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MANUFACTURE OF ARTIFICIAL TEXTILE FIBRES

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Alien Property Custodian

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This invention is for improvements in or relating to the manufacture of artificial textile fibres.

The artificial textile fibres that are at present manufactured on a large scale throughout the world consist solely of cellulose dissolved by various methods in order to obtain a viscous mass which is successively transformed into yarns or fibres according to various methods. Accordingly, these artificial products have an elementary composition nearly identical to that of the vegetable textile fibres and especially to that of cotton, which is constituted by pure cellulose.

Consequently, apart from certain differences in outward appearance, the properties of these artificial fibres are nearly identical with those of vegetable textile fibres, viz. the said artificial textile fibres are cold like cotton, are inflammable, are not adapted to be dyed with the dyeing stuffs in use for the textile fibres of animal nature, such as wool and animal hair generally, do not contain nitrogen etc.etc.

One object of the present invention consists in the production of a novel artificial textile fibre consisting solely of a nitrated substance of animal nature, having an elementary composition nearly identical to that of natural wool, as will be seen hereinafter. This artificial textile fibre is therefore warm like natural wool, is not inflammable, is adapted to be dyed with the same dyeing stuffs as natural wool, contains about the same percentage of nitrogen etc., This novel artificial textile fibre may therefore with good reason be called synthetic wool, since it stands in the same relation to natural wool as the cellulose artificial textile fibres stand to the vegetable textile fibres in general and to cotton in particular.

A second object of the invention consists in the production of a very important full series of novel artificial textile fibres consisting of a nitrated substance of animal nature and of a substance of vegetable (non-nitrated) nature, intimately combined with one another, the properties of which fibres are intermediate those of the "rayon", which consists of vegetable substance alone, and those of the synthetic wool just described, which consists (solely) of nitrated organic substance of animal origin.

A further object of the invention consists in the production of artificial textile fibres as defined in either of the two immediately preceding paragraphs, but with additions of mineral substances.

According to the invention, the above objects are attained by the manufacture of an artificial textile fibre starting from casein as the basic substance and which is suitably treated to produce a fibre of desired softness and strength.

The above and other features and advantages of the invention will be clearly understood from the following explanation of the various basic materials and steps followed in the manufacture of artificial textile fibres according to the invention.

In the production of the artificial fibres according to the invention, the manufactureing process is divided into the following essential phases:

The first phase consists in the preparation of the basic substance constituted by a nitrated organic substance of animal origin.

The raw material employed for this purpose according to the invention is the casein obtained from cow milk after the milk has been skimmed, for example, for the manufactura of butter.

The following is a comparative table giving the elementary composition of casein and of natural wool.

Elementary composition

	Natural wool	Casein
	Per cent	*Per cent*
Carbon	49.25	53
Hydrogen	7.57	7
Oxygen	23.66	23
Nitrogen	15.86	15
Sulfur	3.66	0.79
Phosphorus		0.80
	100	100

However, the various types of casein that are at present produced in the cheese factories of the whole world are but little suitable for a regular production of artificial textile fibres.

The casein obtained by coagulating the skimmed milk with rennet is used in the manufacture of galalite. This casein is insoluble in alkalis and for this reason it is impossible even to try to employ the same in the manufacture of textile fibres.

The other caseins of the trade, obtained by acid coagulation of the skimmed milk (these casein are more or less de-mineralised), are soluble in the alkalis and are suitable for the preparation of viscous glues for the manufacture of plywood, satined paper, tissue sizes etc.

As a result of numerous experiments, it has now been ascertained that these caseins can be transformed into yarns and fibres by the method according to the invention, but generally are—among others—too viscous, so that a regular spinning is difficult. In addition, it has been found that the filaments obtained from these caseins through the acid coagulation bath and through multifilament spinning nozzles are difficult to isolate from one another, since they often stick together and in this case, after drying, present themselves in the form of compact, hard and brittle masses.

Such difficulties are encountered both when lactic casein is employed (viz. casein obtained by coagulation of the skimmed milk by means of spontaneous acid, or fermentation at suitable temperatures) as well as when using caseins obtained by direct acidification of the milk by means of additions of acids according to the generally known methods. Hence the necessity of devising a method for procuring a textile casein, viz. a casein which is perfectly suitable for a regular manufacture of artificial textile fibres.

In the production of lactic casein the coagulation is obtained with the lactic acid which is progressively formed by the lactic ferments present in the milk. The coagulation of the casein takes up a period of time which is variable according to the temperature and to the amount of ferments present in the milk. When the temperature is maintained between 25°C and 30°C, and the milk contains a normal amount of lactic ferments, the coagulation generally takes from 12 to 24 hours from the beginning of the fermentation.

When the coagulation is completed, the development of lactic acid spontaneously ceases because the acid produced has progressively reduced to impotence the lactic ferments by which it is originated.

At this point the casein is heated in its serum up to but not above 65°C. in order to avoid the coagulation of the albumin contained in solution in the serum. The casein is then washed one or more times and extracted from the serum and pressed in order to remove as much as possible the liquid present in the casein, which is finally dried and ground.

At present the de-mineralised casein is generally prepared by the method above described, that is to say through spontaneous acidification of the skimmed milk (lactic casein). In some countries, however, in order to shorten the time taken by the coagulation, the casein is prepared by means of additions of mineral or organic acids to the skimmed milk, whereby an immediate coagulation is obtained (acid casein). The amount of acid to be added to the skimmed milk varies according to the neutralising power of the acid employed and according to the temperature of the milk at the moment the acid is added. The higher the temperature of the milk, the smaller is the amount of acid necessary to bring about the coagulation of the casein. Of course, if a strong mineral acid is employed, for instance sulphuric acid, the requisite amount of acid is much lower than when a weak organic acid is employed, such as for instance lactic or acetic acid.

