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PRODUCTION AND TREATMENT OF THREADS, ETC.

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This invention relates to the production and treatment of threads, etc., especially threads and like materials having a basis of casein or other protein or protein-like substance.

I have found that the physical properties of materials of the kind referred to above can be improved by bringing the protein base of the materials into reaction with sulphur, preferably in the elementary state. It is of considerable advantage for the sulphur with which the protein is to combine to be liberated within the threads or the like as this facilitates the reaction.

According to the present invention, improved artificial materials are made by a process which comprises increasing the resilience of artificial filaments or fibres of proteinaceous material by bringing said filaments or fibres into reaction with sulphur or its equivalents.

The invention may be illustrated with reference to the production of casein threads of improved water-resistance and resilience. The solvent for the casein is an aqueous solution of polysulphides of sodium or potassium. The solution is spun into a coagulating bath containing dilute sulphuric acid preferably buffered with ammonium sulphate or other soluble sulphate. The resulting filaments are drawn from the coagulating bath by a godet which is preferably arranged to rotate at such a speed as not substantially to stretch the threads. From the coagulating bath the threads are passed through a washing bath. They may at this stage or at a later stage be subjected to the usual formaldehyde hardening treatment. This is not, however, essential since the sulphur treatment of the invention to some extent replaces the formaldehyde treatment but with an effect on the physical properties which has not previously been obtained by the action of formaldehyde alone.

The washed materials, whether or not they have been subjected to a formaldehyde treatment, are dried and subjected to dry heat, for example, at a temperature between 100 and 120° C., to effect the desired reaction between the protein and the sulphur. The heat treatment can conveniently be effected by supporting the thread in loose coils or in hank form on perforated trays in a chamber heated by steam pipes. Live steam could be used but dry heat is preferred since in a moist hot atmosphere there is a possibility of undesirable deformation of the materials occurring. With a view to ensuring uniformity the use of a heat atmosphere is to be preferred to direct contact with a heated surface. The time of heat treatment depends upon the

properties required in the product. Up to a point depending on the amount of sulphur available and the temperature of heating the reaction increases the water-resistance as well as the resilience of the materials. If allowed to proceed too far, however, undue hardening of the materials may occur. For any particular composition of spinning solution and temperature of heating a simple measurement of extension under load of a sample will indicate the optimum time of exposure.

With a view to reducing the time of exposure it is of advantage to have present in the spinning solution substances capable of acting as sulphur carriers. For example, thiocarbonyl, and phenyl thiocarbonyl can with advantage be used for this purpose, as can other nitrogenous substances containing sulphur or capable of taking up sulphur and parting with it readily provided they are soluble in a solvent for the protein. Further examples of such substances are hexamethylene tetramine and aldehyde ammonia. Inorganic sulphur carriers can also be employed, e. g., oxides and iodides of amphoteric metals. The heating step may be carried out at temperatures below the range specified particularly when such sulphur carriers are present. Temperatures above this range, though not excluded, are, in general, less satisfactory. Other things being equal the higher the temperature the shorter is the exposure needed.

The following example illustrates the invention.

Example

An approximately 20% solution of casein in an aqueous solution of sodium polysulphide of alkalinity equivalent to that of a 1-3% solution of caustic soda is made. With this is incorporated 1-3% on the weight of the casein of thiocarbonyl.

This solution is spun into an aqueous bath containing 10% of sulphuric acid and 20% of sodium sulphate. The filaments are withdrawn continuously from the bath by means of a godet driven at such a speed as not substantially to stretch the threads and are passed first through a washing bath containing a dilute aqueous solution of sodium bicarbonate, then through a further, substantially neutral aqueous washing bath, then through a drying chamber and are deposited in coils in a revolving foraminous container by means of a guide which is reciprocated parallel to the axis of rotation of the container.

The container is then transferred to a chamber heated indirectly by steam to a temperature of

100-120° C. The materials are maintained in the heating chamber until the desired physical properties, shown by tests carried out on a sample, have been attained.

If desired the materials may be subjected to the action of formaldehyde or other hardening agent for casein at any suitable stage in the process.

Instead of sodium sulphide, other compounds of alkaline reaction from which sulphur can be liberated by acids may be used, for example potassium sulphide or the sulphides of ammonia and like acting non-metallic bases. The compound from which the sulphur is derived need not itself be alkaline or capable of dissolving the casein provided a solvent for the casein is present in addition. Thus, for example, a water-soluble thiosulphate may be used as the source of sulphur in solution in aqueous caustic soda, caustic potash, ammonia, urea or other solvent for the casein.

In an alternative method of carrying out the invention, the casein is dissolved in caustic soda or a like acting base, for example aqueous ammonia, and the solution is saturated with hydrogen sulphide. Preferably the solution contains an alkali-soluble sulphur carrier such as is referred to above. The solution is spun into an aqueous bath containing a high concentration of sulphurous acid. The subsequent treatment of the threads is as described above.

It is preferred to liberate the sulphur which is to combine with the protein within the threads by reaction of a constituent of the coagulating bath with a substance or substances contained in the spinning solution. The invention includes, however, the treatment of fully formed threads and the like. One method of treating such materials is to impregnate them in a bath containing sulphur dissolved in carbon bisulphide (other solvents for sulphur which do not attack the protein base, for example benzene, may be used instead). The impregnated materials are hydro-extracted to remove excess of the treating liquid and are then subjected to dry heat as described above. Sulphur carriers may be introduced together with the sulphur.

