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XANTHATED CELLULOSE DERIVATIVE AND PROCESS OF COATING WITH SAME

Leon Lilienfeld, deceased, late of Vienna, Germany, by Antonie Lilienfeld, administratrix, Winchester, Mass., assignor to Lilienfeld Patents, Inc., Boston, Mass., a corporation of Massachusetts

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In U. S. Patents Nos. 1,589,606, 1,682,292, 1,682,293 1,682,294, 1,683,831, 1,722,927, 1,722,928, and 2,095,524 and in British Patent 374,964 (corresponding to French Patent 715,551, delivered September 29, 1931), this inventor has described many types of cellulose ethers which are insoluble or substantially insoluble in water, but soluble in dilute caustic alkali solutions.

In these patents he further showed that this "alkali soluble" type of cellulose ethers can be successfully used as basic material for treating fibrous materials, including textile materials and paper, for coating, impregnating, filling, dressing, weighting, printing, sizing fabrics, yarns, threads, loose fibres or yarn. In the appended claims the term "textile material" is intended to embrace yarns, threads, fabrics and paper.

This field of synthetic and applied cellulose chemistry has been further developed by this inventor and the results of the continuation of his research work in this domain are disclosed in U. S. Patents 2,165,392, 2,231,927 and 2,265,914 to 2,265,919, and in British Patents 462,456 (including cognate specifications), 462,712, 474,223 and 503,830.

Furthermore, in U. S. Patents 1,858,097, 1,910,440, 2,021,861, 2,163,607, 2,165,392, 2,165,393, 2,265,914, 2,265,915, 2,265,917, 2,265,918, and 2,296,857 and in British Patents 367,920, 459,122, 462,283, 462,456 (and cognate specifications) 462,712, 474,223 and 503,830, xanthates of suitable cellulose ethers, including xanthates of alkali-soluble cellulose ethers, are described and processes for making such xanthates and processes or methods for treating fibrous material therewith, are also described. These xanthates may be included under the expression "xanthates of those ethers of cellulose in which the content of hydroxyl hydrogen substituted by organic radicals is much below one hydroxyl hydrogen per one $C_6H_{10}O_5$-molecular unit of cellulose.

The experience gathered hitherto with regard to the application of alkali-soluble cellulose ethers to the treatment of fibrous materials including textile materials has taught that they are very valuable basic materials for the production of all finishes in which stiffness or at least a certain degree of stiffness is required.

On the other hand, the alkali-soluble cellulose ethers share with all other cellulose derivatives soluble in aqueous media, the incapability of yielding impregnations, coatings, fillings, dressings, weightings, printings, sizings or any other finishes on fibrous materials, for example fabrics or yarn, which excel by a high degree of

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softness and textile appearance. The term "finishing" will hereinafter be used to cover this entire group of treatments.

All arduous efforts which have heretofore been made with the object of providing a permanent and nevertheless perfectly soft dressed textile having a soft feel, have failed. The lack of a cellulosic material capable of giving a finishing which is permanent, i. e. perfectly (or at least in an appreciable degree) fast to laundering and sufficiently resistant to wear and tear and which nevertheless has a feel to the touch that is not inferior or not substantially inferior to the feel of the untreated materials, such as fabrics or yarn, is a long felt want in the technology and in the industries of finishing textiles.

The present invention supplies this desideratum in the chemistry of alkali-solubule cellulose ethers and, thus, in the technology of treating fibrous materials, particularly in the art of finishing textile materials, for example in the art of finishing textile materials of natural or artificial origin. For, the present invention produces cellulose ethers which are soluble in caustic alkali solution and insoluble or only scarcely soluble in water and which, when used (in the form of xanthates) for treating (finishing) fibrous materials of any kind (especially, however, animal or vegetable, artificial or mixed textile materials), yield finishes of any kind that are sufficiently permanent and having the desired handle, and this without substantially altering the textile appearance or their natural soft feel.

