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TREATMENT OF MATERIALS HAVING A BASIS OF ESTERS

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This invention relates to the saponification of organic esters of cellulose, particularly in the form of filaments, threads, ribbons, fabrics, films and like materials and is a continuation in part of U. S. application S. No. 11,080 filed 14th March, 1935.

Applications S. Nos. 709,335 filed 1st February, 1934, and 752,376 filed 9th November, 1934, describe processes wherein organic esters of cellulose are saponified by organic nitrogenous bases. Many of said bases have a pronounced swelling effect on the cellulose ester. We have found that it is of advantage to employ such bases under such conditions that they exert a swelling effect on the cellulose ester but in the presence of a substance which diminishes the swelling action. The presence of substances adapted to diminish the swelling of the ester is of particular advantage with a view to obtaining products of high tenacity and avoiding "fusion" or coalescence of the filaments of multi-filament yarn which might otherwise occur when using relatively high concentrations of the base.

According, therefore, to the present invention, in the saponification of organic esters of cellulose, and particularly of filaments, threads, yarns, fabrics and like materials having a basis of such esters, the saponification is effected by means of a nitrogenous organic base, having a swelling action on the cellulose ester, in the presence of a substance which is not a saponifying agent for the cellulose ester and which diminishes the swelling of organic esters of cellulose. Among the most useful of agents adapted to diminish the swelling of organic esters of cellulose are water soluble salts of organic acids, and polybasic inorganic acids, for example the sodium, potassium and ammonium salts of phosphoric acid, boric acid, acetic acid, tartaric acid, citric acid, lactic acid, sulphuric acid, thiosulphuric acid and sulphurous acid.

Other suitable swelling repressing agents include the barium, strontium, calcium, magnesium and zinc salts of the organic acids referred to above, the sodium, potassium and ammonium oxalates, sodium and ammonium chloride, sodium, potassium and ammonium formate and the sugars, for example, cane sugar, glucose, fructose, mannitol and sorbitol.

The sodium and potassium salts of strong inorganic acids, such for example as hydrobromic, hydriodic, nitric, perchloric and thiocyanic acid, have a tendency to swell the cellulose derivative. This tendency is even more evident in the corresponding strontium, calcium and barium salts. Such salts are not therefore in general suitable as swelling repressing agents. Sodium chloride can however be used and the ammonium salts of all these acids except thiocyanic can also be used. A simple experiment will of course indicate the suitability or unsuitability of any particular substance.

Among the nitrogenous organic bases which may be used mention may be made of methylamine, ethylamine, propylamine butylamine, isopropylamine, isobutylamine, di-isobutylamine, amylamine, di-isoamylamine, the ethanolamines, particularly mono-ethanolamine, diamines of relatively low molecular weight, for example ethylene diamine, propylene diamine and trimethylene diamine, heterocyclic bases, for example pyridine and piperazine and poly-methylene amines, for example cyclohexylamine. In general, water-soluble organic nitrogenous bases in which each carbon atom directly attached to the nitrogen atom is directly attached to three other carbon atoms are suitable. The base may for example be an aliphatic amine containing up to six carbon atoms or may be a diamine in which the two nitrogen atoms are separated by up to four carbon atoms. Bases which contain aromatic groups attached to the nitrogen through aliphatic groups are also suitable. For example, excellent results have been obtained with the benzylamines, particularly monobenzylamine. Such bases in common with the benzylamines are entirely new as saponifying agents for organic esters of cellulose. These two classes of base are of great utility even in the absence of swelling repressing agents.

The process of the invention enables saponification to be effected, even with high concentrations of organic base e. g. between 20 and 40% and at high temperatures for instance 60 to 90° C., not only without damage to the materials but so as to improve their serimetric properties. Thus, materials saponified by the process of the invention may have high tenacity, extensibility and elasticity. The use of high concentrations of organic bases at high temperatures enables saponification to be conducted more rapidly than would otherwise be possible. The invention is not however limited to the use of high concentrations of base or high temperatures. The presence of substances which diminish the swelling action of the bath is of advantage even at low or ordinary temperatures and with low concentrations of organic base.

The concentration and temperature of the saponifying medium will depend on the nature of

the materials treated and the rate at which saponification is to be effected. With methylamine for instance the concentration may range from below 5% to over 30% and the temperature from below 15° C. to above 90° C. Baths containing 15–20, 25 or 30% methylamine have been found useful at temperatures between 20 and 30° C. as well as at higher temperatures e. g. 40–50 or 60–70° or 80° C. Other bases of somewhat similar strength for instance ethylamine and benzylamine may be used at the same temperatures and concentrations. In general the stronger the base the lower the concentration and/or temperature required for a given speed of saponification. With ethylene diamine for example though concentrations below 5% and temperatures below 15° C. can be used saponification under these conditions is very slow and higher concentrations and temperatures e. g. 20 or 25 to 30 or 35% and 40–50 up to 95° C. or more are more generally useful.

