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PROCESS OF PRODUCING ARTIFICIAL THREADS

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This invention relates to new artificial threads, films and the like; and it comprises new and improved artificial threads, films and the like composed of cellulose esters and ethers and having a fibrous internal structure under Roentgen ray examination, high tensile strength and fine titre; and it further comprises processes wherein finished or preformed artificial threads, films and the like are simultaneously swollen and substantially stretched to produce such a fibrous structure and finer titre, together with enhanced tensile strength and other desirable improvement; all as more fully hereinafter set forth and as claimed.

Artificial threads, films and the like, heretofore made from cellulose esters and ethers, are in the form of dry gels; and are characteristically different from natural fibrous textiles, such as cotton, etc., in that they are of amorphous and non-fibrous structure. These non-fibrous artificial threads and the like are made by various processes. In some processes in which artificial threads are made from cellulose esters and ethers by dry spinning, the threads are drawn as they leave the spinning cell, giving a slight stretching of the thread. This stretching does not exceed the normal limit of elongation, being about 25 per cent. In such cases there is no substantial improvement in the thread, such as increased strength. In other known processes, in some instances the finished thread is given a limited stretching, not exceeding 25 percent. This stretching likewise does not give any substantial improvement in titre and in strength. In other processes, it has been sought to improve yarns prepared from cellulose esters by treating the finished thread or yarn with acetic acid and then subjecting the thread to a slight stretching and finally removing the acid while maintaining or increasing the tension of the thread. Again, in still other processes, such threads are treated in certain swelling baths, and the swollen thread slightly stretched; the stretching not exceeding about 100 per cent. However, in such cases the subsequent stretching of the cellulose thread is necessarily limited to the extension mentioned, as during this stretching the swollen body rapidly loses the greater part of its plastic properties, so that further stretching without rupture is practically impossible.

By none of these prior processes is it possible to obtain the new and improved artificial threads and the like, such as are made in the present invention.

We have now found that such threads and the like may be given a fibrous internal structure, as evinced by Roentgen ray examination, with substantial improvement in titre and tensile strength, by new processes discovered by us. Our new processes may be applied to any preformed or finished thread, film or like material made from cellulose esters and ethers or similar compounds, preformed or finished materials being advantageously dry. In our process, such finished or preformed threads and the like are simultaneously swollen and substantially stretched, the stretching being above 200 per cent elongation; stretching to, at least, 200 per cent giving substantial improvement in the thread and producing the desired characteristics. This stretching may be to an unlimited extent; to 1,000 per cent or more.

Our new process may be applied to threads and the like made from cellulose esters and ethers, such as nitrocellulose, acetyl cellulose and the like. It may also be applied to such articles made from viscose (xanthate), the process being somewhat modified for this type of material.

Tests have shown that an already prepared and dried thread or film, that is, one in the dry gel condition and freed from all solvent, can be considerably improved if it be greatly stretched after swelling while still retaining the gel condition. A quite general improvement takes place in this, which embraces above all the strength, the fineness and the lustre, it being possible by a suitable choice of the conditions of working, to influence one or more of these properties above the others. According to the invention, the process for the improvement of artificial threads of cellulose esters and ethers consequently consists in the threads being changed from their original condition which under the Roentgen rays appear amorphous, by mechanical treatment in combination with chemically inert steam or liquid baths, without chemical change, into the axially arranged crystalline condition. The mechanical treatment which can be carried out in the chemically inert bath or directly thereafter in a second bath, consists in a practically unlimited stretching, in any case, however, considerably exceeding the natural plasticity limit, with if necessary additional cross stressing in which both continual, discontinuous as well as partial stretching may be used. The natural plasticity of prepared artificial thread of cellulose esters and ethers permits, as is known, of extensions of about 20 to 30 per cent. If, however, these threads are treated according to the new process, then it is possible to stretch the threads a

great deal over 200 per cent and even up to several 1000 per cent. This astonishingly large stretching capacity is also present even with non-uniform threads with largely varying sections, and the stretching then comprises not only the parts with thin initial sections but also the whole thread, so that a remarkably uniform thread is produced from the original uneven thread.

