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PRODUCTION OF FILAMENTS, YARNS, FABRICS, AND LIKE MATERIALS

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4 Claims. (Cl. 8—20)

This invention relates to improvements in the production of filaments, yarns, fabrics and like materials, and is directed to the production of filaments, threads, yarns and the like, or fabrics or like materials containing the same, which consists of or substantially consist of regenerated cellulose, or which at least have an affinity for the cotton colours, and which have a high tenacity.

In recent years considerable attention has been directed to the production of filaments, threads and yarns of artificial silk, and particularly of artificial silk of the viscose or regenerated cellulose type, which have high, dry and wet tenacities, and in particular dry tenacities of 3 to 5 grams or more per denier. While some success has been achieved in the production of such yarns, nevertheless the processes involved in their production present considerable disadvantages, and the products, while possessing high tenacities, have disadvantages which may outweight this advantage. In general these processes have involved the use at some stage of concentrated acids. Not only are such acids difficult to work with on a commercial scale, but in addition they involve the use of expensive apparatus, and moreover in general yield products which possess the serious disadvantages of being brittle and lacking the flexibility desirable in textile products. The present invention aims to produce filaments, threads, yarns and the like and fabrics containing the same which have high tenacities or at least higher tenacities than ordinary viscose silk and are of the regenerated cellulose type, or consist substantially of regenerated cellulose, or at least have an affinity for the cotton colours.

The prior processes referred to involve the use of aqueous spinning solutions, and notably solutions of viscose as the starting material. The present invention, on the other hand, uses as starting material cellulose acetate or other organic esters of cellulose.

I have found that products of the character referred to may be obtained by saponification of filaments, threads, yarns, or fabrics containing the same, made of or containing cellulose acetate or other organic esters of cellulose of high viscosity characteristics. Thus the cellulose acetate used should have a viscosity exceeding 30 as measured by comparing the rate of flow of a 6% solution in acetone at 25° C. against a standard of glycerine taken as 100. Yarns of such cellulose acetate or other organic esters of cellulose may have a relatively high tenacity, for example a tenacity exceeding 1.5 grams per denier, and preferably exceeding 2 grams per denier. The best results are obtained according to the present invention by saponifying yarns of a cellulose acetate having a viscosity exceeding 50 and, still better, of the order of 75, 100, 150 or 200 or more on the above scale. The saponification of yarns and other materials containing cellulose acetate by means of caustic soda or caustic potash has been known for many years, but in general the application of such saponification processes to the ordinary cellulose acetate yarns results in a decrease, and in some cases a very serious decrease, in the dry tenacity of the yarn under treatment. In the present invention, on the other hand, it is found that provided the conditions of saponification are not unduly drastic the tenacity of the high viscosity yarn may not only be maintained but may even increase very considerably as a result of the saponification treatment. This is a very remarkable observation, since owing to the fact that high viscosity yarns of cellulose acetate or other organic esters of cellulose are somewhat less amenable to saponification than ordinary yarns, and hence have to be subjected to conditions during saponification which are somewhat more drastic than those applicable to ordinary yarns to obtain a similar degree of saponification, or have to be subjected to the ordinary conditions for longer periods, it would be expected that as a result the tenacity, far from being increased by the saponification treatment, would be decreased to a still greater extent than in the case of ordinary yarn. Again while in the treatment of ordinary yarn with caustic alkalies for the purpose of saponification particular attention has been paid to restricting the concentration of alkali, for example to under 1% solution, for the purpose of maintaining as far as possible the tenacity, it is found that in the treatment of high viscosity yarns according to the present invention concentrations considerably above 1% may be applied, and still substantial increases in tenacity are obtained. Thus, concentrations of 5% or more of caustic soda and temperatures up to 90° C. have been used with success and yield products of relatively high tenacity.

The high viscosity cellulose acetates or other cellulose esters may be produced by any suitable methods and particularly methods involving a minimum of degradation of the cellulose molecule. In this connection I particularly refer to the process of my U. S. Patent No. 1,708,787, in which esterification is effected in

presence of large bulk of solvent for the ester produced and particularly a weight of solvent exceeding 6 or 8 times that of the cellulose undergoing esterification.

The high viscosity filaments, yarns, threads or the like may be produced by wet or dry-spinning processes. Suitable wet spinning processes are, for example, those described in U. S. applications S. Nos. 402,785 filed October 26th, 1929, 418,414 filed January 3rd, 1930, 437,423 filed March 20th, 1930, 469,622 filed July 21st, 1930 and 601,043 filed March 24th, 1932. When during the spinning operation a considerable degree of stretch is applied to the materials, the process is included in my co-pending U. S. application S. No. 655,775 filed February 8, 1933. Dry spinning of the high viscosity cellulose esters may be effected, for example, by the processes and apparatus of U. S. Patents Nos. 1,601,125, 1,731,317, 1,541,104, 1,814,468 and 1,934,618.

