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MANUFACTURE OR TREATMENT OF ARTIFICIAL MATERIALS

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This invention relates to the manufacture of artificial filaments, threads, fibres, yarns, ribbons and like materials by processes involving the saponification of materials made of or containing cellulose acetate or other organic esters of cellulose.

The agents generally used in the saponification of such materials are caustic soda or other alkaline inorganic compounds. The use of such saponifying agents, however, is attended by certain disadvantages and much research has been carried out in the attempt to find more suitable agents. I have now found that a much more advantageous means of saponifying materials comprising cellulose acetate or other organic esters of cellulose is to employ liquid saponifying agents containing mono-methylamine or other organic bases, particularly aliphatic bases such as the lower aliphatic amines. Saponification by means of such agents can be effected without damaging the materials or decreasing their tensile strength, in fact the treatment may even increase the tenacity. Moreover, the extensibility of the materials may also be increased as a result of the treatment. Materials of particularly valuable textile or serimetric properties may be obtained by applying the treatment to materials of initially high tenacity, for example yarns of cellulose acetate of high viscosity or yarns which at some stage in their manufacture have been subjected to a relatively high stretch in the presence of softening agents in the fully formed condition or in the course of a wet spinning process. Moreover, saponification extending to a considerable distance below the surface or even throughout the whole section of the material, can readily be obtained. Thus, cellulose acetate materials can be rendered insoluble in acetone by a saponification involving a relatively small loss in weight—much smaller in fact than is necessary when saponification is effected by the ordinary processes. These advantages are particularly evident when mono-methylamine is employed. The advantage of this base over other amines which from their constitution might be expected to be equally satisfactory is most remarkable.

The materials treated may be in the form of filaments, threads, yarns, ribbons or the like or of fabrics containing such threads and the like. The organic ester of cellulose employed may be of normal or low viscosity, but particularly where high tensile strength in the product is desired, it is preferable to employ esters of high viscosity, for example in the case of cellulose acetate the viscosity may be of the order of 30 to 50, 100, 200

or even higher, these figures being obtained by comparison of a 6% solution of the ester in acetone at 25° C. with glycerine at the same temperature taken as a standard of 100. Such esters of high viscosity may readily be made by methods in which degradation of the cellulose molecule is substantially avoided during acidylation, for example the methods of U. S. Patent No. 1,708,787. On the other hand, the viscosity of the cellulose acetate employed may be of the order of 10–20 or even lower, or between 20 and 30, measured on the scale referred to above.

Any suitable dry or wet spinning method may be employed in producing the filaments and the like. Special mention may be made of the methods described in U. S. applications S. Nos. 402,785 filed October 26, 1929, 418,414 filed January 3, 1930, 437,423 filed March 20, 1930, 469,622 filed July 21, 1930, and 601,043 filed March 24, 1932, wherein the materials are produced by wet spinning methods in the course of which they are stretched to a considerable extent. The materials may also, particularly when spun by a dry spinning method, be subjected to a stretching treatment prior to saponification. In this connection mention may be made of the methods described in U. S. applications S. Nos. 378,684 filed July 16, 1929, and 602,844 filed April 2, 1932, wherein the materials are subjected to a relatively high degree of stretch in the presence of softening agents. Such treatments are particularly valuable where high tensile strength in the products is required, and for this purpose it is of advantage to stretch the materials to a considerable extent, for example to 200, 300 or even more than 500% of their original length. The stretching may be effected in a single stage or in several stages, with or without a rest interval between the stages, wherein the materials are allowed to shrink as described in U. S. application S. No. 573,424 filed November 6, 1931. If desired after stretching and before saponification the materials may be treated with shrinking agents, as described, for example, in U. S. application S. No. 611,240 filed May 13, 1932. Materials which have been stretched considerably whether as an after-treatment or in the course of their production by a wet spinning process may have a high initial tenacity, e. g. 2.5, 3 or 3.5 grammes per denier or even more.