The speed of stretching must here be so suited to the other factors influencing the softening, viz: temperature, pressure, composition and concentration, that the weakening accompanying the stretching of the moist thread by the reduction of the section is at least compensated by the strengthening of this section simultaneously attained in the bath. To regulate the lustre, the choice of the baths and the manner of the stretching may be correlated together. In particular directly after the stretching, the threads may be treated with salt baths. By suitable mutual correlation of the concentration, the solution additions, the pressure, the temperature, and the speed of drawing off, an increase in the tensile strength or resistance to rupture of the dried thread by at least 100 per cent is obtained.

For the technical utilization of the improving process, the fact is of particular importance that it is not limited to single threads but may be just as well used on twisted artificial threads, hanks, woven material and films, with if necessary the simultaneous shaping and dyeing, without the separate parts adhering together.

The advantages of the new improving process consist in the production of artificial threads, woven materials, films and the like, of cellulose esters and ethers (for example, cellulose acetate, nitrate, xanthate, etc.) being made possible, these having a fineness and resistance to rupture in the dry and wet state not hitherto attained by any process, and in the lustre of these productions being capable of regulation. The reduction of the capacity of swelling and the improvement in the wet strength is also worthy of note. It is thus possible to produce from coarse comparatively cheap artificial threads, because they are lighter and are produced in greater quantities, or from similar woven materials or films, extraordinarily thin and strong products, and this without difficulty.

It is clear that with the new improving treatment, the known supplementary treatments may be combined, such as are usual with artificial threads, woven materials or films for various purposes. For example, there may be simply mentioned: The production of staple fibers, of crepe threads, curling, dyeing, regulation of lustre on stretching by the aid of weak acids, the treatment with weak alkaline media for the purpose of removing the last traces of acid, or the treatment with direct electric current, and the like. Furthermore, after the improvement has taken place, the goods may be regenerated by known processes to cellulose and for example the acetyl cellulose threads be de-acetylized by dipping in alcoholic potash lye. This regeneration treatment can be carried out with the stretching in the same crystallization bath.

As crystallization baths which, in combination with the mechanical treatment described, produce the improvement of the artificial thread, woven material or films, chemically inert vapour or liquid baths are suitable which consist of a non-solvent and a solvent, preferably an organic solvent, the solvent effect of which, by the choice of suitable temperatures or pressures, but in particular of additions, for example precipitants, is, with an incease in the swelling capacity, reduced until a prepared artificial thread of a cellulose-ester or ether becomes capable of stretching in the bath to a practically unlimited extent, at any rate considerably over the natural limit of plasticity. As chemically inert baths those are in particular understood which neither produce a chemical change in the material stretched, nor are otherwise chemically active, as is for example the case with acids. Mixtures of pure or commercial dioxane (diethylene dioxid) containing ethylene acetal, and water or mixtures of acetone and carbon tetrachloride have proved themselves as particularly suitable crystallization baths for acetyl cellulose threads and films.

As one component of the crystallization bath, as already mentioned, exercises a dissolving effect on the goods being stretched and the other component a precipitating effect, or behaves inertly, it is often difficult, on account of these opposing properties, to attain a sufficiently good mixing of the two components since temperatures or concentration conditions come into consideration, so that the choice is extraordinarily limited. In addition to this, one of the two components is generally absorbed in the crystallization treatment by the goods being crystallized in preference to the other and is withdrawn with the goods, and this has as a consequence an alteration of the concentration in the bath, and under certain circumstances a separation of the mixture. These disadvantages can be overcome according to the invention by adding to difficultly miscible or immiscible systems, substances which produce a complete mixing at least within the limits of temperature and concentration coming into consideration. Such additions or blended agents may themselves act as solvents or be inert. As solvent components of such three or more component mixtures, it is desirable to use organic liquids, in particular the lower members of the homologous series of aliphatic esters, ketones, ketoles; and various heterocyclic compounds, as, for example, furfuran and pyridine come into consideration, while as inert components, water or a precipitant for the crystallization goods, soluble in the solvent components, come into question.

Particularly advantageous for the purposes of the invention, have been proved solvent and inert or precipitant components which enter into molecular combination with each other. As most of the solvent components are easily volatilized organic bodies of low flash point it is desirable for reasons of safety, especially with the use of crystallization goods also easily inflammable, as for example, nitro-cellulose, to reduce the flash point of the baths. For this purpose a further substance acting in this manner can be added to the baths. If necessary this may also facilitate the miscibility of the components in the sense of the invention.