The saponification treatment may be carried out by means of any suitable basic reagent. The most important for this purpose are caustic soda and caustic potash. When using caustic soda or caustic potash in aqueous solution or in mixed aqueous-alcoholic solution it is advisable, particularly when the concentration of the caustic alkali is relatively high, for example over 1%, to include in the saponifying medium a buffer salt, for example sodium chloride, sodium acetate, or sodium salts of other fatty acids, including the soaps or sodium salts of higher fatty acids, or other substance adapted to repress any destructive action which the caustic alkali may have upon the cellulose material under treatment. Thus, it is highly advantageous to have present in the saponifying medium sodium chloride in a high concentration, for example in a concentration of 20%–25% or more depending upon the solubility of the sodium chloride at the temperature of the saponification treatment. Sodium acetate may be dissolved in similar high concentrations. In fact it is of great advantage to use as a buffer salt in the saponifying medium the salt which is produced by the action of the saponifying agent, for instance caustic soda, upon the cellulose ester, for instance cellulose acetate, since such a salt is always present in the spent saponifying liquor, and its use as a buffer salt considerably facilitates regeneration of the spent liquor. The concentration of the caustic alkali in the aqueous or aqueous-alcoholic medium may be adjusted in accordance with the required degree of saponification, the temperature used in the saponification and the time available for treatment. I have obtained very good results by employing as saponifying medium a 4–5 or even 5½–6% solution of caustic soda in a 25% aqueous solution of sodium chloride or sodium acetate at temperatures ranging from 75–90° C., the time of treatment being of the order of 1 minute, this time being very suitable for treatment of travelling filaments, threads or yarns in a bath at a speed of about 40 metres per minute. Again good results are obtainable by employing concentrations of the order of 10–12% caustic soda or caustic potash together with about 18% of sodium chloride or as much sodium chloride as will dissolve in the caustic alkali or corresponding concentrations or even higher concentrations of sodium or potassium acetate at temperatures ranging from 75–90° C., the time of treatment being correspondingly shorter, for example of the order of 20 seconds. This treatment may be applied with filaments, threads or yarns travelling in a bath at a speed of the order of 100 metres per minute. However, the invention is not limited to these specific concentrations, and the caustic soda may be used in lower concentrations preferably at higher temperatures or in higher concentrations preferably at lower temperatures.

The application in a bath treatment of relatively high concentrations of caustic alkali, i. e. concentrations of about 2% or over, ranging upwards to 10–12 or even 15% or more, particularly when combined with the use of high concentrations of buffer substances, for instance sodium or potassium chloride or acetate or soaps, for example concentrations of buffer substances of the order of 10%, and particularly 15–25%, or to saturation, at high temperatures, and particularly temperatures above 65° C. up to the boiling point, for example the temperature range mentioned above of 75–90° C. for relatively short periods, such as periods ranging from 10 seconds to 1 minute, constitutes an entirely new saponification process, and is applicable not only to high viscosity filaments, threads, yarns and other products with which the present invention is particularly concerned, but also to materials containing esters of low, ordinary or any other viscosity, for example ordinary dry-spun cellulose acetate yarn, with highly satisfactory results. As with the high viscosity yarn a bath saponification under these conditions, contrary to all expectation, may result not only in maintenance of the initial tenacity of the yarn or other material, but in a substantial increase in the tenacity. The invention therefore includes the application of these saponification conditions in a bath treatment whatever be the character of the textile material under treatment. Thus, the cellulose ester contained in the textile material may be of any viscosity, for example relatively low viscosities of 6–10 or ordinary viscosities of 10–20 or 30 or high viscosities of 40 or 50–100 or 200 or more are measured by comparing the viscosity of a 6% solution of the cellulose acetate in acetone at a temperature of 25° C. with that of glycerine at the same temperature taken as a standard of 100. Further, the yarn or other material may be stretched or unstretched. In this special process, instead of using the above concentrations of caustic alkali solutions, other alkaline substances, for instance sodium silicate, trisodium phosphate, may be used in concentrations giving similar degrees of alkalinity.