The reference in the last above paragraph, to textile materials of artificial origin is intended to embrace viscose rayon, acetate or other ester threads and fabrics, "nitro-silk" or threads (reduced nitrocellulose), cellulose ether textiles, including the organic solvent soluble and alkali soluble varieties, including those made from xanthates of alkali soluble ethers, cuprammonium threads, and textiles made from long chain amines. Here the "soft feel" of the product is also of particular interest.

This novel effect of the present invention is the more surprising and important.

(1) Since the alkali-soluble cellulose ethers prepared according to the present process give this soft effect also in absence of softening agents or plasticizers, and

(2) Since the alkali-soluble cellulose ethers prepared according to the present process produce this effect even when they are introduced into the fibrous materials in extraordinarily large

amounts, for example in a proportion of 30 or 50 per cent, or even more, calculated on the weight of the fibrous material.

The present invention resides in the discovery and recognition that, when the degradation of alkali-soluble, water-insoluble cellulose ethers, cellulose esters or cellulose thiourethanes, is carried so far that they are deprived of their capacity to form coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or when they are at least made incapable of giving films suitable for practical use, but always short of becoming soluble in water, alkali-soluble degraded cellulose ethers, esters and/or thiourethanes are obtained which are unusually valuable materials for use in dressing fibrous or textile materials, as herein defined. For, when applied as herein defined, preferably in the form of their solutions or pastes in dilute caustic alkali solution, to fibrous materials of any kind as herein defined which, in most cases, do not impair or do not substantially impair the soft feel of the fibrous materials to which they are applied, the finishes thus obtained being in most cases fast (or at least fast to an appreciable degree) to commercial laundering. In addition, in many cases they do not or do not substantially change the textile appearance of the fibrous materials as herein defined to which they are applied. Such treatment also does not greatly stiffen the fibrous materials so treated.

In all the known processes of making cellulose ethers, and in purifying or isolating same, and in some of the processes of making products (artificial regenerated structures) therefrom, it has long been recognized that there was some small amount of degradation of the cellulose molecule inevitably produced, but heretofore the factors in such processes have been so adjusted as to prevent any large amount of degradation, because it was recognized that degrading of the cellulose molecule produced a lowering of the quality (wet and dry strength, elasticity, flexibility, etc.) of the said structures (films, threads etc.). Now in the present process, the prime factor in the production of soft finishes on textiles resides in the carrying of the degradation to such an extent (short of producing water solubility) that the ethers are no longer capable of producing commercially usable films. In order to produce dressed textiles that are laundry-fast, it will be readily understood that the dressing on the textile must be composed of material which is insoluble in water.

The inventor has further found that, when cellulose ethers of the very lowest degree of etherification, i. e. such cellulose ethers as cannot be dissolved in caustic alkali solution (even by freezing) nor in water nor in organic solvents, are treated according to the present process, they can be also successfully used for treating textile materials, for example for the production of finishes as herein defined. The ethers considered in this paragraph are characterized as having a great number of $C_6H_{10}O_5$-molecular units of cellulose to one substituted alcohol group, e. g., such low-alkyl ethers of cellulose as contain not substantially below 15 (and often 20 to 50 or more) $C_6H_{10}O_5$-molecular units of cellulose, to 1 methyl or ethyl group as described in British Patent No. 462,283. Such ethers are of a substantially lower degree of substitution than those described in British Patent 374,964.

The present invention resides further in the recognition that, on being xanthated, i. e. treated with carbon bisulphide in presence of caustic alkali, the cellulose ethers prepared (degraded) according to the present invention yield xanthates which, when applied as herein defined to fibrous materials of any kind, give finishes that in many cases are far softer than the finishes obtained with the cellulose ether xanthates known hitherto.

