This invention relates to improvements in the manufacture or treatment of artificial materials, and is more particularly concerned with processes in which artificial materials are subjected to stretching processes for the purpose of improving their properties and particularly their tensile strength.

U. S. Patent No. 1,709,470 describes the stretching of artificial materials of cellulose acetate and states that the stretching may be facilitated by agents which swell the cellulose acetate. The swelling agents may be employed in aqueous solution, in solution in organic diluents, or in the form of vapour. Aqueous acetone, ethyl alcohol, formaldehyde and glycine are instanced as examples of swelling agents. By such a process products of lower density and increased tensile strength are obtained.

According to the present invention the stretching of threads or other artificial materials containing organic derivatives of cellulose is effected while the materials are under the influence of a solvent or a swelling or other softening agent under super-atmospheric pressure. All such agents, whether or not they have a softening action at atmospheric pressure, are hereinafter referred to generically as softening agents. The pressure may, for example, be 5, 10, 15 or 20 or more pounds per square inch in excess of atmospheric pressure, and may even amount to several atmospheres. By this means it is found that the rate of penetration of the materials by the softening agent is materially increased and/or the concentration in which the softening agent is applied may be substantially reduced to obtain similar results. Furthermore, the rate at which stretching can be carried out may be increased and in addition the use of pressure renders possible the use of certain volatile softening agents at temperatures which are impossible or impracticable when working at atmospheric pressure. Again, the process of the present invention enables certain agents to be used for softening the materials which are not available as softening agents at ordinary temperatures and pressures owing to their lack of softening power under such conditions.

The present invention includes the use of any temperatures coupled with super-atmospheric pressures provided that under the pressure and temperature conditions employed the particular softening agent, at the concentration in which it is employed, does not have such a strong action upon the material under treatment that disintegration or other damage occurs. Under such conditions softening media which at atmospheric temperature and pressure have substantially no softening action may be employed to effect a high degree of softening. Thus, for example, stretching of cellulose acetate materials may be effected with aqueous acetone or dioxane of a very low concentration such as 5-10 or even 3% or less at a relatively high temperature such as 70 or 80°C. to 100°C., 120°C. or more, coupled with the use of super-atmospheric pressure. If desired, much higher temperatures, for example up to 130°C. or even 150°C. or more, may be employed under the appropriate pressure and with the concentration of the acetone or other softening agent so adjusted that stretching takes place readily and yet the softening action is not so far-reaching as to produce disintegration of the material. At such temperatures concentrations of acetone of about 1% or less may be employed. Media containing considerably higher concentrations of softening agents may also be employed, e.g. an aqueous or other solution of acetone or dioxane under pressure, of a concentration of 15 or 20-40% or higher. In general the higher the temperature and pressure, the lower may be the concentration of the agent. At high temperatures and pressures a trace of softening agent dissolved in water or other diluent may produce the desired softening.

The invention is particularly valuable in stretching while the materials are under the influence of a vaporous softening agent. Here again the invention enables conditions such as temperature or speed of stretching to be attained which are difficult of attainment at atmospheric pressure, and further it enables agents to be used which are of little or no value at atmospheric pressure. The vapour of the softening agent may be dry or wet or just saturated. The vaporous softening agent may be employed without dilution or diluted with any appropriate gas or with a non-solvent vapour, e.g. steam.

The present invention is more particularly concerned with the stretching of products made of or containing acetone-soluble cellulose acetate or other cellulose acetates but may also be employed in the stretching of artificial materials containing other organic derivatives of cellulose, for example cellulose formate, propionate, butyrurate, nitrocellulose, cellulose nitro-acetate and other esters and mixed esters of cellulose, cellulose ethers, for example methyl, ethyl and benzyl cellulose, mixed cellulose ethers and mixed ether-
esters of cellulose, for example oxy-ethyl cellulose acetate.

As examples of suitable softening agents for use with cellulose derivatives in accordance with the present invention, the following may be instanced:—aceton, methyl ethyl ketone and other ketones, ethers, including cyclic ethers, etheresters and esters of olefins and poly-olefine glycols, for instance methyl ethylene ether, dioxane, the mono- and dimethyl ethers of ethylene glycol or of propylene glycol, and ethers which are substantially non-solvents at ordinary temperatures for cellulose derivatives, for instance ethylene and propylene glycol, glycol mono-acetate and methyl glycol mono-acetate; formaldehyde, acetaldehyde, methylene chloride, ethylene chloride, dichlor-ethylene, mono- and tri-actins, acetic acid, methyl alcohol, ethyl alcohol, propyl and isopropyl alcohol and other alcohols, hydrocarbons, especially cyclic hydrocarbons, for instance benzene, toluene and xylenes, and ethers, for example isopropyl ether and higher aliphatic ethers. Many of the above agents may be employed in aqueous solution or in the vaporous state mixed with steam, and in accordance with the present invention, it is preferred to employ them so diluted. However, other diluting agents may be employed, or, where the agents have not too great a softening power, they may be employed undiluted. Some of the above agents have little or no softening power at ordinary temperatures and may be used as diluents at such temperatures in association with other agents, or may be used as softening agents at relatively high temperatures. Such agents are, for example, the higher alcohols, hydrocarbons and higher aliphatic esters mentioned above.

