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PROCESS OF PRODUCING ARTIFICIAL PROTEINACEOUS FIBER UTILIZING FINELY DIVIDED MATERIAL IN THE COAGULATING BATH

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This invention relates to the manufacture of synthetic proteinaceous fibers. More particularly it relates to a process of manufacturing such fibers in such a manner as to prevent the adherence of the fibers to each other during their early stages of manufacture in which the surfaces of the fibers have a soft adherent nature.

Processes have been propsed heretofore, and developed commercially, for making synthetic fibers from proteinaceous materials, such as the proteins from milk and soybean. In such processes the protein is dispersed in an aqueous medium with an alkaline material, spun into an acidic coagulating bath, and finally hardened with formaldehyde or other protein tanning agents.

The process of making these proteinaceous fibers is to be distinguished from the manufacture of rayon in which the chemical or physical reactions transforming the filaments into a set shape takes place rapidly in a single operation. In the manufacture of viscose rayon, for instance, the chemical reaction proceeds promptly and setting takes place rapidly to form the fiber in a finished state in a single operation. In making cellulose acetate type of rayon, the fiber is completely formed immediately upon the evaporation of the solvent.

In the manufacture of artificial filaments from such protein as zein, the zein is dissolved in alcohol and extruded into a solution of formaldehyde where the reaction proceeds rapidly to form the finished fiber.

In the manufacture of filaments from an alkali-dispersible acid-coagulable protein, such as casein, the setting of the filaments takes place more slowly in a plurality of operations in the preferred type of process. The protein dispersion, for example, is spun into an acidic coagulating bath, following which the fibers are elongated, and then passed to a hardening bath. The protein dispersion is very glue-like in nature and the freshly coagulated filaments as they are removed from the acidic coagulating bath have a somewhat soft and sticky surface. This characteristic remains more or less until the fibers are hardened.

In the commercial manufacture of filaments from a protein, such as casein, the output from a large number of spinnerettes is combined into a tow which may contain from 50,000 to 300,000 filaments. After these filaments are withdrawn from the coagulating bath and combined in the tow, they are then passed over suitable stretching apparatus which elongates the fibers to any

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desired length. During this elongation the fibers are placed under considerable tension and the force applied for stretching the fibers causes them to press upon each other and the surfaces of the fibers tend to adhere to each other. When the fibers in this condition enter the hardening bath, they have a tendency to remain adhering to each other and the individual filaments are not adequately and completely hardened. At the conclusion of the hardening operation, the fibers in a tow often remain adherent in which is referred to as "tight" bundles. They do not open up readily into soft fluffy wool-like masses of fiber which can be processed in the usual fiber fabricating techniques.

This difficulty is peculiar particularly to fibers formed from alkaline-dispersible acid-coagulable proteins which are made in a plural stage manufacturing process, i. e., a coagulating stage and a subsequent hardening stage. As has been explained heretofore, this is to be contrasted with rayon manufacture in which a single action, either physical or chemical, takes place to precipitate or set the material in filament form.

In the case of casein fibers, for example, they remain in the somewhat sticky adherent stage from the time they leave the coagulating bath until they are hardened. The adherence is aggravated when any attempt is made to elongate the protein fibers before setting or hardening them. Although adherence is not a problem after hardening, it is desirable, as a practical matter, to accomplish most of the elongation while the fibers are in the coagulated but unhardened state. In this state, while "non-set," the fibers are easily elongated. However, they are apt to adhere to each other.

We have conceived that materials which would keep the filaments from sticking together during the coagulating and elongation stage would be highly desirable. Such materials, if of a chemical nature, must not modify the protein undesirably so that it will deleteriously affect in any way its physical properties, such as strength, color, etc., and it must not affect the chemical properties, and in particular, the dyeing properties. Physical agents which might separate the fibers but which adhere and which are attached to the finished fibers would be undesirable. The sticky glue-like nature of the fiber during spinning and elongating is normally thought to have a pronounced adhesive action, and the firm adherence of foreign substances on the surface of the finished fiber in the large amount that would be

necessary for adequate separation is not desirable.