The present invention is important because it makes possible for the first time to convert a fabric which has a certain fullness, density, thickness and weight or a yarn which has a certain thickness, fullness and weight into a fabric which has a greater and even far greater fullness, density, thickness and weight or into a yarn which has a greater thickness, fullness and weight and which (fabric or yarn), in regard to the softness of their feel, their lack of stiffness, their appearance and their dyeing properties are not (or not considerably) different from the fabrics and yarn before treatment according to the present invention and which (fabric and yarn) are fast or at least in an appreciable degree fast, to commercial laundering and sufficiently resistant to wear and tear.

The present invention further enables one to impregnate or fill loose fibres (for example in the form of a fleece) with a cellulosic material, thus, giving fibres which, according to the nature and properties of the cellulose ether used for the impregnation or filling are conglutinated or conglutinated to a small extent only or are not conglutinated, and which also are soft to the touch, sufficiently fast to laundering and which, even if in a conglutinated state, can be worked up into useful articles and, if in the non-conglutinated state, can be even spun and, if desired, thereafter woven into fabrics or knitted into knitted goods.

In summing up, it is possible, according to the present invention, to produce perfectly novel textile materials cheaper than textile materials which, owing to a larger amount of textile fibres contained therein, have the same fullness, density, weight and thickness and which, with regard to appearance, feel and fastness are not or not considerably superior to the textile materials after being treated according to the present invention.

The degraded cellulose derivatives of the present invention may be also used in conjunction with other dressings applied to textile material, e. g. colloidal or binding substances of cellulosic or non-cellulosic nature, for instance, celluose precipitated from cellulose solutions (including viscose, cuprammonia, urea, thiourea, cyanates or others), starch, dextrin, tragasol etc.

In this modification of the present process the cellulose ethers produced according to the present invention are capable of accomplishing the following two tasks different from each other:

(1) Insofar as they are added to a solution of a colloidal substance of cellulosic or non-cellulosic nature, in which solution they are insoluble or only scarcely soluble, they act as pigment or filler or as a loading material.

(2) Insofar as they are added to a solution of a colloid or of a colloidal substance of cellulosic or non-cellulosic nature in which they are soluble or partially soluble or in which they can be made soluble or partially soluble by an appropriate method or process, (e. g. with viscose) they act

as a dissolved or partially dissolved admixture to the solution of the colloidal substance in hand.

Ad. (1) In this modification of the present invention the degraded cellulose ethers prepared according to the present process by far outshine the mineral fillers (such as china clay, zinc white, tacl (French chalk), lithopone, etc.) and the organic fillers (such as powdered cellulose or the like) used heretofore in the finishing art. For, owing to their softness and flexibility, they do not or do not substantially stiffen the textile finishes as herein defined obtained by means of the inorganic or organic fillers known hitherto and, owing to their physical character, they do not occupy the surface of, and, thus, do not overlie the fibres of which the fibrous material in question consists. Consequently, contrary to all fillers known hitherto, they do not disguise the true nature and appearance of the fibrous materials, such as fabrics, knitted goods, yarn, paper, loose fibres etc., but in most cases improve their appearance in the direction of density.

Furthermore, since owing to their physical nature, particularly their softness and flexibility, they are easier fixable on and in the textile material, than the more or less hard and rigid mineral or organic fillers used hitherto, the resistance to mechanical influences such as rubbing, bending, etc. of the finishes produced thereby is in some cases greater than the resistance of the finishes of equal covering power produced by means of the mineral and organic fillers used hitherto. And, last but not least, the voluminosity of the cellulose ethers produced according to the present invention in their solid state is so much greater than the voluminosity of the mineral or organic fillers used hitherto, that it is possible to produce finishes as herein defined with far smaller proportions (by weight) of the cellulose ethers produced according to the present invention and used as fillers, than the proportions of the hitherto used mineral or organic fillers necessary for the preparation of finishes as herein defined exhibiting the same degree of covering.