The invention offers the advantage that a regeneration of the used crystallization baths by producing an intentional separation after the removal of the addition, is extraordinarily facilitated. A further advantage consists in that there is a large field offered in the choice of the conditions in the temperature and concentration.

As already mentioned in the introduction, the production of an at least partially crystalline structure with artificial threads or films of cellu-

lose esters and ethers can also be attained during the producing process thereof (crystallization spinning process).

Of all the hitherto known spinning processes for artificial threads, only that one permits an improvement combined with the actual spinning by excessive stretching, in which the cellulose esters and ethers contained in the spinning solution are regenerated into hydrate cellulose during the stretching. This holds good in particular for the process of production for viscose silk and cuprous silk. With the other dry or wet spinning processes on the other hand it has not been possible to effect any improvement at all by stretch spinning. It has now been proved that any spinning process whatever can be changed into a crystallization spinning process if the excessive stretching improving the spun goods is carried out in a crystallization bath, in which a prepared air dried thread can be stretched, with improvement. These crystallization baths do not need to exert a regenerative action on the threads produced. It is only necessary that the stretched goods have a certain swelling condition imparted thereto and that the draw off speed, temperature and pressure be suitably adjusted together. The new crystallization spinning process can be carried out both in the so-called single bath as also in the so-called multiple bath process. In the latter case, with viscose the stretching takes place in one or more baths which do not contain substances regenerating cellulose.

In the spinning of the other cellulose esters and ethers, the stretching can be carried out with or without regeneration. The selection of the swelling medium must be controlled in the first place by the nature of the threads to be produced. Thus for artificial threads of cellulose esters or ethers organic non-acid solvents have been found particularly suitable which exert their action in the vapour condition also, so that instead of the second bath a vapour treatment can be employed. Threads of regenerated cellulose on the other hand are preferably transformed into the desired swelling condition by means of strongly alkaline baths, in which they can be subjected to a thorough stretching.

By suitable concentration of the baths in combination with a proper stretching speed, with the strengthening of the thread an extraordinary improvement is simultaneously obtained. Artificial threads are obtained in this way up to a fraction of a denier with strength of between 300 to 700 g/100 den. The products obtained from cellulose esters and ethers are, contrary to those made in the known ways, largely crystallized and arranged axially. By the selection of the swelling medium, and the length and speed of the stretching it is possible to considerably influence the lustre of the products, when if necessary a supplementary treatment with salt baths may follow directly after the stretching.

It is not absolutely necessary for the stretching to take place in the crystallization bath itself. The thread can be subjected to the stretching directly after leaving the bath. The swelling action of the bath or vapour may be regulated within wide limits by, in addition to the alteration of the concentration, the choice of the temperature and the duration of the swelling. Similarly to the above improvement in the spinning of cellulose and cellulose compounds, the improvement in the spinning of spinning solutions of all kinds as for example glue, albuminous substances, etc., can be also carried out.

In the same way as with artificial threads, films may also be produced and shaped according to the new process, with a far reaching improvement.

Furthermore, other properties, in particular the heat conductivity of the products can also be influenced by the incorporation of suitable substances during the improving treatment. Thus, for instance the swelling medium taken up by the goods being stretched can be transformed by heating or by a vacuum treatment into the vapour state. The expansion thus taking place effects at the same time a mechanical stressing of the goods being stretched in the above-mentioned sense crossways to the stretching direction and therefore a further extensibility.

Known additions as for example for the purpose of increasing the plasticity lustre, colour and the like, can be added to the spinning solution or to the swelling bath or to both.

Examples

Example 1.—A single thread acetyl cellulose silk of 10 deniers was swollen in a bath of equal parts of commercial dioxane (diethylene dioxid) and water and then stretched to 30 times the length, that is to 0.33 den. The time of stretching lasted 8 seconds. There consequently resulted an improvement coefficient (that is initial standard to final standard) of 30.

Example 2.—A thread of 800 parallel arranged threads spun from a spinning solution of 20 parts of acetyl cellulose and 80 parts of dioxane and having a standard of 5.7 den. and a resistance to tearing of 140 g/100 den. after drying is swelled in a mixture of equal parts of dioxane and water and then stretched for 12 minutes to 20 times the length. This was then washed with a 30 percent sodium sulphate solution and cold water. The stretched, dry thread has a standard of 0.285 den., and a strength of 610 g/100 den. The improvement coefficient amounted consequently for the titre to 20 and that for the strength to 4.35.