We have discovered, contrary to what might be expected from the known state of the prior art and the above considerations, that a protein fiber, such as a casein fiber, may be formed by spinning a dispersion into an acidic coagulating bath containing an extremely finely divided solid material inert with reference to the coagulating bath to prevent adherence of the fibers to each other. This material adheres to the freshly formed surface of the casein filaments during this stage and the finely divided material which adheres is sufficient to prevent the adherence of the fibers to each other and eliminates the formation of "tight" bundles. Furthermore, and this is surprising, during the hardening of the fiber, at least a part and generally a major portion of the finely divided material sloughs off or is removed from the surface of the fiber. Thus the finished fiber is not modified by the material to such an extent as to interfere with its normal use.

In practicing our invention, the proteins to which it may be applied are the so-called alkali-dispersible acid-coagulable proteins. Outstanding examples are casein from milk, sometimes referred to as animal casein, and the caseins from certain seeds, such as soybean, peanuts, cottonseed, etc., which are often referred to as vegetable casein. These caseins have the characteristic of being dispersible in an alkaline material and coagulable in an acid.

The invention will be particularly described with reference to milk casein as a preferred illustrative embodiment. It is to be understood, however, that other alkali-dispersible acid-coagulable proteinaceous substances may be used alone or in admixture. The raw material need not be from a single source; for instance, mixtures of soybean casein and milk casein may be used, and in addition, natural protein fibers, such as wool shoddy may be dispersed and blended with a dispersion of milk or soybean casein. The invention also includes dispersions containing a minor proportion of cellulosic dispersions, such as viscose, but in which the problems incident to the manufacture of proteinaceous fibers predominate.

The casein may be dispersed in any of a number of ways known in the art and the particular technique employed is not critical. Any alkaline material may be used, preferably caustic soda.

After the dispersion has been appropriately filtered, deaerated and cooled, if necessary, it is pumped through the minute orifices of a spinnerette which is immersed in an acidic coagulating bath.

This bath comprises essentially an acid, such as sulfuric acid in aqueous solution. Other acids may be used, such as acetic, hydrochloric, sulfamic, or the like; sulfuric acid is preferred. The bath may also contain advantageously a soluble salt, such as sodium sulfate or sodium chloride which augments the action of the acid and possibly has a dehydrating action. The acidity of the solution will depend somewhat on the rate of travel of the fibers through the coagulating liquid and the pH of the protein dispersion. Solutions having an acidity of 1.3 to 2.0 pH value or higher are preferred. If any tanning agents are included, they should not be in an amount to accomplish any appreciable or substantial hardening action.

Included in the coagulating bath, in accordance with the invention, is a finely divided solid material. This must remain as a solid under the acid and other conditions prevailing in the coagulating bath, and materials having this property are referred to as inert. Illustrative of these materials are finely ground clay, kaolin, feldspar, diatomaceous earth, talc, soap stone, gypsum, silica, bentonite, asbestos flour, calcium and barium sulfates, etc., which are referred to as inorganic materials. Preferably these should be sufficiently finely divided to stay in suspension in the bath during coagulating, such as a size of the order of a few microns. Preferably a major portion of the inorganic particles should be smaller than 5 microns; even colloidal size particles are desirable. The circulation of the coagulating bath, due to the passage of fibers through it, is generally sufficient to keep the finely divided material in a state of suspension. Forced circulation, however, may be used. Other materials, such as ground wood flour, leather flour, ground rabbit's hair, and other organic inert substances may also be used. Because they are lighter they may be larger in size, such as 200 to 300 mesh.

The amount of the finely divided material in the coagulating bath varies somewhat with the one selected, the rate of fiber withdrawal and the extent to which the adherence of the fiber is troublesome. In general, the amount will be within the range of 0.1 to 10% by weight, based upon the total coagulating bath, preferably 0.2 to 4%.