Since the lack of fillers capable of having the qualities specified above is a long-felt want in the finishing art, besides the desideratum which they supply to the art of finishing fibrous materials as herein defined when used in their dissolved or semi-dissolved state for the production of finishes as herein defined, the cellulose ethers prepared according to the present invention supply another desideratum in the finishing art as herein defined of fibrous materials as herein defined, when used in their solid state as fillers for finishing materials.

Ad. (2) Contrary to modification (1) in which they act as fillers suspended or distributed within the finishing material, in this modification of the invention the alkali-soluble cellulose ethers prepared according to the present process are not in the form of finely divided particles or fibres suspended or distributed throughout, but form an integral part of, the finishing material as herein defined and thus contribute towards its binding effect, to its fastness towards laundering and resistance to wear and tear.

Hence, when in this modification of the present process a mineral filler is added to the solution of the finishing material compounded of a colloidal substance, for example an alkali-soluble celluose ether of any kind or viscose or the like, the cellulose ether prepared according to the present invention and incorporated with the solution of the finishing material cooperates with the other colloidal substance in binding or fixing the mineral filler in question.

From this it can be seen that, if desired, modification (1) may be combined with modification (2), that is to say, a cellulose ether prepared according to the present invention may be dissolved or at least partially dissolved in a solution of another colloidal substance suitable for finishing fibrous materials as herein defined and to this solution there may be added a smaller or larger proportion of the same cellulose ether in a finely divided but solid state under such conditions that no dissolution of the cellulose ether thus added takes place or dissolution of only part thereof takes place, and that it or the undissolved part can act as a soft filler.

From the foregoing, it can be gathered that one object of the invention is to prepare cellulose ethers which are soluble in dilute caustic alkali solution but insoluble in water, and which have no capacity to form coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or alkali-soluble cellulose ethers which form films that, with regard to their properties, are unsuitable for practical use, (as films),

That another object of the present invention is to prepare finishes as herein defined which do not impair or do not substantially impair the feel of the fibrous materials as herein defined to which they are applied and which are fast or to an appreciable degree fast to commercial laundering and sufficiently resistant to wear and tear, and

That the third object of the invention is to supply the art of finishing fibrous materials as herein defined with a filler or loading material which does not stiffen or does not substantially stiffen textile products, and which does not impair or otherwise unfavorably influence the appearance and handle of fibrous materials as herein defined.

Other objects of the invention will become apparent from the following description.

As far as it is concerned with the preparation of degraded alkali-soluble or alkali-dispersible cellulose water-insoluble ethers as herein defined, the carrying out of the invention in practice consists in treating an alkali-soluble water-insoluble cellulose ether with one or more agents which are capable of depriving the cellulose ether of its capacity to form coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or at least making the cellulose ethers incapable of giving films suitable for practical use, i. e. treating the cellulose ether with a "degrading agent."

A great variety of substances exist, which are well known in the art to be capable of degrading cellulose ethers, either during or after the formation and/or isolation of such ethers.

It is further to be understood that also such cellulose ethers can be used as initial materials in the present invention as contain not more than one alcohol radical, for example one alkyl group or hydroxy-alkyl group, or not more than one hydroxy-acid residue introduced ether-fashion into the cellulose molecule per 2 or 3 or 4 or 5 or 15 or 30 or even 50 or more $C_6H_{10}O_5$-molecular units of cellulose. In the prior literature, those ethers containing from 2 to about 14 $C_6H_{10}O_5$-molecular units of cellulose to one substituent alcohol radical were known as "ethers of low de-

gree of etherification," such ethers being described for example in British Patent No. 374,964 (and the corresponding U. S. Patents 2,327,911 and 2,327,912). Also in the prior literature, those ethers containing over about 15 (e. g. 15 to 50) $C_6H_{10}O_5$-molecular units of cellulose per one substituent alcohol radical linked ether fashion to the cellulose molecule, have been referred to as "ethers of extremely low degree of etherification." The latter kind of ethers are shown for example in British Patent No. 462,283. The former class of ethers can usually be dissolved in dilute caustic alkali solution by refrigeration or freezing, and the latter class cannot be so dissolved. Both these classes of ethers are insoluble in water and in the usual organic solvents (alcohol, benzene, acetone, chloroform, carbon tetrachloride, ethylene chloride, etc.), as well as in mixtures of such organic solvents with each other, and in mixtures of alcohol or acetone with water.