In other words, in the preparation of acid casein, the aim is to realise in a few minutes the same result that is achieved in about a day with the preparation of lactic casein through spontaneous acidification.

Both methods realise the coagulation of the casein by means of acid agents and consequently hitherto the amount of acid added to the milk or spontaneously produced by acid fermentation of the milk is deliberately confined to the amount strictly necessary to achieve, at a determined temperature, the coagulation of the casein, any excess of acid being carefully avoided since it might give rise to the so-called "acid redissolution of the casein" which is affirmed by all writers and technicians in the art dealing with milk.

The lactic casein necessarily remains a considerable time in contact with the acid in its serum, and this favours the demineralisation which is desired in order to obtain a casein adapted to supply good viscous glues. Also, in the production of acid casein some manufacturers prolong the duration of the contact of the coagulating casein with the acid added to the milk, and sometimes energetically stir the casein in the acid serum, always solely in order to achieve a better de-mineralisation, but of course in this case there is lost a good portion of the time that had been gained through the rapid acid coagulation.

The acid and lactic caseins produced by the methods above described are sufficiently de-mineralised and usually contain only 2–3% ashes.

In order to obtain a pure casein, that is to say an almost completely ash-free, casein, the lactic and acid caseins are again dissolved in alkalis and then precipitated with an acid. The operation may be repeated two or three times, a substantially pure casein being thus obtained. The cost of this pure casein, however, is so high that the method could never be introduced itself into the industrial pratice.

It has now been endeavoured to ascertain if at least this pure casein was suitable for the manufacture of artificial textile fibres. As a result of numerous experiments, however, it has been found that also this pure casein presents the same disadvantages as the other trade caseins previously referred to.

As a result of numerous other experiments, however, it has now been found that in order to obtain a casein (and even a full series of caseins) suitable for the manufacture of artificial textile fibres, it is necessary to introduce into the skimmed milk an excess of acid over the amount which is strictly requisite to bring about the coagulation of the casein.

The acid coagulation of the casein must thus be carried out in such a manner as to bring about what the makers of trade-casein carefully seek to avoid and what the writers and technicians have inappropriately called "acid redissolution of the casein" which acid re-dissolution it has been found, as a result of numerous experiments, does not exists actually but only apparently.

The above will be more fully understood from the following examples.

Example I

In order to coagulate 100 (one hundred) litres of skimmed milk heated to 40°C., 110 (one hundred and ten) cm^3. of 66° Be sulphuric acid are sufficient previously additioned with 90 cm^3 of water. The acidity of the serum at the moment of the coagulation is equal to about 4.9–5 PH. The casein thus prepared is, among other, but little de-mineralised and is absolutely unsuitable for a regular and convenient manufacture of textile fibres.

Example II

In order to coagulate the same 100 litres of skimmed milk, but heated to 20°C, about 160 (one hundred and sixty) cm^3 of 66° Be. sulphuric acid are used previously additioned with 1440 cm^3. of water. The acidity of the serum at the moment of the coagulation is equal to about 4.6–4.7 PH. This is the minimum PH, viz. the maximum acidity used for the coagulation of all the lactic and acid caseins of the trade.

This casein is better than the one obtained by the method indicated in Example 1, especially from the standpoint of the de-mineralisation, but also this casein presents, in the manufacture of artificial textile fibres, the same disadvantages and difficulties that are encountered when employing the lactic and acid caseins of the trade.

The amount of sulphuric acid used being left unaltered, various experiments have been made with various modifications of the above examples, as follows: introducing the sulphuric acid into the skimmed milk in various portions and at time intervals one from the other; letting the coagulating casein remain in its serum; heating the coagulating casein in its serum to all temperatures comprised between 20 and 69°C. and for durations comprised between 5 minutes and 96 hours; letting the said casein mature in pressed conditions only or also, in ground, washed and unwashed conditions at the most various temperature and for the most various periods of time; drying the casein slowly or quickly, the temperature and ventilation being varied. In many cases a deterioration of the desired qualities has been found, but in no case has a casein been obtained with such substantial modifications as would result in overcoming the disadvantages above referred to.

Example III

It has been found, however, that if to the same 100 litres of skimmed milk and at the same temperature of 20° C. as in Example II, there are added, preferably in two amounts, 250 (two hundred and fifty) cm^3 of 66° Be. sulphuric acid, previously additioned with 2250 cm^3 of water, a casein is obtained which is perfectly adapted to be transformed into artificial textile fibres. The acidity of the serum at the moment of coagulation is equal to 2.9–3 PH.

The amount of acid used for the coagulation of the casein in the above Example, represents an excess of 56% over the amount strictly necessary to obtain the coagulation as indicated in the preceding Example II.

The coagulation of the casein takes place completely and in small flocons when into the 100 litres of skimmed milk heated to 20°C, 160 cm^3. 66° Be. sulphuric acid have been introduced as indicated in Example II. The addition of the acid then being continued until the 250 cm^3 of Example III are reached, it is observed that the coagulated casein dissolves itself again, but only apparently, due to the excess of acid.