As indicated above the sulphur required is preferably provided by a sulphur compound present in the materials treated or in the spinning solution from which they are to be made. The compound in question may introduce into the protein molecule other elements in addition to sulphur. Thus compounds, e. g. thiophosgene and the halogenated mercaptans and alkyl sulphides, which are capable of introducing carbon and/or a halogen as well as sulphur may be used as well as mercaptans and disulphides themselves.

Instead of sulphur, other substances which are similar in chemical behaviour can be used. Thus other non-metallic elements of the sixth group of the periodic classification, for example selenium or tellurium, can be used.

The invention has been described with particular reference to the production and treatment of threads having a basis of casein. Other proteins or protein-like substances may, however, form the basis of the materials, for example zein, the protein from ground nuts, gelatine, long chain polypeptides obtainable by condensing acid chlorides of chlor fatty acids with amino acids, replacing the chlorine in the product by an amino group by the action of ammonia and repeating the process, and the similar bodies

obtainable by condensing polyamines with dicarboxylic acids. Owing to the different solubility properties of certain of these protein-like substances as compared with those of casein, their use may involve the use of different solvents and coagulants in spinning from those specifically referred to above. The necessary modification of the process specifically described, for any particular filament-forming protein-like substance, however, presents no difficulty once the solubility properties of the substance are known.

The protein or protein-like substance need not constitute the sole filament-forming base present in the threads or the like. These may, for instance, be formed from spinning solutions containing in addition to the protein or protein-like substance an unstable alkaline solution of cellulose or other non-protein-like film-forming substance. The threads may, for example, be spun from solutions containing in addition to casein or the like viscose or cuprammonium cellulose. Stable cellulose derivatives which are soluble in the solvent for the casein or the like, for example alkali-soluble cellulose ethers, may also be present.

It is not essential that the materials should be treated in thread form. The invention includes treating the materials in other than thread form, e. g. in the form of fabrics or of staple fibres.

Having described my invention, what I desire to secure by Letters Patent is:

1. Process for the manufacture of improved artificial materials which comprises increasing the resilience of artificial filaments of a proteinaceous substance, by heating said filaments with elementary sulphur to cause reaction between the protein and the sulphur.

2. Process for the manufacture of improved artificial materials which comprises increasing the resilience of artificial filaments of a proteinaceous substance substantially free from combined sulphur, by heating said filaments with elementary sulphur to cause reaction between the protein and the sulphur.

3. Process for the manufacture of improved artificial materials which comprises increasing the resilience of artificial filaments of casein, by heating said filaments with elementary sulphur to cause reaction between the protein and the sulphur.

4. Process for the manufacture of improved artificial materials which comprises increasing the resilience of artificial filaments of peanut protein; by heating said filaments with elementary sulphur to cause reaction between the protein and the sulphur.

5. Process for the manufacture of improved artificial materials which comprises increasing the resilience of artificial filaments of zein, by heating said filaments with elementary sulphur to cause reaction between the protein and the sulphur.

6. Process for the manufacture of improved artificial materials which comprises forming filaments by spinning a solution of a proteinaceous substance in a solvent containing a compound of sulphur into a coagulating medium, liberating sulphur in said filaments by reaction between said sulphur compound and said coagulating medium and heating the coagulated filaments to cause reaction between the protein and the sulphur.

7. Process for the manufacture of improved artificial materials which comprises forming fila-

ments by spinning a solution of casein in an aqueous solution of an alkaline polysulphide into an acid bath, liberating sulphur in said filaments by reaction between the polysulphide and the acid and heating the coagulated filaments to cause reaction between the protein and the sulphur.

8. Process for the manufacture of improved artificial materials which comprises forming filaments by spinning a solution of peanut protein in an aqueous solution of an alkaline polysulphide into an acid bath, liberating sulphur in said filaments by reaction between the polysulphide and the acid and heating the coagulated filaments to cause reaction between the protein and the sulphur.

9. Process for the manufacture of improved artificial materials which comprises forming filaments by spinning a solution of casein in an aqueous solution of an alkaline polysulphide and an organic sulphur carrier into an acid bath, liberating sulphur in said filaments by reaction between the polysulphide and the acid and heating the coagulated filaments to cause reaction between the protein and the sulphur.

10. Process for the manufacture of improved artificial materials which comprises forming filaments by spinning a solution of peanut protein in an aqueous solution of an alkaline polysulphide and an organic sulphur carrier into an acid bath, liberating sulphur in said filaments by reaction between the polysulphide and the acid and heating the coagulated filaments to cause reaction between the protein and the sulphur.

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11. Process for the manufacture of improved artificial materials which comprises forming filaments by spinning a solution of casein in an aqueous solution of an alkaline polysulphide and thiocarbanilide into an acid bath, liberating sulphur in said filaments by reaction between the polysulphide and the acid and heating the coagulated filaments to cause reaction between the protein and the sulphur.

12. Process for the manufacture of improved artificial materials which comprises forming filaments by spinning a solution of peanut protein in an aqueous solution of an alkaline polysulphide and thiocarbanilide into an acid bath, liberating sulphur in said filaments by reaction between the polysulphide and the acid and heating the coagulated filaments to cause reaction between the protein and the sulphur.

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