Example 3.—The same initial material as in Example 2 was swelled in a bath of equal parts of dioxane and water and stretched for 12 minutes to 11.1 times the length. After washing with cold water and drying a thread was obtained of 0.51 den. and 616 g/100 den. The improvement coefficient amounted consequently for the titre to 11.10 and for the strength to 4.40.

Example 4.—The same initial material as in Example 3 resulted, with 11.1 times the stretching in a bath of equal parts of dioxane and water and subsequent washing with cold water in a resistance to rupture of 616 g/100 den. as well as an extensibility of 9.4 per cent, while the initial material had a strength of 140 g/100 den. and an extensibility of 20 per cent.

Example 5.—The initial material used in Example 2 gave with 20 times the stretching in the dioxane water mixture and subsequent washing with 30 per cent sodium sulphate solution and cold water, a resistance to rupture of 610 g/100 den., and an extensibility of 10 per cent, while the initial material had a resistance to rupture of 140 g/100 den. and an extensibility of 20 per cent.

Example 6.—A thread spun from 20 parts acetyl cellulose, 40 parts dioxane and 40 parts acetone was stretched in a bath of equal parts of acetone and carbon tetrachloride, for 9 minutes, from 12.05 to 5.2 den. that, is to an extent of 2.3 times. After washing with cold water and dry-

ing, the stretched thread showed a resistance to rupture of 230 g/100 den. and an extensibility of 21 per cent.

Example 7.—A particularly beautiful lustre similar to natural silk is obtained from the initial material according to Example 6 by swelling and stretching in a bath of equal parts of acetone and carbon tetrachloride by stretching for 9 minutes to 2.3 times. After stretching the goods are washed with cold water.

Example 8.—A slightly less lustre is given by the process under the conditions of Example 2.

Example 9.—A matted silk lustre and soft touch is given by treatment of a commercial acetate silk (12 twisted single threads of 5.2 den.), if 160 such threads twisted and lying in parallel are stretched for 8 minutes in a bath of equal parts of dioxane and water to an extent of 3.06 times, the titre falling from 5.2 to 1.7. This is followed by washing with hot water (80° C.).

Example 10.—A perfectly matt thread is given by the same commercial acetate silk as in Example 9 if it is stretched in a bath of equal parts of dioxane and water for 8 minutes to 3.24 times the length, and then washed with cold water. The thread produced is characterized by its marked soft and down-like character.

Example 11.—A similar appearance but with a slightly harder touch is shown by a thread which is stretched as in Example 10 but is washed out with methyl alcohol.

Example 12.—A down-like character but greater lustre is given by a thread stretched according to Example 11, washed out with a 30 per cent sodium sulphate solution and hot water (80° C.).

Example 13.—The acetyl cellulose threads stretched as in Example 3 are in known manner de-acetylized by steeping them for 12 hours under tension in alcoholic potash lye, which contains 32 g. of caustic potash to the litre. The cellulose threads so regenerated show an additional improvement of the strength properties.

Example 14.—Acetyl cellulose threads of 5 den. are during stretching simu'taneously de-acetylized in the 50 per cent dioxane bath, the known additions for de-acetylizing being made to the dioxane bath. The threads produced of regenerated cellulose show an improvement of the strength properties.

Example 15.—An acetyl cellulose thread is carried through a 50 per cent dioxane solution and then passed through a funnel through which quicksilver flows in the same direction. The quicksilver exercises a strangling effect on the thread which favours the stretching. The titre of the thread is consequently still further reduced.

Example 16.—A lustrous acetyl celulose thread is first stretched in a bath of 48 parts dioxane and 52 parts of water to 4 times the length. It is then washed with cold water and allowed to dry. A completely matt thread is thus produced. If this thread is now again stretched in a 50 per cent dioxane solution to a further 5 times the length, that is, altogether to 20 times the original length, then after washing and treating with 30 per cent sodium sulphate solution, the original lustre is recovered, while the strength properties as well as the titre are considerably improved.

Example 17.—The treatment described in Example 16 is altered by one stage of the two part processes being carried out by rolling.

Example 18.—The treatment described in Example 16 is altered by the second partial treatment being carried out in a swelling bath with added de-acetylizing media.