All writers and technicians of the milk branch affirm this re-dissolution of the casein if an excess of acid is introduced into the skimmed milk. It is herein affirmed, on the contrary, that it is a question, not of a re-dissolution proper, but only of an extremely fine subdivision of the flocons of coagulated casein. The coagulation of the casein remains intact even with an excess of acid; only an extremely fine subdivision of the casein particles in the serum occurs. Nothing is changed in the fact, even if the excess of acid is pushed to exaggeration, as has been ascertained by introducing into the skimmed milk an amount of sulphuric acid which was several times the amount sufficient to realise a normal coagulation of the casein. There is only the illusion of a re-dissolution, but the casein coagulated by means of the acid absolutely does not dissolve itself again in an acid medium, and consequently can be extracted and separated from its serum, no matter what may have been the amount of acid employed for its coagulation.

Anyhow it remains established by the above that caseins specially adapted for a rational and regular production of artificial textile fibres have been prepared by coagulating the skimmed milk with an excess of acid over and above the quantity that is strictly sufficient to bring about the coagulation of the casein at the temperature of 20° C., that is to say it is necessary to go down to a PH lower than the one (4.7 PH) used for the coagulation of the lactic and acid caseins of the trade.

Of course the percentage of acid excess may be varied above or below the 56% indicated in Example III, according to the effect desired. For instance, the other factors of the process remaining unaltered, by coagulating 100 litres of skimmed milk heated to 20° C. with 250 cm^3 66° Be. sulphuric acid, a textile casein is obtained, viz. a casein capable of supplying textile fibres of excellent softness and strength, and by progressively reducing the amount of acid used for the coagulation, the strength of the fibres will be increased but the softness progressively reduced until the resulting fibres are glued together and brittle (and therefore unserviceable) when the amount of 66° Be. sulphuric acid employed is confined to the amount strictly requisite to bring about the coagulation of the casein, viz. is confined to about 160 instead of 250 cm^3. Conversely, by employing greater amounts of acids, the softness is, up to a certain amount, improved but to the prejudice of the fibre strength which decreases according to the greater quantity of acid employed.

All strong mineral acids (salpetre acid, hydrochloric acid etc.) may be used for coagulating the casein suitable for the manufacture of textile fibres. According to the invention, the quantity thereof being of course varied according to their degree of concentration and to their greater or smaller neutralising power, it remaining understood that it is necessary to carry out the coagulation with an excess of acid as indicated above in connection with the sulphuric acid.

The organic acids can also serve for the purpose, but are less suitable and, besides, the cost of the casein would become far greater owing to the greater amount of acid required as well as owing to their higher cost.

Finally, it is pointed out that the coagulation of textile casein may be obtained also with a mixture of two or more mineral or organic acids, provided that the neutralising power of the acid mixture be equivalent, for each 100 litre of skimmed milk, to that of 250 cm^3 of 66° Be. sulphuric acid or to that greater or smaller quantity of the same sulphuric acid which it is desired to employ in order to secure a greater or smaller strength or softness of the fibres as above explained.

For instance, always for each 100 litre of skimmed milk at a temperature of 20° C., there may be employed 125 cm^3 66° Be. sulphuric acid and 260 cm^3. salpetre acid (likewise concentrated). The result is about the same as when using 250 cm^3 66° Be. sulphuric acid. The expense, however, is many times superior to that incurred when using sulphuric acid alone.

Again, it is pointed out that the trade caseins, (lactic or acid) may be modified in order to make them suitable for the manufacture of textile fibres, by means of a supplementary acid treatment so as to make up for the insufficient amount of acid employed at the moment of the coagulation. In the case of lactic casein, the acid supplement—preferably strong mineral acid—may be added after the coagulation brought about by spontaneous fermentation of the casein, before or during the normal heating of the casein in its serum, the mass being energetically stirred in order to distribute the acid uniformly. Alternatively, the acid supplement may be added to the casein after the casein has been extracted from its serum, preferably after pressing and grinding. Such processes, however, would only constitute makeshifts in practice and uncertain ones at that, since the measuring of the acidity for each lot of coagulated milk in order to determine the requisite acid supplement would involve an onerous and delicate work. In the case of acid casein, the work would be easier because, once the amount of acid employed for the coagulation of the normal acid casein is known; it is easy to determine the acid supplement necessary to transform the same into textile casein according to the invention.

It must further be pointed out that there are certain kinds of ferments which, if added to the skimmed milk under favourable temperature conditions, are capable of producing a considerable acidity which may sometimes attain the pH value necessary for the obtention of a textile casein. However, this caseing does not fulfil always the requirements for its transformation into textile fibres because the acidity, being produced by micro-organisms, may vary within too wide limits so that a regular spinning would be rendered impossible, but this possibility of adding special ferments adapted to produce strong acidities has also been referred to in order to lay stress on the feature according to the invention that in order to obtain a textile casein from milk it is necessary to coagulate the milk with an acid excess comprised between the limits stated above.

Also, the serum left from a first lot of coagulated milk can be used for the coagulation of a subsequent milk lot, by making the necessary additions of acid.

After the casein has been coagulated, it is heated in its serum in order to facilitate the draining and subsequent pressing thereof.

The temperatures for these operations may be the most various, but it must be avoided to exceed 65–68° C. because already at 70° C. the coagulation of the milk-albumin begins in the serum and this albumin mingling in considerable quantities with the casein disturbs the subsequent spinning operations.

It is sufficient, for instance, to gradually heat the casein in its serum up to a temperature of 61°C. and to then immediately drain the serum in order to collect the casein. The permanence of the casein in the serum at 61° C. may be extended to half an hour or even more, but this is disadvantageous since a too prolonged permanence, at the said temperature, impaire the strength of the fibres in the final product.

It has been further ascertained that it is preferable to heat the casein in the serum, for an hours duration at 45°C.