As indicated above, the saponifying agent preferably comprises mono-methylamine, with which particularly advantageous results have been obtained. The invention is not limited to the employment of this base however. Thus bases con-

taining more than one carbon atom can be usefully employed, particularly bases of about the same order of alkalinity as methylamine. Among other lower aliphatic mono-amines mention may be made of dimethylamine, trimethylamine, ethylamine, diethylamine, propylamine, amylamine and alkylamine. Of these the stronger bases are to be preferred, and even very strong bases such for example as tetramethyl ammonium hydroxide may be employed with care. The base may contain hydroxy groups, as for example in the ethanolamines, and particularly triethanolamines. Preferably the bases are non-aromatic but heterocyclic bases such as piperidine are useful but not to the same extent as the lower aliphatic amines. Cyclic bodies such as cyclohexylamine are also included.

The base is preferably applied in aqueous media but other media containing available hydroxyl may be employed, e. g. aqueous alcoholic or even alcoholic media. The process may be effected at atmospheric temperatures or even at temperatures below atmospheric, but generally it is of advantage to employ somewhat higher temperatures. Thus when substantially complete saponification is to be effected I prefer to work at temperatures of 50-60° C. with methylamine and with the weaker bases even higher temperatures are in general preferred. For example, in the case of triethanolamine, temperatures in the neighbourhood of 100° C. have been successfully employed. In general, the upper limit of the temperature range is determined by the difficulty of avoiding undue loss of the base by evaporation. When, however, it is intended only partially to saponify the materials, and particularly when the object is to effect a deep seated change in the properties of the materials which yet involves only a small loss in weight, it appears preferable to work at somewhat lower temperatures unless employing the base in low concentration. Thus when it is desired to render cellulose acetate insoluble in acetone by a saponification involving a relatively small loss in weight, temperatures of the order of 30° C. are recommended, working with 20% aqueous methylamine.

This is a very advantageous concentration to work with whether the saponification contemplated is partial or complete. Lower concentrations, e. g. concentrations of 15%, 10%, 5% or even less can be employed, but saponification is then in general slower, and in some cases less uniform, so that concentrations much below 15% are not recommended. Higher concentrations may be used, particularly in the case of the weaker bases. Certain organic bases, however, including methylamine, have solvent or swelling properties for organic esters of cellulose, so that as temperature and concentration increase they become capable of dissolving the materials, reducing them to a jelly-like form, or at least reducing their tenacity to a very considerable extent. With methylamine, for instance, if the concentration be raised much beyond 20 or 25% there may be danger of damaging the materials, specially at temperatures near the boiling point of the solution. This possibility should be borne in mind. Again, with high concentrations and high temperatures the difficulty arises of maintaining the concentration of the bath. Rapid loss of the organic base from the saponifying medium apart from other disadvantages may affect the uniformity of the product. Evaporative losses may be greatly reduced by covering the surface of the saponifying medium with a layer of

an inert substance liquid at the desired temperature but of high boiling point, e. g. an unsaponifiable oil, as described in U. S. application S. No. 690,122 filed September 19, 1933. It is preferred, therefore, in the case of methylamine to work with concentrations of the order of 20%, and whatever the nature of the base, conditions which result in incipient solution of the materials are to be avoided. In general, the effect of increasing either the concentration or the temperature starting from a given set of conditions is to increase the speed of saponification and up to a point to increase the depth to which saponification extends. It appears, however, that a point may be reached, beyond which further increase in speed involves a less deep seated saponification. Thus it is preferred to work at concentrations and temperatures at which the base is capable of swelling the cellulose ester without incipient solution occurring.

The temperature and concentration should preferably be such, subject to the considerations set out above, that the desired degree of saponification can be effected in a treatment lasting a relatively short time, e. g. 2-3 minutes or even less. On the other hand, more prolonged treatments are not excluded and may even be necessary in the case of the weaker bases. Rapid saponification, apart from other advantages, enables the treatment to be carried out continuously and under conditions in which uniformity as between a number of yarns or the like to be subjected to the same treatment can more easily be ensured than if a batch treatment be adopted. Thus, even when saponification takes 4 or 5 minutes, it may be of advantage to employ a continuous (bath) treatment. Treatments lasting considerably longer than this, for instance from 10 or 15 minutes up to several hours are best avoided, but if for particular reasons they are employed, a batch method should be used.