The coagulating bath may contain any of a plurality of auxiliary agents suggested in the prior art and its composition is not critical, except that it must coagulate the fibers without an appreciable hardening action.

After the fiber is so coagulated, it may be elongated and passed to a hardening bath or baths. The hardening bath generally contains an aldehyde or a compound yielding one, such as formaldehyde, paraformaldehyde, hexamethylenetetramine, acetaldehyde, paraldehyde, etc. It may also contain a salt, such as sodium sulfate or sodium chloride which has a dehydrating effect, and one or more mineral tanning agents, such as alum, etc.

The hardening may be carried out in a plurality of baths, the first bath containing a lesser concentration of the hardening agents and the second bath containing a larger amount. During this treatment, the fiber is hardened sufficiently so that there is no adherence even when passed through squeeze rollers. After it is removed from the hardening baths, it may be washed and dried.

After the hardening, the fiber may be acetylated or otherwise treated, in accordance with processes known in the art.

During the hardening action, it has been found that a large portion and generally a major portion of the finely divided inert material is removed from the fiber during the hardening action and possibly also in a subsequent washing operation. Apparently during the hardening action, the surface of the protein fiber shrinks and becomes more firm and the particles of finely divided solid which have adhered to it, slough off. It appears that these particles adhere to the fiber surface while the fiber is in its coagulated unhardened adhesive stage but that during the hardening, the adhesive character of the surface is eliminated and the ability to hold the finely divided solid is greatly reduced. This is surprising, since it might have been expected that the hardening would adhere the particles to the surface all the more firmly. This is also highly advantageous, because fiber containing an appre-

ciable amount of the solid would be undesirable for many purposes, due to the modification of its physical surface characteristics and its chemical properties, particularly its dyeing and coloring properties.

As illustrative of this property of removing the finely divided solid from the fiber, a dispersion of casein was spun into an acidic coagulating bath containing 1% of finely divided aluminum silicate. Samples of the fiber after coagulation but before hardening were analyzed and were found to contain 0.77% (average) calculated as clay. After the fiber had been hardened in a formaldehyde bath, washed and finished, in accordance with a commercial method, it was analyzed and found to contain 0.29%, calculated as clay. This shows that the amount of the clay removed during the hardening action is more than half. The removal of the inert material during the hardening was also evidenced by the fact that large quantities accumulated in the hardening tanks.

The fiber produced in accordance with the invention may be put to any use for which synthetic proteinaceous fiber is now employed. It has good dyeing properties and the small amount of the finely divided solid which adheres to it does not interfere with any of its normal uses.

It will be obvious that the invention contemplates many variations in the exact procedure that can be employed, in the composition of the dispersion and various treating baths, and in the finely divided solid material, and the invention is intended to cover all of the same as are included within the following claims.

We claim:

1. In a process of manufacturing synthetic proteinaceous fiber comprising an alkali-dispersible acid-coagulable protein, in which process the fibers are elongated after spinning and before hardening and during which there is a marked tendency for the fibers to adhere to each other, the steps comprising spinning a dispersion of said

protein into an acidic coagulating bath in which is suspended particles of a finely divided solid material inert with respect to the coagulating bath and said protein to form filaments in a coagulated but unhardened state and upon the freshly coagulated surface of which filaments said particles adhere, elongating a plurality of said filaments by stretching the filaments while they are in said unhardened condition during which the particles on the filament surface inhibit the adherence of the fibers to each other, passing the elongated filaments into a protein hardening bath comprising formaldehyde, holding the filaments in the hardening bath so as to harden the protein and cause the filaments to lose the adhesive character of their surface, whereby a major portion of said particles slough off from the surface of the filaments during the normal hardening and subsequent washing steps and the fiber is not modified by the treatment with the particles to such an extent as to interfere with its normal use.

2. The process of claim 1 in which the particles of finely divided solid are particles of finely divided clay.

3. The process of claim 1 in which the alkali-dispersible acid-coagulated protein comprises milk casein.

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