One may operate through the temperature or through the duration of the heating in order to make small corrections in the viscosity and density of the successive colloidal solutions of the casein, but it is preferable to carry out these small corrections by varying the temperature during the preparation and subsequent maturation of the alcaline colloidal solution of the casein. Of course, when it is desired to previously vary the viscosity and density of the alkaline colloidal solution of the casein, it is better to operate by reducing or increasing the acid excess during the coagulation of the milk according to the end in view.

After the casein has been coagulated and subsequently heated as already described, it is extracted from the serum and then pressed with suitable means in order to reduce the serum content left in the casein.

The acid and lactic caseins of the trade are generally washed one or more times before pressing, and after pressing are dried in order to reduce to 10–12% the moisture contents which generally are 50–70% after pressing.

The textile casein prepared according to the invention retain, in the draining and pressing operation, a greater serum percentage than the normal trade caseins according, up to a certain point, to the greater or smaller acid excess used during the coagulation of the milk.

For the manufacture of artificial textile fibres it is not indispensable to wash the casein in order to free the same from its serum, nor to dry it. It has been found that it may be used without further ado, after the pressing and subsequent grinding, for the preparation of the alkaline colloidal solutions from which the textile fibres are obtained. Of course, as will be described hereinafter in this case the percentage of acid serum left in the casein must be taken into account in determining the addition of alkali requisite for its neutralisation. It is preferable that the serum percentage after the pressing should not exceed 200% of the dry weight of the casein, in order to leave a sufficient margin for the solvent to be used for the preparation of the alkaline colloidal solution.

It is obvious that once a serum percentage has been fixed, this percentage should be adhered to in order to facilitate a regular work.

It is preferable that the casein intended for the production of textile fibres should not undergo the slightest fermentation during the operations performed after the coagulation when the casein is still in the unwashed condition and consequently still contains a determined percentage of acid serum, it can be readily preserved at the temperature of running water for some days, viz. for about the time necessary for its transfer to the spinning works and for its successive use in the preparation of the colloidal solution. If the same casein containing acid serum is dried in suitable drying plants at a convenient temperature, there is no danger of fermentations being originated.

On the contrary, when the casein—for any reason whatever— is washed, it is convenient to add an antiseptic or sterilising agent to the casein, in order to prevent fermentation which would readily set in, especially at the beginning of the drying and during the summer months.

A suitable sterilising agent may in all cases be used, either during the coagulation or afterwards.

A specific process and apparatus for the manufacture of casein suitable for the production of textile fibres according to the invention will now be described by way of example.

In the first phase of the process, a determined quantity of skimmed milk is put into a suitable vessel, the latter being provided with a stirring device and with a double bottom and double walls for the circulation of water necessary to adjust the temperatures during the coagulation.

The milk temperature is raised to 20° C.

In a separate vessel, a solution is prepared with, for each 100 litre of skimmed milk, 250 cm^3 66° Be. sulphuric acid preferably diluted with 9 times its volume of water. This acid solution is also raised to 20° C. It remains understood that the amount of water added to the acid is not a hard and fast one but may be varied between very wide limits.

The stirring device is started, in order to keep the milk in motion so as to facilitate a uniform and rational distribution of the acid solution in the milk.

One half of the prepared acid solution is now slowly introduced into the milk, preferably by means of several tubes uniformly distributed in the milk mass, the agitation of the liquid mass being continued.

After about half an hour's contact of the milk with the first portion of the acid, the remaining portion of the prepared acid is added in the same manner.

When the addition of the acid is completed, the heating to the desired temperature is started at once, the agitator being preferably kept going in order that the casein may remain mingled with the serum. As previously stated, a certain time may elapse before starting the heating of the mass after completion of the coagulation.

When the heating is completed, the casein is extracted from the serum by suitable means and is then pressed in order to reduce the moisture content, after which the casein is ground in order to facilitate the subsequent colloidal solution.

The casein prepared in the manner above described is adapted to furnish textile fibres of excellent strength and softness.

When for any reason whatsoever it is desired to produce fibres of greater strength and less softness, the amount of sulphuric acid should be reduced down to a minimum limit of about 170 cm^3., for each 100 litre of milk, thus obtaining fibres that are gradually stronger and less soft according to the smaller quantity of acid employed.

At the said minimum limit, however, the risk already exists of an irregular spinning and above all of endangering the quality of the final product.

Conversely, a greater amount of acid is used when it is desired to increase the softness, to the detriment, however, of the strength of the fibre.

During the coagulation the temperature may also be lower than the 20° C. named in the example, or slightly higher.

The second phase of the process consists in obtaining the colloidal solution, dilution and maturation of the casein.

All caseins, lactic or acid inclusive, of the textile caseins according to the invention, provided they have been sufficiently de-mineralised, are soluble in all the alkalis and in conjunction with these give more or less viscous colloidal solutions.

In order to realise a colloidal casein-solution adapted to be spun, it has been found that only hydrated sodium and hydrated kalium are suitable. All other alkaline agents, even if combined together in the most varied proportions, supply colloidal casein-solutions which cannot be spun. This fact ascertained by numerous experiments, applies not only to the textile casein produced according to the invention but to all trade-caseins, whether lactic or acid.

In practice, it is preferable to use as alkaline solvent the hydrated sodium only, because it is cheaper than hydrated kalium, while the results are identical. It has also been found, however, that a mixture of hydrated sodium and hydrated kalium in the most varied proportions to each other may be used, the only difference consisting in the greater expense incurred according to the proportion of the hydrated kalium employed in lieu of the hydrated sodium.