Preferably, saponification is effected by means of a bath treatment, and where the process is sufficiently rapid, it is of advantage to pass the materials continuously through the bath in the course of their passage between two points. This is the preferred method, whether the materials treated are in fabric form or in the form of threads, ribbons or the like. Threads and like materials are most advantageously treated in warp formation. Thus, for example, a number of threads may be drawn off from a creel, passed through a reed, and then in the form of a warp or sheet of threads over a roller, which may conveniently dip into a bath containing the saponifying medium, through the bath, through a further reed and over a further roller, from which they may be wound in suitable form, preferably after undergoing washing and drying treatments and/or any other treatment which it is desired to effect after saponification. By treating the materials in warp formation it is possible to ensure that each thread is subjected to identically the same treatment as its neighbours. To ensure uniformity of tension during the process all rollers, guides or like devices adapted to control or modify the speed of travel of the materials should extend right across the warp or sheet of threads. The speed at which the materials pass through the bath should preferably be such that the desired degree of saponification is effected by the time the materials leave the bath. During their passage through the bath the materials may be under applied tension or simply under the tension introduced by shrinkage of the materials,

or again means may be taken to reduce the tension, for example by causing the speed of travel of the materials to diminish along their path. 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, palmittates 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.

As indicated above, batch methods may be employed and may even in some circumstances be preferable to continuous methods such as that described above. Thus, for example, the materials in hank form may be suspended from rods which are caused to traverse the length of the bath and at the same time to rotate so as to expose each portion of the yarn to the same depth in the bath for the same period. Again, the materials may be treated in the form of bobbins, cheeses or like packages, or in the form of cakes from centrifugal spinning boxes.

Although the above methods are to be preferred, other methods of effecting saponification according to the invention may be employed. Thus, for example, the saponifying medium may be applied to the materials, for example during a bath treatment or by padding methods under such conditions that saponification, or the whole of the saponification to be effected, does not occur during the application, and the materials may be passed continuously from the point of application of the saponifying agent through a heated zone or in contact with a heated surface so as to bring about or complete the saponification required. Processes in which this method is applied in connection with mineral saponifying agents are described in U. S. Patents Nos. 1,884,622 and 1,884,623.

The extent of the saponification may vary considerably depending upon the object in view. An affinity for the cotton colours may be acquired by the process of the invention with a very small loss in weight, such as 10% or even less, which is remarkable since such low degrees of saponification are in general only effective in conferring affinity for the cotton colours when the saponification is mainly superficial, which does not appear to be the case here. The invention is not limited to such small degrees of saponification, or indeed to any particular degree. Thus for example, the loss of weight may be from 5-8%, or even less than 5%, or may be of the order 20-50% or more up to complete saponification. Again, the range between 14% loss of weight and

18% has been found a useful one, and particularly, in the case of saponifying cellulose acetate by means of mono-methylamine the range from 8-12% affords very valuable products.

The following example illustrates the invention, which is not however to be regarded as limited to the method therein set forth:

Example

Cellulose acetate yarns which after their formation have been softened and stretched to a considerable extent, are led continuously from a 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 a bath containing a 20% solution of methylamine in water at 60° C. The materials then pass through the saponifying bath, through a further reed close to a feed roller, and out of the saponifying bath to suitable washing, drying and winding devices. All the rollers referred to extend across the whole breadth of the warp. The surface of the bath between the two rollers is covered with a layer of non-saponifiable oil. The speed of travel of the materials and length of bath are such that the yarn takes between 2½ and 3 minutes to pass through the bath. A completely saponified yarn of high tenacity and improved extensibility is obtained.

In a similar manner the invention may be applied to the production of filaments, threads, yarns and other materials from saponifiable cellulose esters other than cellulose acetate, for instance cellulose formate, cellulose propionate or cellulose butyrate. 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 nitro-acetate or mixed ether-esters of cellulose, for example oxyethyl cellulose acetate or ethyl cellulose acetate. 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.