Example 19.—A suitable crystallization bath for artificial threads or films of cellulose ethers or esters at 20° C. has the following composition:

1. Solvent component: 10 vol. methylethyl ketone (or acetone),

2. Inert or precipitating component: 10 vol. water,

3. The addition producing miscibility: 1 vol. alcohol. The alcohol serves as a blending agent, for the ketone-water mixture.

Example 20.—A 20 per cent acetyl cellulose solution in pure or commercial dioxane is spun through a nozzle for 80 threads in a crystallization spinning bath of approximately 50 per cent dioxane and 50 per cent water, with a speed of 5.5 g. spinning solution per minute (corresponding to 1.1 g. acetyl cellulose per minute) with a taking off speed by the stretching roller of 200–300 metres per minute. There is produced a total thread of 33 den. thickness which is composed of 80 separate threads of 0.4 den. By changing the concentration of the crystallization bath, the plasticity of the thread may be regulated within wide limits.

What we claim is:—

1. A process of preparing artificial thread formed of an organic derivative of cellulose and characterized by a fine denier, high tensile strength and a fibrous structure under Roentgen ray examination which comprises treating a thread formed of an organic derivative of cellulose with a bath comprising dioxane and water in such proportions as to swell and plasticize the thread, and stretching the thread until the length thereof is at least 200% of the original length.

2. A process of preparing artificial thread formed of an organic derivative of cellulose and characterized by a fine denier, high tensile strength and a fibrous structure under Roentgen ray examination which comprises treating a thread formed of an organic derivative of cellulose with a swelling bath comprising approximately equal parts by weight of dioxane and water and stretching the thread until the length thereof is at least 200% of the original length.

3. A swelling bath for treating artificial thread formed of an organic derivative of cellulose and comprising dioxane and water in such proportions as to swell and plasticize said thread, whereby said thread can be stretched until the length thereof is at least 200% of the original length.

4. A swelling bath for treating artificial thread formed of an organic derivative of cellulose and comprising dioxane, ethylene acetal and water in such proportions as to swell and plasticize said thread, whereby said thread can be stretched until the length thereof is at least 200% of the original length.

5. A swelling bath for treating artificial thread formed of an organic derivative of cellulose and comprising approximately equal parts by weight of dioxane and water to swell and plasticize the thread, whereby the thread can be stretched until it is at least 200% of the original length.

6. A swelling bath for treating artificial thread formed of an organic derivative of cellulose and comprising approximately equal parts by weight of acetone and carbon tetrachloride to swell and plasticize the thread, whereby the thread can be

stretched until it is at least 200% of the original length.

7. A process of preparing artificial thread formed of a cellulose derivative and characterized by a fine denier, high tensile strength and a fibrous internal structure under Roentgen ray examination which comprises treating a thread formed of an organic derivative of cellulose with a swelling bath comprising equal parts by weight of acetone and carbon tetrachloride and stretching the thread until the length thereof is at least 200% of the original length.

8. A method of preparing artificial thread characterized by a fine denier and a high tensile strength which comprises spinning a solution of an organic derivative of cellulose into a bath comprising dioxane and water and taking off the thread at a speed sufficient to stretch the freshly produced yarn at least 100% of its original length.

9. A method of preparing artificial thread characterized by a fine denier and a high tensile strength which comprises spinning a solution of an organic derivative of cellulose into a bath comprising equal parts by weight of dioxane and water and taking off the thread at a speed sufficient to stretch the freshly produced yarn at least 100% of its original length.

10. A method of preparing artificial thread characterized by a fine denier and a high tensile strength which comprises spinning a 20% solution of cellulose acetate in dioxane into a bath comprising dioxane and water and taking off the thread at a speed sufficient to stretch the freshly produced yarn at least 100% of its original length.

11. A method of preparing artificial thread characterized by a fine denier and a high tensile strength which comprises spinning a 20% solution of cellulose acetate in dioxane into a bath comprising approximately equal parts by weight of dioxane and water and taking off the thread at a speed sufficient to stretch the freshly produced yarn at least 100% of its original length.

12. Process for the manufacture of artificial filaments, threads, yarns, ribbons and like products, which comprises extruding a solution of cellulose acetate in dioxane through a shaping device into an aqueous solution of dioxane, stretching the products continuously with their production, and thereafter drying the products.

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