Also, small quantities of other alkaline agents may be used, added either directly to the aqueous solution of hydrated sodium or hydrated kalium, or a mixture of these two hydrates, or to the colloidal casein-solution previously prepared with hydrated sodium or hydrated kalium, or a mixture thereof, these additions being made in order to modify slightly the properties of the colloidal casein-solution. It is necessary, however, to confine these additions within narrow limits, because otherwise the colloidal casein-solution would lose its spinning capability.

In other words, it is necessary that the alkaline agent employed for the colloidal casein solution shall preponderantly consist of hydrated sodium or hydrated kalium, the said preponderance being referred, not to the volume of the solvent solution used, but only to its neutralising power.

The amount of hydrated sodium to be preferably used for obtaining a colloidal casein-solution suitable for the manufacture of textile fibres has been established—on the basis of a temperature of 24° C. used for the solution of the casein and for its subsequent maturation. However, the amount of hydrated sodium may be slightly reduced if the adopted temperature is higher than the temperature indicated above, and conversely the said amount may be slightly increased for a lower temperature. No true reverse proportion, however, exists between the amounts of alkali and the temperature adopted, because the alkali amount chiefly influences the solubility of the casein, whereas the temperature chiefly influences the viscosity, density, volume and maturation of the colloidal solution.

The amount of hydrated sodium used remaining unaltered, to a higher temperature there corresponds a greater volume and density as well as a lesser viscosity and more rapid maturation of the colloidal solution.

Yet it is not advisable to depart considerably from the so to say centre temperature of 24° C. For instance, if the temperature of 35° C. is progressively exceeded, the density progressively becomes excessive and the viscosity unduly great as compared with the viscosity necessary for the spinning operation and, above all, the risk is incurred of seriously endangering the quality of the ultimate product. Conversely, with a temperature below 14°C., there results an unduly great and useless delay in the maturation and it is difficult, not to say impossible, to realise the desired volume of colloidal solution.

It is possible to increase the density of the colloidal casein solution without altering its spinning property (and even improving the same) by using special diluting agents hereinafter specified. These diluting agents, however, always act in the same measure on the density and on the volume of the colloidal solutions whatever may have been the preparation and maturation temperature, so that the differences of the colloidal solutions of the textile casein in density and volume remain practically unaltered relatively to one another at the various temperatures.

Various examples of colloidal solutions of textile casein will now be given for a clear understanding of this part of the invention.

Example A

When using dried casein that has not been washed after coagulation.

A determined quantity of dried and ground casein is placed in a suitable vessel, the vessel being fitted with a stirring device and with a double bottom and double walls for the circulation of the water necessary to regulate the temperature during the solving, diluting and ripening of the colloidal-casein solution.

For each 100 kilos of dried casein containing a normal moisture percentage of 10%, 200 litres of water are poured into the vessel, the water having been previously heated to 24° C. and being uniformly distributed in the casein previously placed in the vessel. However, it is also practicable to pour first the water into the vessel and then the casein.

After two or three hour contact of the water and casein, there is introduced into the vessel a solution comprising 23 (twenty three) litres. 35° Bé. hydrated sodium and 77 (seventy seven) litres water, previously heated to 24° C., for each 100 kilos dried casein referred to above, the mass being energetically stirred in order to rapidly and uniformly incorporate the hydrated sodium with the casein solution. When the mixture has become uniform, the stirring may be slowed down or be effected only at intervals. The temperature is preferably maintained constant at 24° C. It may be mentioned that, of course, instead of 35° Bé. hydrated sodium, a corresponding amount of dry hydrated sodium previously solved in water may be used. Likewise, the procedure is the same if instead of hydrated sodium, hydrated kalium is used, bearing in mind that the temperature of 24° C. remaining unaltered, the amount used must correspond to the alkalinity or neutralising power of 23 litres. 35° Bé. hydrated sodium for each 100 kilos dry casein containing 10% moisture. If the moisture percentage in the casein used is higher or lower, the amount of water and alkali to be added to the casein must be varied accordingly.

When the casein has been dissolved and the mass has gradually become more dense and viscous (this taking place in a few hours according to the type of casein used, viz. whether coagulated with a greater or smaller quantity of acid, and the temperature of 24° C. remaining unaltered), a slow and gradual dilution is effected so as to compensate for the increasing density of the colloidal solution during its maturation.

The addition of diluting agents previously heated to 24° C. are preferably made little by little in order to avoid a momentarily unduly high dilution which would delay the regular and gradual development of the density necessary to allow of the subsequent additions of diluting agents until there is obtained the desired volume of the colloidal solution and without causing this solution to lose its spinning property.

When the desired volume and density of the colloidal solution have been attained, the development of the density can be stopped by slightly lowering the temperature of the solution, the solution thus remaining stabilised for a certain time so that it can be transferred to the spinning machines with the properties and characteristics previously established. This is of the greatest importance for a regular spinning which otherwise would be difficult to obtain.

The concomitance of the above said factors, the time requisite for the dissolution, maturation and increase in volume of the colloidal casein-solution may vary between sufficiently wide limits, since the said time depends not only upon the desired volume and density but also upon the types of the caseins used, upon the types of diluting agents used and upon the temperature adopted during the alkaline dissolution of the casein and its subsequent maturation.

A casein obtained with 250 cm^3 66° Bé. sulphuric acid for each 100 litre of skimmed milk by the methods above described, dissolved in the manner above indicated and at the constant temperature of 24° C., and diluted with town water, generally takes 48 hours maturation in order to reach a density and viscosity suitable for spinning and a volume of 550–600 litres for each 100 kilos dry casein used. When a smaller volume is desired, all other factors remaining unaltered, the maturation time may be somewhat reduced. When a greater volume is desired, the maturation time may be increased but only up to a certain limit because it has been found that after 96 hours, for instance, the risk is incurred of prejudicing the quality of the textile fibres obtained.

