the said band intermittently, for example, at points located one metre apart, making it move upwards and downwards so as to enter the bath over a distance of 10 to 15 centimetres only of its travel, with a distance of one metre between successive immersions.

In the passage of the band of fibers through the baths, two factors are of high importance:

1. That the band be under tension when passing through the baths, so that it cannot shrink.

2. That the temperature of the bath be greater than 25° C., and preferably between 35° C., and 40° C. for the first bath composed of sodium chloride or other salts, and between 50° C. and 65° C. for the preparatory or for the complete baths for rendering the fibers insoluble.

When these two factors are complied with, the continuous or the intermittent immersing operation of the band is effected in less than five minutes, in conformity with the spinning velocity, and the fibers are sufficiently hard to prevent adhering together, even when coagulation baths of low concentration are employed. The fibers could be cut to the desired lengths immediately and only shrink in so far as the best twist is to be obtained. If, however, a greater twist is required, to the detriment of the fineness of the fibers, the passage of the band through the baths may be effected without maintaining it under tension.

By the above described treatment short fibers can also be derived from casein which are finer than those which can be obtained during spinning. For instance, when the spinning operation is regulated so as to obtain a fiber the count of which is three denier and it is not possible to spin a finer number, the band of fibers should be drawn with a speed which is 50% higher than that of the spinning velocity, and the count, which during the spinning was three denier, will be reduced to two denier. But when the band is then immediately cut, the fibers will shrink to a point at which the count has returned to three denier. Instead, when the said band is made to pass through the above described baths, under tension and at the prescribed temperature, the fiber will maintain the count of two denier.

In view of the fact that the price of wool increases as the count increases it will readily be appreciated that it is of considerable importance to be able to obtain a higher count without any increase in cost.

As a result of the preceding statements it is important that the temperature of the bath into which the hardened fibers are introduced when cut should be greater than 25° C., it being preferable to employ a temperature between the range 35° C. to 40° C.

The treatment for rendering the casein fibers insoluble extends over a very long period, even several days, when carried out in a bath at room temperature, which is usually less than 25° C., nevertheless the fibers offer little resistance to boiling extending over a long period. On the contrary, it is found that when the temperature of the baths for rendering the fibers insoluble is raised, for example to between 60° C. and 70° C., perfect insolubility is obtained in less than nine hours, and the fiber which has been treated at that temperature completely resists boiling which may extend over many hours. Before proceeding to this strong treatment it is preferable to pass the fibers for some hours into the collecting bath of the cut fibers at a temperature of between 35° C. and 40° C.

Complete resistance to the extensive boiling could also be obtained, when the casein fibers, which have been rendered insoluble at a temperature which is lower than that indicated, for instance at 25° C. to 50° C., are treated, preferably after being washed and dried, with an aqueous solution of formaldehyde at a temperature of about 60° C. to 70° C. for several hours, for exam-

ple, five hours. In this case, the addition of the aluminium salts, of sodium chloride or of other soluble alkaline metal salts or earthy alkalies, to the formaldehyde solution is unnecessary.

This treatment could be effected with the dried casein fibers at any desired time, that is to say, even after a period of many months or years from the manufacturing date of the fiber has elapsed.

Above all, it is of great importance that the treatment for rendering the fibers insoluble should be effected at temperatures which are greater than 25° C., and that, when a temperature above 25° C. is applied, the described operation should take place in an autoclave (digester) which should preferably be rotary, so as to maintain the fibers in motion, while at the same time the bath for rendering the fibers insoluble is made to circulate in the interior of the autoclave.

From the foregoing statements it is clear that in order to avoid deterioration of the casein fibers when they are just coagulated, they should not be rendered insoluble in aqueous solutions which contain more or less high percentages of formaldehyde alone, but other salts such as sodium chloride and aluminium salts should be added to the aqueous solutions of formaldehyde. This is more important when the fibers are rendered insoluble at temperatures above 25° C.

After the casein fibers have been rendered insoluble it is advantageous to treat them with aqueous solutions of monosodium, bisodium, or trisodium phosphate, together with or without the addition of formaldehyde, and this treatment should preferably be effected after the fibers have been dried.

All of the above described processes could be applied to the manufacture of fibers derived from casein, whatever may be the kind of casein employed (textile casein, lactic casein or acid casein etc.).

Moreover, some of the above stated processes are very important not only for the manufacture of fibers from casein alone but also, although to a less degree, for the mixed casein and cellulose fibers, because better quality products are obtained together with a reduction of the production costs.

In the case of fibers of mixed casein and cellulose, the desulphurating operation, which is normally employed in known manner for rayon which is produced by the viscose system (cellulose xanthogenate), is detrimental. It has been found that such deterioration of the mixed casein and cellulose fibers can be avoided, when sodium chloride or other soluble alkaline metal salts or alkaline earth salts, either with or without the addition of formaldehyde, are added to the desulphurating solutions. This is suitable also for the fibers of casein alone when they contain sulphur which has to be removed.

It is to be understood that the present invention may be modified or supplemented in various ways without departing from the spirit of the invention. Various matters of process and product, ingredient, composition and step, hereinabove disclosed but not herein claimed have been made the subject of divisional or continuation applications as follows: Serial Numbers 330,725, and 330,726, and 330,727, and 330,728, all filed April 20, 1940.

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

1. In a process for the manufacture of artificial textile fibers from material containing casein, the stage of maturation under heat of an alkaline solution containing the casein to afford spinnable viscosity thereof, which stage comprises the step of adding to the solution a chemical agent which sterilizes and prevents fermentation thereof, thereby greatly stabilizing the spinnable viscous solution pending the stage of spinning and coagulating the fibers; said sterilizing agent being a hydrosulphite having also a reducing influence in the solution, selected from the group consisting of sodium hydrosulphite and aldehyde hydrosulphite.

2. In a process for the manufacture of artificial textile fibers from casein, the stage of maturation under heat of an alkaline solution of the casein to afford spinnable viscosity thereof, which stage comprises the step of sterilizing by adding to the solution a chemical agent of the group consisting of sodium hydrosulphite and aldehyde hydrosulphite, thereby stabilizing the spinnable viscous solution pending the stage of spinning and coagulating the fibers.

3. In a process for the manufacture of artificial textile fibers from casein, the stage of maturation and volume expansion of an alkaline solution of the casein to afford an increased volume of spinnable viscosity, which stage comprises the steps of diluting the solution progressively with water and introducing formaldehyde in very small proportions thereby maintaining spinnable viscosity throughout dilution to an excess volume, and adding to the solution a chemical agent selected from the group consisting of sodium hydrosulphite and aldehyde hydrosulphite, which sterilizes and prevents fermentation thereof, thereby greatly stabilizing the expanded spinning viscous solution pending the stage of spinning and coagulating the fibers.

4. The process stage as in claim 3 and wherein the formaldehyde present is in the proportion of about 1.7 to 2 kilograms of 100% formaldehyde for each unit of about 3150 liters of diluted solution.

5. The improvement set forth in claim 1 applied to a mixture of casein and cellulose in alkaline solution.

6. The improvement set forth in claim 2 applied to a mixture of casein and cellulose in alkaline solution.

7. The improvement set forth in claim 3 applied to a mixture of casein and cellulose in alkaline solution.

8. In a process for the manufacture of artificial textile fibers from material containing casein, the stage of maturation under heat of an alkaline solution containing the casein to afford spinnable viscosity thereof, which stage comprises the step of sterilizing by adding sodium hydrosulphite to the solution, thereby to stabilize the spinnable viscous solution pending the stage of spinning and coagulating the fibers.

ANTONIO FERRETTI.