In this respect, by way of further examples, it is expressly pointed out that also the initial or final cellulose ethers described in either U. S. Patent 2,265,919 or British Patent No. 503,830, and also any one of the products produced by the methods described in U. S. Patents 2,231,927 or 2,265,916, in any one of the examples thereof for the production of the initial cellulose ethers, and also in any one of the products described in U. S. Patents Nos. 1,858,097, 1,910,440, 2,100,010, 2,163,607, 2,265,915 and 2,296,856, and in British Patents 367,920 and 462,283, and in any one of the examples thereof for the production of the cellulose ethers, may be used as starting materials for the preparation of the degraded cellulose ethers used as initial materials in the present invention.

In other words, not only such cellulose ethers of the aforementioned types as can be prepared or modified by the processes and methods described in those patents given in the last paragraph above, but also cellulose ethers of the aforementioned types or ethers having substantially similar properties, can be used herein, however prepared.

It is further to be understood that, in the present invention, either simple or mixed cellulose ethers of the aforementioned types can be used as initial materials. As mixed ethers the following may be named by way of example.

Cellulose ethers containing in their molecule two different alkyl or hydroxy-alkyl groups, hydroxy-acid residues, or cellulose ethers containing in their molecule a plurality of said kinds of radicals.

The most effective way of carrying the present invention into effect, i. e. of depriving the cellulose ethers of the aforementioned types of their capacity to form coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or at least making them incapable of giving films suitable for practical use, so far as now known, is the treatment of the cellulose ethers of the aforementioned types, with such agents or mixtures of agents as exert a hydrolyzing or degrading or an oxidizing or a hydrolyzing and oxidizing or a degrading and oxidizing action on cellulose ethers of the aforementioned types, (such agents being hereinafter referred to for brevity, as "degrading agents") the conditions, particularly the temperature and/or duration of the treatment and concentrations, being such as to deprive the cellulose ethers of the aforementioned types of their capacity to form coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or at least to make the cellulose ethers incapable of giving films suitable for practical use. Such result will be hereinafter referred to, for brevity, as being "sufficiently converted."

The oxy-organo derivatives of cellulose (e. g. cellulose ethers, cellulose esters, cellulose ether-esters and cellulose thiourethanes), degraded to the extent indicated in the preceding paragraph, will hereinafter be termed "water-insoluble alkali-soluble non-coherent-film-forming oxy-organo derivatives of cellulose (cellulose ethers)."

Among the hydrolyzing and/or degrading agents which may or may not have an oxidizing effect on the cellulose ethers of the aforementioned types, substances having an acid reaction, such as acids or acid salts and also substances, for instance salts, capable of generating acids, have proved very suitable for the treatment according to the present invention.

The acids (inorganic and organic) or mixtures of acids may be used in the concentrated state or in moderately concentrated or dilute state (i. e. as solutions, e. g. aqueous solutions).

When, instead of acids, one or more acid salts by themselves or together with one or more acids are used as means of the carrying of the present invention into effect, they may be applied to the collulose ethers of the aforementioned types in concentrated solutions or in moderately concentrated solutions or in dilute solutions.

As is well known, strong acids or strong solutions of acid salts are far more powerful as degrading agents, applied to cellulosic substances, but dilute solutions of acids or acid salts are more easily controlled in their actions. It is important to note that in the present invention, it is important to effect a very far-going degradation of the cellulose derivatives (e. g. ethers), but it is equally important that the degrading be stopped short of converting the bulk of the cellulose derivative into water soluble products. Since an object of the invention is to produce laundry-fast dressings, any cellulose derivatives that are converted into a water soluble condition are effectively lost.