The amount of swelling repressing agent used will depend on the strength and concentration of the base, the temperature of the bath and the nature of the materials treated and of the final products required. For example, in the saponification of cellulose acetate yarns, by means of baths containing 10–20% of methylamine or ethylamine at 25–65° C., concentrations of sodium acetate of 2–20% and particularly 5–15% have been found to enable a considerably higher tenacity to be obtained in the products than would otherwise result. Considerably higher concentrations have also been used e. g. 20–35% or even more. On the other hand a marked increase in tenacity has resulted from the presence even of 1% of sodium acetate. The more sensitive the materials and the higher the strength and concentration of base and temperature, the higher the concentration of swelling repressing agent required to give the maximum tenacity.

The saponification may be effected by any suitable means. Thus, for example, yarn and like materials may be treated in hank form in a vessel containing the saponifying medium and the sodium acetate or other salt which diminishes the swelling effect of the base, and allowed to remain therein until the desired saponification is effected. Again, the materials may be drawn continuously through the saponifying bath at such a rate that the desired saponification is effected by the time the materials leave the bath. It is of advantage when adopting this method to treat a number of threads in warp formation, that is in parallel alignment in the same plane. This method facilitates uniform saponification as between thread and thread.

The saponification, whether conducted as a continuous operation or as a bath process, may be conducted under pressure, as described in U. S. application S. No. 11,080 filed 14th March 1935. By this means higher concentrations of volatile bases and/or higher temperatures may be employed than would otherwise be practicable. When in a continuous process saponification is effected under pressure a convenient method is to pass the threads through a vessel partly filled with the saponifying medium, the threads entering and leaving the vessel through small holes above the level of the liquid. To facilitate threading up, the holes are preferably formed in members readily detachable from the apparatus. Thus in one form of apparatus there is at each end of the saponifying vessel an aperture over which, when the apparatus is in operation, is clamped a detachable perforated plate, the perforations being sufficiently large to take the threads without permitting an excessive loss of pressure. Guides or rollers may be provided in the vessel so that the greater part of the path of the materials lies below the level to which the saponifying liquid will rise. When working with this type of apparatus in its simplest form, the materials are threaded through the perforations in the one plate, passed under the guides, or rollers, which are conveniently situated near the bottom of the vessel, and through the perforations in the other plate. The plates are then clamped in position and the saponifying liquid is run into the vessel up to the required level. Heating coils or other suitable attemperating means are provided for use when the process is to be carried out at a temperature differing from atmospheric temperature. If the process is to be carried out at a temperature sufficiently high, it may be unnecessary to apply external pressure to the liquid, its own vapour pressure at that temperature being sufficient. In general, however, with a view to maintaining the composition of the saponifying medium constant, the required pressure may be obtained by supplying air or other suitable gas under pressure to the space above the liquid.

Saponification may be effected under little or no applied tension, so as to facilitate contraction of the materials during saponification. With this in view it is of advantage to provide intermediate rollers which are preferably positively driven at speeds which progressively decrease along the path of the materials. On the other hand, if the saponifying medium is such as to exert the necessary softening effect upon the materials, they may even be stretched during saponification. Whether the saponification is to be carried out so that the materials contract, or so that they are stretched, or so that no lengthening or contraction takes place, it is of advantage to provide a series of positively driven rollers along the path of the materials, since it is found that such an arrangement leads to great uniformity in the properties of the saponified materials along their length, and particularly uniformity in their tenacity, extension and dyeing properties.

Threading-up of the materials before admission of the saponifying liquid to the vessel may be avoided by adopting a slightly more elaborate apparatus in which the guides or rollers are attached to a frame so that they can be lifted above the surface of the liquid for threading up and depressed and fixed in position below the surface of the liquid when this has been accomplished.

As indicated above, saponification may be carried out as a batch process. Thus yarns in hank or other package form, or fabrics, may be suspended within a saponifying medium maintained under pressure in a closed vessel. The pressure may be obtained by any suitable means, for example by means of pumps or compressors or by means of compressed air. On the other hand, as in the continuous process, when a saponifying liquid at a sufficiently high temperature is employed, the vapour pressure of said liquid may be sufficient to provide the necessary pressure, or the pressure may be obtained by introducing a compressed gas into the space above the liquid.

The following example illustrates the invention:—

Example

Cellulose acetate yarn is completely saponified in hank form by treatment in an aqueous bath

containing 15–20% methylamine and 2–5% sodium acetate at 40–60° C. The tenacity of the yarn is considerably higher than if the sodium actate is omitted. The amount of sodium acetate may be increased up to 15 or even 20%. Instead of sodium acetate other salts of organic acids may be used for instance sodium lactate. Instead of methylamine ethylamine may be used.

Although the invention has been described with particular reference to the saponification of filaments, threads, ribbons, fabrics, films and like materials of cellulose actate, it is also applicable to the treatment of materials comprising other esters of cellulose, particluarly organic esters, i. e. esters containing acidyl groups, for example simple esters such as cellulose formate, propionate or butyrate, ether-esters, such as ethyl cellulose acetate and oxy-ethyl cellulose actate, and mixed esters, such as cellulose acetate propionate, cellulose acetate-propionate-butyrate and nitrocellulose acetate. The cellulose acetate or other base of which the materials to be saponified are made may be of high, medium, or low viscosity. For example in the case of cellulose acetate the viscosity may be above 30 to 50 or even 100 or more, measured by comparing the viscosity of a 6% solution of the cellulose acetate in acetone at 25° C. with that of glycerine at the same temperature, taken as 100; or may be considerably lower, for example 10 or 15 to 20, on the same scale.