In addition to including saponification by caustic alkali in aqueous or aqueous-alcoholic media the invention further includes saponification in a purely alcoholic medium. As is known in such a process the caustic soda may be present in the alcoholic medium, for example in a medium of methyl or ethyl alcohol, in a proportion less than that theoretically required to produce the required degree of saponification. Thus, in order to produce substantially complete saponification the caustic soda may be present, for example, in a proportion ranging from about 3–35% or more of that theoretically necessary to eliminate all the ester groups. The concentration of the caustic alkali in the alcoholic medium may vary very considerably, for example from the very low concentration of under .05% to 5% or more. The saponification in a purely alcoholic medium may be effected at atmospheric temperature or at any convenient higher temperature. In this method of carrying out the saponification it is, however, of great advantage to effect the saponification at relatively low temperatures and to allow the sa-

ponifying medium to act for a considerable time so that this process lends itself more particularly to batch processes in which, for example, the yarns, threads or the like are treated in the form of hanks or cakes. Similarly instead of employing methyl alcohol or ethyl alcohol as the medium in which to dissolve the saponifying agent other alcoholic or even phenolic media may be employed, for example monohydric alcohols higher in the series than ethyl alcohol, or di- or polyhydric alcohols, for example the glycols, glycerine or the like. With the higher monohydric alcohols and still more with the di- and polyhydric alcohols the best results are obtained at temperatures exceeding atmospheric, for example temperatures of the order of 50–80 or even 90° C. Higher temperatures do not in general lead to the best results according to the present invention. The term "alcoholic medium" is to be understood to include the use as medium of certain cyclic alcohols. As already indicated, phenolic media may be used, but it is desirable to use the phenols in very low concentration in aqueous solution and to employ relatively low temperatures.

While in the above description caustic soda and caustic potash have alone been referred to as the saponifying agents, the invention is not limited to these agents, but includes quite broadly the use of alkaline saponifying agents. Other suitable agents include sodium silicate, trisodium phosphate and ammonia. Such reagents may be applied in aqueous, alcoholic or aqueous-alcoholic media. Ammonia or volatile organic amines may be used in the vapour state, particularly when mixed with steam or water vapour to effect the saponification.

The saponifying mixture may be applied to the threads by any suitable method, for example by bath treatments, padding methods particularly followed by a batching process during which the saponifying mixture has time to effect the requisite degree of saponification, spraying methods followed by batching, gaseous or vaporous application of the saponifying agent as previously referred to, or the methods described in U. S. Patents Nos. 1,884,622 and 1,884,623 in which the saponifying mixture is applied to the materials and immediately afterwards the materials are heated, for example by passage over heated drums or like devices to effect a quick saponification. In methods involving batching or subsequent heating to effect saponification, the concentration in which the caustic alkali or other saponifying agent is applied is relatively immaterial provided that there is enough of the medium to enable uniform application of the saponifying agent.

The extent of the saponification may vary considerably depending upon the object in view. An affinity for the cottom colours is acquired with a comparatively small loss in weight, such as 5–10 or 20%, though such low degrees of saponification are in general only effective in conferring affinity for the cotton colours when the saponification is mainly superficial. If, as in the case of using an alcoholic medium for the saponifying agent, the saponification is relatively uniform, a somewhat higher degree of saponification, for example up to 50% or more of the ester groups, is generally necessary to confer affinity for the cotton colours. The invention particularly contemplates complete or substantially complete elimination of the ester groups, since, as already indicated, the main object of the invention is to produce filaments, yarns, threads or the like which are of high tenacity and are of the regenerated cellulose type.

The best method of carrying the present invention into effect is to use a bath saponifying treatment and to treat a warp of yarns in one operation. It is found that great advantages accrue from treating the travelling threads, particularly when travelling in the form of a warp or sheet of threads. Thus, the threads from a creel of bobbins may be carried through a reed, round one or more rollers, for example nip rollers or feed rollers, into the saponifying bath, preferably through a further reed, traverse an appropriate length of bath, the length depending upon the desired degree of saponification, the speed of travel, the temperature of the bath and the concentration and character of the saponifying agent, then through a further reed, round a feed roller, out of the bath and finally to a washing device, and preferably to a drying and reeling or beaming device. It is desirable in order to utilize the full length of the saponifying bath to wet out the materials thoroughly either on entering the saponifying bath or before entering. For this purpose the yarns may be carried into a short wetting out bath in which they are carried through a pair of nip rollers, one at least of which dips into a wetting out liquid. The nip rollers are preferably so arranged that one is in advance of the other so that their rotation causes a trough of liquid to collect in the nip of the rollers. By this means very efficient wetting out may be obtained. The rollers may be metal rollers or may be covered with fabric or with rubber or similar materials to assist wetting out. The wetting medium may be water, or may be an aqueous solution of a wetting agent, as for example the soaps, for example sodium potassium or ammonium oleates, palmitates or stearates, sulphonated soaps, for example Turkey red oil or Monopol soap, the naphthalene sulphonic acid wetting agents, and particularly the propyl and butyl naphthalene sulphonic acids or their salts, or the ω-amino-alkylamides of oleic, stearic, palmitic or other fatty acids. A small proportion of the saponifying agent itself may be included in the wetting out bath.