The invention is especially valuable for the treatment of filaments, threads and similar textile materials, whether these consist of continuous filaments or of spun yarn, for example yarn spun from short lengths of artificial filaments or the type of product obtainable according to the process of U. S. application S. No. 120,264 filed 18th May, 1934. The textile materials may contain finely divided substances, e. g. barium sulphate, titanium dioxide and other delustering agents, and tin compounds and other weighting agents. The invention, however, includes the treatment of other materials, for example films, sheets or the like, so as to effect a stretching while the materials are under the influence of the softening agents under pressure. The stretching of the films or like sheet materials may be carried out so that the permanent elongation is purely longitudinal, in which case the film, sheet or the like may be held laterally against shrinkage, or may be carried out so that the stretching takes place both laterally and longitudinally. Preferably the conditions of pressure and temperature existing during the application of the softening medium are the same as those during the stretching operation. The materials may, for example, be introduced directly into the desired medium under pressure and stretched while therein. Alternatively, however, the material may be impregnated with the desired medium at any desired temperature and pressure, and the impregnated material subsequently brought to the desired pressure or the desired temperature and pressure for effecting the stretch.

The stretch produced according to the present invention may be of a low order, for example a stretch so as to produce a permanent elongation of 30-70% of the original length of the materials, or very considerable stretches may be effected, for example of the order of 100 up to 500, 700 or 1000% or more of the original length of the materials. In order to achieve these higher stretches high pressures and/or high pressures are in general desirable, coupled with the use of comparatively low concentrations of the softening agents.

The stretching operation may be carried out on the materials under any suitable conditions, and textile materials being stretched may be untwisted or twisted. The stretching operation may be applied to a single thread or bundle of filaments proceeding, for example, from a dry spinning cell or other spinning apparatus, or a number of threads or bundles may be stretched in a single apparatus. Artificial filaments, yarns and the like may be stretched in yarn form, for example between rollers positioned in a pressure vessel containing the liquid or vaporous softening medium. Alternatively stretching of the materials may be effected during the course of their travel from one point to another, e. g. during the winding of a yarn from bobbin to bobbin. A number of artificial threads or the like may be subjected to the stretching operation in warp formation, i. e. in parallel alignment in the form of a sheet, during the course of their travel from one point to another. The stretching operation, whether applied to a warp of threads or otherwise, may be carried out in a single stage or may be effected in a number of stages with or without removal or reduction of the stretching tension between two or more of the stages.

The speed of the materials entering the stretching vessel may be controlled by a positively driven feed device which may be positioned either inside or outside the vessel, and stretching may be effected by one or more stretching devices. In the case of single stage stretching the means for applying the stretching may be located either inside or outside the stretching vessel, or if stretching is being effected in stages the final stretching means may be located outside and the remainder inside or all the stretching means may be located inside.

The stretching tension may be allowed to act on the materials immediately upon their exposure to the liquid or vaporous softening medium or, in order that the materials may have time to reach a sufficiently softened condition before being subjected to the stretching tension, the tension may be prevented or substantially prevented from acting upon them during the first part of their travel in the softening medium, e. g. by passing them in substantially non-slipping contact with one or more rollers driven at a peripheral speed substantially equal to that of the feed device.

Examples of apparatus which may be employed in carrying out the processes of the present invention are described in U. S. applications S. Nos. 4,510 filed 1st February, 1935, and 4,511 filed 1st February, 1935, to which reference is made in this connection.

The present invention is particularly valuable for the treatment of cellulose derivative materials which have been produced by dry spinning processes, but it may also be applied to the treatment of materials obtained by wet spinning processes, as described, for example, in U. S. Patents Nos. 1,465,994 and 1,467,493 and U. S. Patents Nos. 1,465,994 and 1,467,493 and U. S.

The materials may be treated in the form in which they are obtained from the spinning machines, or after they have been subjected to after-treatment processes, e.g., to a shrinking operation.