With a view to obtaining materials of high tenacity, it is of advantage that the materials treated should have been stretched to a relatively high extent at some stage in their manufacture. They may, for example, have been stretched considerably during their formation by a wet spinning process such as those described in applications S. Nos. 402,785 filed 26th October, 1929, 418,414 filed 3rd January, 1930, 437,423 filed 20th March, 1930, 469,622 filed 21st July, 1930, and 601,043 filed 24th March, 1932, or again stretching may have been effected as a separate operation subsequent to their production. Further, the materials may be softened by means of steam or hot water, and stretched, as described, for example, in application S. Nos. 4,510 and 4,511 both filed on 1st February, 1935. The materials may have undergone a shrinking operation e. g. after stretching.

The degree of saponification effected will depend to some extent upon the object of the process; whether, for example, it is required merely to impart to the materials an affinity for cotton dyes, or to increase their tenacity, or to produce materials consisting substantially of regenerated cellulose. The degree of saponification may, for example, reduce the original acid radicle content by 15–20% or less, or may be more extensive involving a reduction of 25 or 30 up to 40 or 50% or from 60 to 75 or 80% or may even effect substantially complete removal of the acid radicle groups. By the process of the invention it is possible to obtain a deep-seated saponification extending to a considerable depth beneath the surface of the materials or even throughout substantially the whole section of the material.

Having described our invention, what we desire to secure by Letters Patent is:—

1. Process for the saponification of organic esters of cellulose, wherein the saponification is effected by means of a nitrogenous organic base having a swelling action on the cellulose ester, in the presence of a substance which is not a saponifying agent for the cellulose ester and which diminishes the swelling of the cellulose ester.

2. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of organic ester of cellulose, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose ester and a substance which is not a saponifying agent for the cellulose ester and which diminishes the swelling of the cellulose ester.

3. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of organic ester of cellulose, wherein saponification is effected by means of an aqueous liquid containing a water-soluble nitrogenous organic base in which each carbon atom directly attached to a nitrogen atom is directly attached to three other atoms and which has a swelling action on the cellulose ester, and a substance which is not a saponifying agent for the cellulose ester and which diminishes the swelling of the cellulose ester.

4. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of organic ester of cellulose, wherein saponification is effected by means of an aqueous liquid containing a water-soluble nitrogenous aliphatic base containing not more than six carbon atoms which is a swelling agent for the cellulose ester, and a substance which is not a saponifying agent for the cellulose ester and which diminishes the swelling of the cellulose ester.

5. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose acetate and a substance which is not a saponifying agent for the cellulose acetate and which diminishes the swelling of the cellulose acetate.

6. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing a water-soluble nitrogenous organic base in which each carbon atom directly attached to a nitrogen atom is directly attached to three other atoms and which has a swelling action on the cellulose acetate, and a substance which is not a saponifying agent for the cellulose acetate and which diminishes the swelling of the cellulose acetate.

7. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing a water-soluble nitrogenous aliphatic base containing not more than six carbon atoms which is a swelling agent for the cellulose acetate, and a substance which is not a saponifying agent for the cellulose acetate and which diminishes the swelling of the cellulose acetate.

8. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of organic ester of cellulose, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose ester and a water-soluble salt of an inorganic polybasic acid, said salt being one which is not a saponifying agent for the cellulose ester and which diminishes the swelling of the cellulose ester.

9. Process for the saponification of filaments, threads, yarns, fabrics and like materials having

a basis of organic ester of cellulose, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose ester and a water-soluble salt of an organic acid, said salt being one which is not a saponifying agent for the cellulose ester and which diminishes the swelling of the cellulose ester.

10. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of organic ester of cellulose, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose ester and a sugar, which sugar diminishes the swelling of the cellulose ester.

11. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose acetate and a water-soluble salt of an inorganic polybasic acid, said salt being one which is not a saponifying agent for the cellulose acetate and which diminishes the swelling of the cellulose acetate.

12. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose acetate and a water-soluble salt of an organic acid, said salt being one which is not a saponifying agent for the cellulose acetate and which diminishes the swelling of the cellulose acetate.

13. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing a nitrogenous organic base having a swelling action on the cellulose acetate and sodium acetate, the sodium acetate diminishing the swelling of the cellulose acetate.

14. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing monomethylamine which has a swelling action on the cellulose acetate and sodium acetate, the sodium acetate diminishing the swelling of the cellulose acetate.

15. Process for the saponification of filaments, threads, yarns, fabrics and like materials having a basis of cellulose acetate, wherein saponification is effected by means of an aqueous liquid containing ethylene diamine which has a swelling action on the cellulose acetate and sodium acetate, the sodium acetate diminishing the swelling of the cellulose acetate.

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