Also the quantity of acid employed for the coagulation of the casein, and in a slight degree also the types of acid employed, play an important part on the viscosity, density and volume of the alkaline casein solution. The greater the amount of the acid employed for the coagulation of the casein, the lower and less rapidly obtained are the viscosity, density and volume of the subsequent alkaline colloidal solution.

Conversely, to a gradually smaller quantity of acid there corresponds a gradually more rapidly obtained and greater viscosity, density and volume of the solution. By exaggerating in one or the other direction, solutions can be obtained which are difficult to spin, apart from the lower quality of the resulting fibres.

Accordingly, when caseins having the different properties above indicated are used, it is preferable and—in the named extreme cases indispensable—to modify also the initial volume of casein. In the example above indicated the initial volume after the addition of the hydrated sodium solution is 400 litres for each 100 kilos casein employed. This volume may be slightly increased or reduced, but only between narrow limits because by increasing the volume by a greater addition of water, while the other factors are left unaltered, the perfect dissolution of the casein and the development of the viscosity and density requisite for proceeding to the successive additions of diluting agent are delayed. If an exaggeratedly great initial volume is adopted, the regular development of the process may be irreparably spoiled. On the other hand, a reduction of the initial volume renders more difficult (and impossible, if the initial volume is exaggeratedly small) a regular incorporation of the alkali in the casein and thereby a perfect solution.

The volume referred to above is rationel for the type of casein indicated. For caseins that have been coagulated with a greater amount of acid it is advisable to reduce slightly the volume of the initial solution, and conversely to increase the same for caseins that have been coagulated with a smaller amount of acid.

The casein that has been washed prior to the drying is dissolved in the same manner as the unwashed casein, with the difference that the quantity of alkali used is reduced according to the lesser quantity of acid left in the casein in consequence of the washing.

Example B

The dissolution of non-dried casein, that is to say, casein which still contains a percentage of acid serum, is carried out with the following modifications.

The casein, coagulated and heated in its serum as above indicated and previously drained, is pressed so as to reduce its serum content, preferably to not above 200% of the weight of the dry casein, this also being effected in order to facilitate the subsequent grinding of the pressed casein.

The casein is placed in a vessel constructed as previously described, without addition of water which in this case is replaced by the serum left in the casein. The 35° Be hydrated sodium solution is then added, this solution having been previously additioned with the quantity of water necessary to attain, as indicated in the preceding example, the volume of 400 litres for each 100 kilos casein, always referred to the dry weight of casein including the normal moisture of 10%. For the rest, the procedure is the same as in Example A.

Numerous diluting agents can be used for diluting the colloidal casein solution during its maturation. Water represents, of course, the cheapest diluting agent and it may be used such as it is, if it is town water or purified water. Distilled water does not offer advantages sufficient to outweigh its cost. The serum itself, left in the casein after its coagulation and extraction, may also be used after being duly neutralised. In this case, the density and volume of the resulting colloidal solution are slightly greater than those obtained when using water as diluting agent.

The water or serum used as diluting agent may also be very slightly alkalised, but previously deducting a corresponding amount of alkali from the alkaline solution of hydrated sodium prepared for the dissolution of the casein.

If, as diluting agent, non-neutralised acid serum, only partially neutralised acid serum or slightly acidulated water is used, the spinning capacity of the final product is impaired, but the coagulation capacity of the colloidal-casein solution is slightly increased.

There may also be used as diluting agents (according to the effects desired) neutral or slightly alkaline or acid solutions, prepared with alkaline salts combined with acids, such as for instance sodium lactate, sodium formiate etc.

The solutions containing quite small proportions of certain sulphates or of sodium bisulphite or the like when used as diluting agents increase the density and thereby the volume of the colloidal-casein solution and may therefore be employed when it is desired to obtain this result. Soap solutions act in the same manner and can be used preferably when it is desired to obtain a greater density and to introduce at the same time a saponified fat into the casein solution.

Sometimes it is important to introduce coagulation accelerators into the colloidal-casein solutions, in order to obtain a more rapid and perfect coagulation of the filaments without modifying the coagulation acid bath.

Some of the diluting agents above indicated are suitable also for slightly increasing the coagulability of the colloidal-casein solution, yet when a more rapid and energetic coagulation of the filaments is desired, it is preferable to introduce carbon sulphide into the colloidal casein solution by the means and at the moment most appropriate.

For instance, it is practicable to treat soap with carbon sulphide in the presence of hydrated sodium and a small quantity of water and to heat the mass to a moderate temperature. When the reaction is completed, further water is added in order to attain the desired volume of the soap solution, which will have taken up an orange tint if the reaction has been regularly accomplished.

According to the effects desired, a determined quantity of this soap solution is added to the colloidal-casein solution, preferably a few hours before it is passed on to the spinning process.

In this manner three results are simultaneously achieved viz: a greater volume of the colloidal casein solution without lowering its density; an acceleration of the coagulability in spite of the retarding action of the soap; and a greater softness of the resulting textile fibres (other substances such as glycerine etc. may be used for the same purpose, always with treatment with carbon sulphide).

Instead, if it is not desired to introduce any saponified fats into the colloidal-casein solution, a solution of hydrated sodium can be treated with carbon sulphide and this solution may be used instead of those indicated above, taking note of the amount of hydrated sodium used in order to deduct the same, at least in part, from the amount of alkali to be employed in the previous casein solution.

The carbon sulphide may also be introduced, preferably in vapour form, directly into the colloidal casein solution or in any other form adapted for the end in view.