Instead of applying a continuous treatment as described above, batch treatments, for example with the yarn in the form of hanks or cakes may be applied. Such batch processes are particularly useful where it is desired to extend the saponification treatment over a considerable period of time, as for example from 10 minutes to many hours. Thus, for instance, the high viscosity yarn may be built up into cakes in a centrifugal spinning box. These boxes may themselves be used for the saponifying treatment in which case they should be made of or lined with a material reistant to alkali, as for example copper, or the cake may be removed from the centrifugal spinning box, and while being supported on the outside or inside or both be subjected to the saponifying treatment. Thus, for example, the cake removed from the box may be supported from the interior by means of a swift which may be made expansible for insertion in the cake. Thus, for instance, the swift may comprise a small end plate, the periphery of which is perforated with holes for the insertion of a number of wires which after insertion in the interior of the cake may be expanded umbrella-fashion by means of a conical piece sliding on a shaft fitted to the end plate. Alternatively the centrifugal spinning box before winding of the yarn therein may be provided with a removable copper gauze lining in which the cake is built up and in which it can be removed from the spinning box. The cake with its supporting gauze

outside may if necessary be fitted with top and bottom plates to enable saponifying liquor to be circulated through the cake. Such a gauze may be used whether or not the cake is supported from the interior, as for example by means of the expansible swift referred to. Another means of supporting the cake from the interior consists in constructing a number of small segmental gauzes to fit inside the cake, for example at opposite ends of two perpendicular diameters, the gauze being attached to each other in pairs by a spring distance piece. Such a device is of value for supporting the interior of the cake whether or not the cake is removed from the spinning box for saponification. The saponifying liquor may be circulated through the cake, as for example by means of a pump, for the requisite time. In a similar manner the stretched yarn may be wound upon perforated bobbins or on a perforated spool tube and the liquor circulated through the bobbin or other package. In all such packages, whether of the bobbin, spool or cake type, it is sometimes advantageous to employ a cross wind with a quick traverse so as to obtain a relatively porous package.

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

Example 1

Yarn dry-spun from cellulose acetate which has a viscosity of 55 is wound on bobbins from which a creel is built up. The yarns are led from the creel through a reed so as to constitute a warp, over the top roller, through the nip and under the bottom roller of a pair of nip rollers, the lower one of which is in advance of the upper one in the direction of travel of the yarn and which dips into water acting as a wetting out liquid. Thence the warp of yarns is carried out of the wetting out bath, over a further roller, down into the saponifying liquor, through a reed and under a roller, thence the whole length of the saponifying bath which may be of the order of 90 feet long, through a further reed, close to a feed roller and out of the saponifying bath to suitable washing, drying and winding devices. The feed roller at the exit end of the saponifying bath is immersed less than half its diameter in the saponifying liquor. The saponifying bath consists of a 4% solution of caustic soda in a 25% aqueous solution of sodium chloride and is maintained at 85° C., and is circulated from end to end of the bath. The speed of travel of the filaments is 40 metres per minute. The threads, after treatment, have an increased tenacity and an increased extension.

Example 2

The saponifying treatment is carried out as in Example 1 with the exception that the saponifying liquor consists of a 5% solution of caustic soda in a 25% aqueous solution of sodium chloride and is maintained at 75° C. and the yarn is wet-spun from a cellulose acetate having a viscosity of 162 without applying substantial stretch.

Example 3

The saponifying treatment is carried out as in Example 1 with the exception that the sodium chloride is replaced by sodium acetate.

Example 4

The saponifying treatment is carried out as in Example 1 with the exception that the saponifying bath consists of a 5.5% solution of caustic soda in a 25% aqueous solution of sodium chloride and is maintained at 75–90° C. and the yarn is made from a cellulose acetate having a viscosity of 120–180.

Example 5

A warp of yarns made from a cellulose acetate having a viscosity of 73 and constituted as described in Example 1 is carried through a 2 or 3 bowl padding mangle, wherein it is impregnated with a 10% aqueous solution of caustic soda. The nip of the mangle is adjusted so that the yarn retains about its own weight of liquor. The warp is carried directly from the padding mangle to a series of hollow steam heated rollers which serve to effect the saponification as described in U. S. Patents Nos. 1,884,622 and 1,884,623.

