This invention relates to the manufacture and production of artificial threads, filaments, fibres and the like, hereinafter referred to as threads, from solutions of proteins, for example milk casein or vegetable seed caseins such as those obtained from soya beans or peas. It is well known to produce threads from proteins by extruding an alkaline solution of the protein into a coagulating bath containing for example sulfuric acid, and subjecting the resultant thread to a treatment known as "hardening," which comprises passing the thread through one or more baths comprising aqueous solutions of one or more suitable substances such as formaldehyde and metallic salts such as aluminium salts. The threads obtained are insoluble in cold water but in boiling water or hot dilute acid the threads become plastic and tend to stick together, or even to dissolve.

Processes are already known for improving the resistance of casein and like protein threads to attack by boiling water or hot dilute acids by treating the threads with hardening baths containing formaldehyde and sulphuric acid. The specification of U.S. Serial No. 440,116 in the names of the present applicant and C. L. Knight, describes and claims a process for this purpose which comprises treating the threads for a considerable time during or after the hardening treatment in a bath containing formaldehyde and an alkal metal bisulphate or an alkal metal sulphate and sufficient sulphuric acid to convert at least a large proportion of the sulphate into bisulphate. In U.S. specification No. 2,293,988 a process for improving the water-resistance of protein fibres is described which comprises subjecting the fibres to the action of an alkaline and an acid such as sulphuric acid in concentrations of up to 10 per cent, and thereupon drying and heating the fibres without previous washing. British specification No. 512,640 describes hardening baths for casein fibres which baths contain formaldehyde, a water-soluble salt and about 2 per cent of sodium sulphate in an amount considerably less than that necessary to react with all the sulphuric acid in the bath with the formation of sodium bisulphate. It desired, aluminium salts may also be added to the treating bath although it is preferred to harden the threads to some extent by means of baths containing aluminium salts before carrying out the process of the present invention.

The time of reaction required to obtain the benefit of this invention depends on the temperature of the treatment bath and on the concentration of the sulphuric acid in the bath. The concentration of the sulphuric acid in the bath must be chosen so as to improve the resistance of the casein threads to boiling water without deleteriously affecting their physical properties or appearance. For example, if the treatment is carried out at room temperature it is advisable to have the concentration of the sulphuric acid above about 600 grams per litre of solution (corresponding to about 48 per cent by weight of sulphuric acid) if the treatment is carried out at a temperature higher than room temperature the concentration of sulphuric acid used may be higher. When working at room temperature with high concentrations of acid the time required to effect the reaction is less than that required using lower concentrations of acid. If the treatment is carried out at room temperature or higher with a concentration of acid much above 600 grams per litre of solution a yellowing of the threads is liable to take place.

The following examples illustrate the present invention, although the invention is not restricted to these examples:

**Example 1**

An 18 per cent solution of milk casein in dilute caustic soda solution is extruded through fine orifices into a bath containing in each litre 350 grams of sulphuric acid and 360 grams of sodium sulphate. After passing for a few minutes first through an aqueous solution containing 230 grams of sodium chloride per litre, and then through an aqueous bath containing in each litre 190 grams of aluminium sulphate and 140 grams of sodium chloride, the resultant threads are given a preliminary hardening treatment for 10 hours at...
28° centigrade in a solution containing in each litre 250 grams of sodium sulphate and 40 grams of formaldehyde. The threads are then immersed for 8 hours at 25° centigrade in a bath containing in each litre 400 grams of sulphuric acid, 300 grams of sodium sulphate and 40 grams of formaldehyde. After washing the threads with water and drying, they show an increased resistance to boiling water.

**Example 2**

Casein threads which have been obtained by extrusion and coagulation, as described in the foregoing Example 1, are passed for a few minutes, first through an aqueous solution containing 230 grams of sodium chloride per litre and then through an aqueous bath containing in each litre 150 grams of aluminium sulphate and 140 grams of sodium chloride. The threads are then cut into short lengths and hardened for 10 hours at 25° centigrade in a solution containing in each litre 250 grams of sodium sulphate and 40 grams of formaldehyde. The threads are then immersed for 1 hour at 25° centigrade in a bath containing in each litre 496 grams of sulphuric acid, 271 grams of sodium sulphate and 38.5 grams of formaldehyde. After washing the threads with water and drying, they show an increased resistance to boiling water.

**Example 3**

Casein threads which have been obtained by extrusion and coagulation, as described in the foregoing Example 1, are passed for a few minutes, first through an aqueous solution containing 230 grams of sodium chloride per litre and then through an aqueous bath containing in each litre 190 grams of aluminium sulphate and 140 grams of sodium chloride. The threads are then cut into short lengths and hardened for 10 hours at 25° centigrade in a solution containing in each litre 250 grams of sodium sulphate and 40 grams of formaldehyde. The threads are then immersed for 1 hour at 25° centigrade in a bath containing in each litre 607 grams of sulphuric acid and 40 grams of formaldehyde. After washing the threads with water and drying, they show an increased resistance to boiling water.

What I claim is:

1. A process for improving the resistance to attack by boiling water or hot dilute acid of artificial threads having a basis of casein or other protein and which have been at least partially hardened which comprises treating the threads with an aqueous solution containing formaldehyde and from 350 grams to 750 grams of sulphuric acid per litre of solution, washing the thus-treated threads acid-free and drying the threads.

2. A process as claimed in claim 1 wherein sodium sulphate is added to the treating bath in an amount considerably less than that necessary to react with all the sulphuric acid in the bath with the formation of sodium bisulphate.

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