For instance, there may be added to the colloidal-casein solution preferably a few hours before the spinning, a determined percentage of the colloidal viscous solution normally used in the manufacture of rayon according to the alkali-cellulose and carbon sulphide method. In this case, however, the resulting textile fibres no longer consist of a mere organic substance of animal origin, owing to the percentage of cellulose that has been added to the casein solution. Also, the percentage of nitrogen is therefore lowered and the properties of the ultimate product are modified, so that the product can no longer be called "synthetic wool."

Owing to the fact that by introducing into the colloidal-casein solution various percentages of cellulose in the form of a viscose solution, a full important series of special types of artificial textile fibres is obtained which show intermediate properties between those of rayon (consisting of cellulose alone) and those of synthetic wool (consisting of casein alone). These novel products may be defined as follows:

(*a*) "Synthetic Silkwool" or "Serinwool" when the casein percentage is greater than the cellulose percentage, because the resulting textile fibres contain nitrogen in an amount upward of 7% and the thermal properties of these fibres are nearer to those of a natural wool and natural silk.

(*b*) "Rayon-wool" or "cotton-wool" when the casein percentage is lower than that of the cellulose percentage, because the resulting textile fibres contain nitrogen in a quantity less than 7% and the thermal properties of these fibres gradually decrease until the cold property of the vegetable textile fibres is reached.

It is an important feature of the invention that for the production of these textile fibres of mixed casein and cellulose, though with greater difficulties, the lactic and acid caseins coagulated without acid excess can also be used. This is due to the fact that the addition of a cellulosic viscose to the casein solution modifies the properties of the latter. In fact the alkaline solutions of these caseins are the more suitable according as the percentage of cellulosic viscose added to the casein solution is greater.

Finally, a mineralised synthetic wool can be obtained by adding to the alkaline-casein solutions, solutions of alkaline silicates, preferably sodium or kalium silicates, or alkaline or neutral solutions of soluble metals.

All colloidal solutions of pure casein or of casein mixed with other substances as described above, before being spun, are preferably filtered one or more times by suitable means.

As described above, the first phase of the process according to the invention consists in the preparation of the basic casein material and the second phase in the preparation of the alkaline-casein colloidal solution. The third phase of the process will now be described, which phase consists in the spinning of the alkaline casein colloidal solution alone, or of the combined solutions of casein and viscose, with or without additions of soluble mineral substances, and coagulation of the filaments.

For spinning the colloidal solution of casein alone, the same machines and apparatus can be employed that are already in use for the production of rayon by the so-called viscose process (aqueous sodic solutions of alkali-cellulose treated with carbon sulphide), with eventual slight modifications of the vessel for the coagulation bath, of the tube carrying the spinning nozzles etc. On the other hand, no modification of such apparatus is required for spinning the mixed solutions of casein and viscose when the viscose is present in the solution in proportions above 35%.

It has been found that the spinning velocity, viz. the velocity of the filaments issuing from the spinning nozzles immersed in the acid coagulation bath, may vary from 80 to 120 m. per min. according to the degree of viscosity of the colloidal solution of casein. The said velocity is nearly twice as great as the velocity generally used for the production of rayon by the viscose method, and hence a first necessity of increasing the length of travel of the various filaments in the acid coagulation bath on their issuing from the spinning nozzles.

Further, the filaments resulting from the casein solutions coagulate more slowly and less easily than the rayon filaments obtained from the viscose. Accordingly, the acidity of the coagulation bath must be greater, viz. the bath must have nearly twice the acid concentration of the coagulation bath used for viscose filaments. Also, the temperature must be higher and must be comprised between 48°C and 58°C. It has been found that temperatures of 52–53°C. may be advantageously adopted.

It is preferable to adopted a lower acidity and eventually also a lower temperature of the bath and to increase, on the contrary, the length of travel and thereby the time of immersion of the filaments in the acid coagulation bath. When, for instance, instead of spinning on bobbins, it is desired to produce loose flocons of synthetic wool, the length of travel of the filaments in the acid coagulation bath can be readily increased, whereby a more certain and smooth product is obtained and waste is eliminated or reduced to a minimum.

When spinning at great velocity and directly on bobbins, it is advisable and sometimes necessary to cause the filaments, immediately on their leaving the coagulation bath, to slide on a rod of glass or other suitable material in order to remove from the filaments portions of the coagulating medium which have been taken up by the filaments.

Examples of coagulation baths which may be used are as follows:

Example (a)

An aqueous solution of sulphuric acid and sodium sulphate is made, the proportions being such that the bath contains 140 cm³ 66° Be. sulphuric acid and 400 gr. sodium sulphate for each litre of the bath. To this solution, aluminium salts may be added, preferably aluminium sulphat or kalium alum. It is also advantageous to add small amounts of tin salts, for instance tin acetate.

Example (b)

An aqueous solution of sulphuric acid, aluminium sulphate (or kalium alum) and sodium chloride is made, the proportions being such that the bath contains, for each litre thereof, 150 cm³ 66 Be. sulphuric acid, 150–200 gr. aluminium sulphate and 75 gr. sodium chloride. The quantity and proportion of aluminium sulphate and sodium chloride may be varied according to the effects aimed at, bearing in mind that the function of the aluminium salts is to rapidly harden the filaments as soon as they have been coagulated, and that the presence of the sodium chloride in the bath facilitates the insolubilising action of the aluminium salts. In preparing this solution, care should be taken not to unduly heat the same, so as to avoid the transformation of a portion of the sulphuric acid into hydrochloric acid. There may likewise be added to this solution small amounts of other salts.