The following examples are given in order to illustrate the invention, but are not to be considered as limiting it in any way:

**Example 1**

Cellulose acetate yarn is passed during its travel from one point to another through a dilute aqueous solution of acetone contained in a suitable vessel and maintained under a pressure of 50 to 60 lbs. per square inch above atmospheric pressure, and is stretched while in contact with the solution. Suitable concentrations and temperatures for the solution are about 6% at 100°-105° C. and about 10% at 90°-95° C. In this manner a yarn of increased tensile strength may be obtained.

**Example 2**

Cellulose acetate yarn is stretched in a manner similar to that described in the preceding example, except that an aqueous solution of methyl alcohol is employed, suitable concentrations and temperatures being about 15% at 110° C. and about 10% at about 115-120° C.

**Example 3**

Cellulose acetate yarn is stretched during its travel through a vessel containing a mixture of acetone and steam at a temperature of about 118° C., the concentration of acetone being about 3% and the pressure being adjusted so that the steam is just wet.

**Example 4**

Cellulose acetate yarn is stretched in a manner similar to that described in Example 3, except that a medium containing wet steam at a temperature of about 110° C. and containing about 5% of methyl alcohol vapour is employed.

The stretched materials may be subjected to any desired after-treatment processes. Thus, they may be treated with shrinking agents, for example as described in U.S. applications S. Nos. 611,240 filed 13th May, 1932, 607,967 filed 26th April, 1932, and 609,255 filed 4th May, 1932, to improve their extensibility or for the production of shrinkage or other effects. Shrinkage may be effected continuously with the stretching operation of the present invention, e.g., as described in U.S. application S. No. 672,805 filed 25th May, 1932. Again, they may be subjected to delustrating operations, for example by incorporating there in finely divided organic or inorganic materials. By suitably controlling the conditions of the stretching operation of the present invention, materials having a modified lustre may, if desired, be produced directly by such operation. Thus, for instance, high speeds of stretching are in general conducive to the production of lustrous products. Again, cellulose ester materials may be subjected to processes of saponification which may be carried out to a relatively small extent, for example to give them an affinity for cotton dyestuffs, or in which a complete or practically complete saponification is effected. In this connection reference is made to U.S. Patents Nos. 1,884,622 and 1,884,623 and U.S. applications S. Nos. 655,773 filed 8th February, 1933, 655,774 filed 8th February, 1933, and 655,778 filed 8th February, 1933.

When cellulose acetate forms the basis of the artificial materials it may be of normal viscosity, for example 8, 15 or 20 as determined by comparison with a 6% solution of the cellulose acetate in acetone at 25° C. compared with glycerine as 100, or it may be of relatively high viscosity, for example a viscosity of 50, 50, 100, 200 or even more. Similarly artificial materials containing other organic derivatives of cellulose of normal or high viscosity may be treated. The production of such high viscosity organic derivatives of cellulose is described in U.S. Patent No. 1,708,787.

What I claim and desire to secure by Letters Patent is:

1. Process for the treatment of artificial filaments, yarns, films and similar materials containing organic derivatives of cellulose, which comprises subjecting the materials to a stretching operation while they are softened under the influence of a medium which is at super-atmospheric pressure and consists of an organic softening agent for the cellulose derivative diluted with a diluent which has no softening action upon the cellulose derivative at atmospheric pressure and temperature, the degree of dilution being such that the mixture at atmospheric pressure and temperature has substantially no softening action upon the cellulose derivative.

2. Process for the treatment of artificial filaments, yarns, films and similar materials containing organic derivatives of cellulose, which comprises subjecting the materials to a stretching operation while they are softened under the influence of an aqueous medium which is at super-atmospheric pressure and which contains an organic softening agent for the cellulose derivative, the concentration of such organic softening agent being such that the aqueous medium at atmospheric pressure and temperature has substantially no softening action upon the cellulose derivative.

3. Process for the treatment of artificial filaments, yarns, films and similar materials containing organic derivatives of cellulose, which comprises subjecting the materials to a stretching operation at atmospheric pressure with an aqueous medium which contains an organic softening agent for the cellulose derivative in such concentration that the aqueous medium at atmospheric pressure and temperature has substantially no softening action upon the cellulose derivative, and subjecting the softened materials to a stretching operation at super-atmospheric pressure.

4. Process for the treatment of artificial filaments, yarns, films and similar materials containing organic derivatives of cellulose, which comprises subjecting the materials to a stretching operation while they are softened under the influence of a medium which is at super-atmospheric pressure and which contains an organic softening agent for the cellulose derivative diluted with wet steam, the degree of dilution being such that the mixture at atmospheric pressure and temperature has substantially no softening action upon the cellulose derivative.

HENRY DREYFUS.