Certain of the advantages obtainable by the process of the invention have been indicated above. Reference has been made to the very desirable tensile or serimetric properties which the products of the invention may show. In addition to exhibiting a high tensile strength, the materials may have a considerably enhanced extensibility, particularly when in some previous stage of manufacture they have been subjected to a relatively high degree of stretch. Moreover, it has been found possible as a result of the process of the invention to obtain materials which not only have a high tenacity and extensibility but have the remarkable property of retaining their elasticity until subjected to a relatively heavy stress, which may be avoided in many processing operations, so that it is possible to manufacture and finish the material without ever having stretched it beyond the elastic limit which it possesses after saponification. By way of example it may be mentioned that by treating according to the invention a cellulose acetate silk which has been stretched to 200 times its original length a product may be obtained having a tenacity of over 2.5-3 or more grammes per denier, an extensibility of 12-15% or more and an elastic limit which is not exceeded until a stress greater than 0.2 to 0.5 grammes per denier is applied. In the ordinary

processing operations to which cellulose acetate yarn is subjected, it is quite easy to avoid imposing stresses greater than this so that the elasticity which the yarn has after saponification may be retained throughout the whole of its subsequent manufacture. The process of the invention is particularly useful in the production of yarns intended to be twisted in the manufacture of crêpe materials. The process of the invention, besides improving the serimetric properties of the material may have other valuable effects. Thus by partial saponification an affinity for cotton dyes may be imparted to the material without loss of affinity for cellulose ester dyes, for example dyes of the dispersed insoluble type. Again, the materials may be rendered insoluble in acetone or even in aqueous acetone by a saponification involving a relatively small loss in weight. The process moreover raises the safe ironing point of the materials and may at the same time lower the scorching point, so that in ironing and calendering operations warning that the iron or calender is too hot may be received before serious damage is done to the material.

If desired, the materials obtained as a result of the saponification process may be treated so as to effect further shrinkage. Special shrinking agents may if desired be used to produce this effect, and in this connection reference is made broadly to the processes described in U. S. application S. Nos. 607,667 filed April 26, 1932, 609,255 filed May 4, 1932 and 611,240 filed May 13, 1932. Uniform shrinkage for the purpose of increasing extension is most useful when applied to yarns which have undergone a relatively high degree of stretch prior to saponification. The shrinking treatment is preferably applied after saponification and to materials in which the degree of saponification is relatively small, for example up to 10 or even 20% loss in weight. When a high degree of saponification or substantially complete saponification has been carried out, swelling agents for the cellulose may be employed.

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

1. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity comprising subjecting materials comprising filaments, threads, ribbons and the like of cellulose acetate or other organic esters of cellulose to saponification by means of liquid media containing lower aliphatic mono-amines.

2. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity comprising subjecting materials comprising filaments, threads, ribbons and the like of cellulose acetate to saponification by means of an aqueous solution containing mono-methylamine.

3. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity comprising subjecting materials comprising filaments, threads, ribbons and the like of organic esters of cellulose to saponification by means of an aqueous solution of mono-methylamine in such concentration and at such temperature as to exert a swelling action on the

organic esters of cellulose without effecting incipient solution.

4. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity, which comprises subjecting materials comprising filaments, threads, ribbons and the like of organic esters of cellulose to saponification by means of an aqueous liquid medium containing a non-aromatic nitrogenous organic base which contains less than seven carbon atoms.

5. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity, which comprises subjecting materials comprising filaments, threads, ribbons and the like of organic esters of cellulose to saponification by means of an aqueous liquid medium which contains a nitrogenous organic base of dissociation constant at least as high as that of tri-methylamine.

6. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity, which comprises subjecting materials comprising filaments, threads, ribbons and the like of organic esters of cellulose to saponification by means of an aqueous liquid medium which contains a water-soluble nitrogenous base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom.

7. Process for the manufacture of improved artificial materials, of improved extensibility and unimpaired tenacity, comprising subjecting materials comprising filaments, threads, ribbons and the like of cellulose acetate to saponification by means of an aqueous solution containing below 30% of mono-methylamine.

8. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity, comprising subjecting materials comprising filaments, threads, ribbons and the like of cellulose acetate to saponification, at a temperature not substantially in excess of 90° C., by means of an aqueous solution containing below 30% of mono-methylamine.

9. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity, which comprises subjecting filaments, threads, ribbons and like materials having a basis of organic ester of cellulose and a tenacity of at least 2.5 grams per denier to saponification by means of an aqueous liquid medium which contains a water-soluble nitrogenous base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom.

10. Process for the manufacture of improved artificial materials of improved extensibility and unimpaired tenacity, which comprises subjecting filaments, threads, ribbons and like materials having a basis of cellulose acetate and a tenacity of at least 2.5 grams per denier to saponification by means of an aqueous solution containing mono-methylamine.

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