Example 6

Yarn dry-spun from a cellulose acetate having a viscosity of 146 is put up into hank or cake form and is then treated with any of the following baths under the conditions stated:—

(*a*) 0.25% solution of caustic alkali in methyl alcohol in a bath volume of 20:1 for 16 hours at 25° C.

(*b*) 0.5% solution of caustic alkali in methyl alcohol in a bath volume of 20:1 for 16 hours at 25° C.

(*c*) 0.5% solution of caustic alkali in methyl or ethyl alcohol in a bath volume of 40:1 for 4 hours at 30° C.

(*d*) 0.25% solution of caustic soda in ethyl alcohol in a bath volume of 20:1 for 24 hours at 26° C.

In all the above examples the tenacity and the extension of the yarn are increased and the material acquires an affinity for cotton colours. In Examples 1–4 the saponification is substantially complete. In Example 5 the saponification corresponds closely with the amount of caustic soda with which the yarn is impregnated, and in Example 6 the degree of saponification varies with the concentration of caustic soda and the time and temperature of treatment.

In a similar manner the invention may be applied to the production of filaments, threads, yarns and other materials from other saponifiable cellulose esters, for instance cellulose formate, cellulose propionate or cellulose butyrate. The cellulose esters may be present in the threads, yarns or other materials either alone or mixed with each other or mixed with other materials not deleteriously affected by the treatment, for instance natural or artificial cellulosic materials. The cellulose esters present in the materials may be either simple cellulose esters as in the case of cellulose acetate, or mixed cellulose esters, for instance cellulose nitroacetate or mixed ether-esters of cellulose, for example oxyethyl cellulose acetate or ethyl cellulose acetate.

The materials in the form of filaments, threads, fabrics and the like may in addition to the above treatments be subjected to a treatment with shrinking agents to improve their extension or for the production of special effects, and in this connection reference is made broadly to the processes described in U. S. applications S. Nos. 611,240 filed May 13th, 1932, 607,667 filed April 26th, 1932, and U. S. Patent No. 2,020,303. Uniform shrinkage for the purpose of increasing extension is particularly advantageous in the case of yarns which have relatively low extensions. The shrinking treatment may be applied after saponification, but is preferably applied be-

fore. When applied before saponification the agents specified in the specifications referred to above may be used with advantage. When the shrinking is applied subsequent to saponification the nature of the reagent will depend upon the degree of saponification. Thus, if a relatively small degree has been applied, such as up to 10 or 20% loss in weight, swelling agents for the cellulose derivative may still be effective in producing the desired shrinkage. When a high degree of saponification or substantially complete saponification has been carried out swelling agents for cellulose should be used to effect the shrinkage.

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

1. Process for the production of filaments, threads, yarns and the like having a relatively high tenacity and an affinity for cotton colors, which comprises subjecting to saponification dry-spun filaments, threads, yarns or the like of acetone-soluble cellulose acetates having a viscosity exceeding 30 as measured by the rate of flow of a 6% acetone solution against a standard of glycerine as 100.

2. Process for the production of filaments, threads, yarns and the like having a relatively high tenacity and an affinity for cotton colors, which comprises subjecting filaments, threads, yarns or the like of acetone-soluble cellulose acetates having a viscosity exceeding 30 as measured by the rate of flow of a 6% acetone solution against a standard of glycerine as 100, to saponification by treating them with relatively high concentrations of alkaline saponifying agents at temperatures not substantially below 60° C. for not more than two minutes.

3. Process for the production of filaments, threads, yarns and the like having a relatively high tenacity and an affinity for cotton colors, which comprises subjecting filaments, threads, yarns or the like of acetone-soluble cellulose acetates having a viscosity exceeding 30 as measured by the rate of flow of a 6% acetone solution against a standard of glycerine as 100, to saponification by treatment with relatively high concentrations of an alkaline saponifying agent at a temperature above 60° C. in the presence of a buffer salt for not more than two minutes.

4. Process for the production of filaments, threads, yarns and the like having a relatively high tenacity and an affinity for cotton colors, which comprises subjecting filaments, threads, yarns or the like of acetone-soluble cellulose acetates having a viscosity exceeding 30 as measured by the rate of flow of a 6% acetone solution against a standard of glycerine as 100, to saponification while they are traveling through a bath of the saponifying agent.

HENRY DREYFUS.

CERTIFICATE OF CORRECTION.

Patent No. 2,053,767. September 8, 1936

HENRY DREYFUS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 15, for the serial number "655,775" read 655,773, and second column, line 41, for "are" read as; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of November, A. D. 1936.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.