When the colloidal-casein solution contains carbon sulphide, it is preferable to employ as coagulating agent the first bath indicated above.

For the mixed solutions of casein and viscose, the first bath is likewise preferable and the amount of sulphuric acid employed can be gradually reduced to 55% of the amount indicated above according to the higher or lower percentage of viscose added to the casein solution. The higher the viscose percentage, the lower can be the amount of acid in the coagulating bath. Also, the bath temperature may be slightly lower.

The fourth phase of the complete process for the manufacture of the textile fibres in accordance with the invention consists in the treatments required for the insolubilisation of the filaments or fibres obtained and for the de-acidification thereof.

The filaments or fibres obtained at the moment of the coagulating operation show a strong acid reaction. It is therefore necessary to remove from the filaments the acidity which would otherwise impair the final product after drying. In order to do this, for the filaments made solely of casein, it is necessary to wash the filaments in running water and to this effect a few hours of washing are sufficient if the product is in flocons, whereas 16 to 24 hours are required if the filaments are wound on bobbins. For the mixed casein and cellulose filaments a washing of several days is required when the filaments are wound on bobbins.

The washing, however, cannot be carried out directly after the coagulation of the filaments, because those consisting of casein alone would get dissolved and those consisting of mixed casein and cellulose would be seriously damaged. The filaments should therefore be previously subjected to treatment having for object to render the same insoluble.

To this end, aqueous solutions of formaldehyde are employed, preferably with additions of sodium chloride in order to regulate or prevent altogether the swelling of the fibres in the first phase of the operation.

An aqueous solution of sodium chloride of less than 10% exercises a swelling action on the casein fibres. On the contrary, a solution with more than 10% exercises an astringent action. It is therefore very useful to regulate the behaviour of the fibres in the insolubilising bath by using a convenient quantity of sodium chloride which also assists the insolubilising action of the aluminium salts when it is desired to use these salts in solution combined with formaldehyde.

It is possible to operate with a solution having but one concentration only, for instance, with 90 parts of a 12% aqueous solution of sodium chloride and 10 parts of 40% formaldehyde, additioned or not with aluminium salts. It is preferable, however, and even very important, to operate with various solutions having progressively increasing concentrations and to begin the treatment of the filaments with weak concentrations, for instance with 99 parts of aqueous solution of sodium chloride and 1 part of 40% formaldehyde, gradually passing to higher concentrations. The procedure is the same in the eventual addition of aluminium salts, whereas for the sodium chloride it is preferable not to go below a 10% concentration in order to avoid an excessive and noxious swelling of the fibres.

The insolubilising solutions prepared in the manner above described may be slightly acidified, preferably with sulphuric acid. On the other hand, the continuous immersions of acid fibres in the insolubilising solution continually increases the acidity of the latter solution so that, once the desired acidity has been fixed, one must from time to time neutralise with alkali the excess of acidity of the insolubilising bath.

When the alkaline-colloidal solutions of casein alone or of casein mixed with cellulose are not spun directly on bobbins or in a centrifugal machine, as is the case for instance in the production of flocons fibres, it is advisable to let the loose fibres fall, on their leaving the coagulation bath, into a bath consisting of a more than 10% aqueous solution of sodium chloride. If, to this solution, small quantities of acid or of aluminium salts are added, even without addition of formaldehyde, the fibres will have been passed into an excellent preparatory insolubilising bath and will separate from one another better than when they are collected in an empty vessel and retained therein for a certain time before they are passed to the insolubilising bath proper.

The fibres consisting of casein alone, when they are not kept in tension on a bobbin, undergo a considerable shortening in the insolubilising bath, especially if after coagulation they are immersed in a highly concentrated insolubilising bath. This is the case with the loose or flocons fibres which receive, it is true, an excellent twisting from the fact that they are not in tension, but lose somewhat of the fineness or titre they had received at the moment of spinning. Already, the immersion of these loose fibres into a first weakly concentrated insolubilising bath reduces a good deal the shortening of the fibre, but if it is desired to eliminate this shortening almost completely, the filaments must not be cut directly after the coagulation. The mass of the filaments should instead be wound on reels that are afterwards immersed in a weakly concentrated insolubilising bath, and then passed to further baths of increasing concentrations until baths of medium concentration are reached. The filament skeins can now be cut to the desired length and then passed to the successive insolubilising baths. In this manner fibres are obtained that are but little shortened and are equally twisted.

After the filaments have been insolubilised, they are washed in running water until complete de-acidification.

After washing, it is preferable to give the filaments a final treatment by a neutral insolubilising bath.

The manufacture of the textile threads in accordance with the invention may be completed by a fifth phase including treatments for increasing the softness of the fibres.

The textile fibres obtained as above described are exeellent in every respect, yet it has been found desirable to treat them with a softening bath at suitable temperatures.

To this end, aqueous solutions can be used of sulphoricinated oils, even mixed with soaps, with emulsional mineral oils, glycerine etc., or oils of fats emulsified by known processes. The percentage of oils or fats used may be varied according to the effects desired.

It is preferable to submit the fibres to the softening bath before drying them and, of course, after they have been completely de-acidified. The bath temperature may be comprised between 45° C. and 60° C. Of course, it is needless to submit the fibres to such a treatment if the softening agents have already been introduced into the colloidal-solution prior to the spinning.

It will be understood that the practical details for carrying the invention into effect are not limited to those above described by way of example only, and which may undergo suitable modifications and adaptations without departing from the spirit of the invention, and furthermore that the present invention relates not only to the processes of manufacture above described and modifications thereof, but also to the products obtained by such processes.

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