The present invention is concerned with the provision of a method for improving the strength of artificial insolubilised protein filaments particularly of the kind wherein the insolubilisation of the coagulated filaments obtained by wet spinning is carried out by means of formaldehyde in the presence of an acidified strongly saline solution.

The invention is especially applicable to insolubilised filaments produced from alkaline solutions of casein and alkaline solutions of vegetable globulins, for instance, peanut globulins or soya bean globulin solutions in dilute sodium hydroxide solution.

The object of the present invention is to increase the strength of the insolubilised protein filaments so as to permit them to be readily processed in the existing machinery employed in the manufacture of textile products.

The insolubilisation of the coagulated wet spun protein filaments can be most effectively or conveniently carried out by means of formaldehyde in the presence of an acidified highly concentrated aqueous saline solution as, for example, according to the method described and claimed in British specification No. 513,910 or 597,497. The insolubilisation of the coagulated wet spun protein filaments can also be carried out according to British specification No. 533,982 according to which coagulated protein or vegetable seed protein filaments are treated with a concentrated aqueous solution of a salt of a hydrohalide containing formaldehyde or a compound which will yield formaldehyde under the conditions of the treatment, a salt of a reducing sulphur acid in which the atomic proportion, reckoned on the anhydrous salt, of oxygen if present, to sulphur does not exceed 2:1, and an acid which does not oxidise the salt of the sulphur acid, and which is sufficiently completely ionised in dilute aqueous solution.

While it is known that stretching of the coagulated wet spun filaments previous to their insolubilisation has a beneficial effect on the strength of the insolubilised filaments obtained from these, and that the strength of the insolubilised filaments can frequently be further increased by treatments involving further stretching, such stretching processes as have heretofore been disclosed with respect to protein fibres not only do not permit the application of extensive stretching but the effects produced are only relatively small.

We have now found that a very marked improvement in the strength of the filaments obtained from coagulated protein filaments that have been insolubilised with formaldehyde in the presence of acidified highly concentrated salt solution, and if desired washed free from surface and uncombined acid or formaldehyde, is obtained if the insolubilised filaments are treated, preferably under tension, with an aqueous solution of a uranyl salt as for example, uranyl acetate in acetic acid, aqueous solutions of salts of the type of zinc uranyl acetate, and of uranium (uranil) salts of hydrochloric acid, nitric acid and sulphuric acid.

According to the present invention, therefore, the method of improving the strength of artificial insolubilised filaments of the kind heretofore defined comprises treating the insolubilised filaments, preferably under tension, in an aqueous solution of at least one uranyl salt.

It has been found, for instance, that insolubilised protein filaments obtained according to the process of specifications No. 513,910, 533,982 or 597,497 when soaked in a solution of for example uranyl acetate in 0.1 N acetic acid produces a large increase in the rigidity in the wet state while the wet tensile strength is increased by about 30 percent. If however, a tow of insolubilised protein filaments obtained for instance according to the aforesaid processes is stretched in said uranyl acetate solution for about half an hour at 70° C, then the wet rigidity is still further increased and the wet tensile strength is increased by about 80 percent and the dry tensile strength is increased by about 20 percent.

The invention is illustrated by the following examples.

**Example 1**
A solution of ground nut protein in caustic soda is extruded into a sulphuric acid/sodium sulphate coagulating bath. These fibres are now given an insolubilising treatment for 16 hours at 38° C. in a solution consisting of 960 ml brine, 40 ml formalin, 14 ml concentrated sulphuric acid. The fibres are now washed free from acid and dried at 105° C. The insolubilised fibre thus obtained is now treated for 15 hours at 40° C. with a solution of 5% uranyl acetate in 0.1 N acetic acid. The fibre is now washed and dried at 105° C. It is found that the wet tensile strength of the insolubilised fibre is increased by about 30% and the rigidity in the wet state is considerably increased.

**Example 2**
A tow of fibre prepared and insolubilised with formaldehyde as in Example 1, is stretched to a
maximum in a bath containing 3% uranyl acetate and 0.1 N acetic acid at 70° C. The stretch is maintained for half an hour and the fibre is washed and dried at 105° C. The fibre produced has an increased wet rigidity and the tensile strength is increased by about 80%.

It will be appreciated that the term “insolubilized,” as used in the foregoing specification and appended claims, refers to filaments which are not only insoluble in cold water, but also are resistant to boiling water and hot dilute acids. In other words, the insolubilized filaments, as referred to herein, must be capable of withstanding the resistance test referred to in each of the above-mentioned British patents, i.e., they should be unaffected by treatment for 90 minutes at 97° C. with a bath containing 0.1% sulfuric acid and 0.25% sodium sulfate. The filaments treated in accordance with the invention are, therefore, to be distinguished from filaments which are simply hardened, i.e., insoluble in cold water but soluble in boiling water and hot dilute acids.

We claim:

1. A method of improving the strength of coagulated protein filaments selected from the group consisting of casein and vegetable globulin filaments which have been insolubilized so as to be resistant to boiling water and hot dilute acids, by treatment with formaldehyde while in contact with an acidified highly concentrated salt solution which comprises immersing the insolubilized filaments in an aqueous solution of at least one uranyl acetate and acetic acid under conditions sufficient to effect a substantial increase in the tensile strength of said filaments.

2. The method of claim 1, wherein the immersion is carried out under tension.

3. A method of improving the strength of coagulated protein filaments selected from the group consisting of casein and vegetable globulin filaments which have been insolubilized so as to be resistant to boiling water and hot dilute acid, by treatment with formaldehyde while in contact with an acidified highly concentrated salt solution which comprises immersing the insolubilized filaments in an aqueous solution of uranyl acetate and acetic acid under conditions sufficient to effect a substantial increase in the tensile strength of said filaments.

4. A method of improving the strength of coagulated protein filaments selected from the group consisting of casein and vegetable globulin filaments which have been insolubilized so as to be resistant to boiling water and hot dilute acid by treatment with formaldehyde while in contact with an acidified highly concentrated salt solution which comprises immersing the insolubilized filament at a temperature of between about 40° C. and 70° C. in a solution containing 3% uranyl acetate and 0.1 N acetic acid for a time sufficient to effect a substantial increase in the tensile strength of said filaments.

5. The method of claim 4, wherein said immersion is carried out under tension.

6. The method of claim 4, wherein said insolubilized filaments are ground nut protein filaments.

7. The artificial insolubilized protein filaments of increased tensile strength obtained by the method of claim 1.

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