Since the carrying of the present invention into effect by treating the cellulose ethers of the aforementioned types with dilute acids is in many cases simpler and easier to control than by treating the said ethers with concentrated acids or moderately concentrated acids, it is often preferable to effect the said conversion of the cellulose ethers of the aforementioned types, by means of media which contain small or very small proportions of the acids or acid substances.

The said conversion of the cellulose ethers of the aforementioned types may be carried out in various ways. Some of these methods are described in the following lines by way of examples to which, however, the present invention is not limited.

First method.—This method consists in treating a cellulose ether of the aforementioned types with an excess of a dilute mineral acid in the cold, i. e. at room temperature or at a temperature not substantially exceeding room temperature or at a temperature below room temperature.

Thus, for instance, the cellulose ether is immersed in, or otherwise mixed with, an excess of a dilute hydrochloric acid or sulphuric acid or phosphoric acid or nitric acid or hydriodic or hy-

drobromic or sulphurous acid or the like and the mixtures allowed to stand at room temperature until the said conversion (degradation) of the cellulose ether is sufficiently effected. In some cases, particularly when the acid is very dilute, the treatment must last 2 to 3 months or even longer until the desired result is attained.

Second method.—This method consists in treating a cellulose ether of the aforementioned types with an excess of a dilute mineral acid, such as dilute hydrochloric acid or sulphuric acid or phosphoric acid or nitric acid or the like, at a raised temperature with or without pressure.

Thus, for instance, a cellulose ether of the aforementioned types is immersed in, or otherwise mixed with, an excess of hydrochloric acid or sulphuric acid of 0.02 to 2 per cent strength and heated in a closed or open vessel or with reflux cooling to 50 to 100° C. or to the boiling point and kept at this temperature until the cellulose ether becomes sufficiently converted.

Or, for instance, a cellulose ether of the aforementioned types is immersed in, or otherwise mixed with, an excess of hydrochloric or sulphuric acid of 3 to 8 per cent strength and heated in a closed or open vessel to 40 to 50° C. and kept at this temperature until the cellulose ether becomes sufficiently converted.

Or, for instance, a cellulose ether of the aforementioned types is immersed in, or otherwise mixed with, an excess of hydrochloric or sulphuric acid of 0.01 to 2 per cent strength and heated e. g. at 50 or 100° C., or to boiling, under pressure (for example a pressure of 1 to 4 atmospheres) until the cellulose ether becomes sufficiently converted. The pressure can be omitted.

The conversion, in this second method is much faster than by the first method.

Third method.—This method consists in impregnating or otherwise mixing a cellulose ether of the aforementioned types with an excess of a dilute mineral acid, for example with dilute hydrochloric acid or sulphuric acid or phosphoric acid or nitric acid or the like (e. g. at room temperature), removing the excess of the acid by pressing, centrifuging or the like, drying the pressed and preferably comminuted material and then leaving it in the air (e. g. at room temperature), until the conversion is sufficiently effected, or the material after being pressed may be heated until the cellulose ether becomes sufficiently converted.

Thus, for instance, the cellulose ether is immersed in, or otherwise mixed with, an excess of sulphuric acid of 1 per cent strength and left in the sulphuric acid for a few minutes, whereupon the excess of the sulphuric acid is removed by pressing or centrifuging until the press cake or residue of the centrifuging retains 0.3 per cent to 0.5 per cent of actual H_2SO_4. Thereupon, it is comminuted or otherwise finely divided and either allowed to remain in the air at room temperature, or with or without intermediate drying at room temperature or at a temperature not substantially exceeding room temperature, heated in a closed vessel at 40 to 100° C., until the cellulose ether becomes sufficiently converted. In the former instance the pressed and comminuted material must remain in the air for about 2 to 3 months, whereas in the latter case the heating must be conducted for several hours or even 1 to 2 days until the desired result is attained.

Or, for instance, the cellulose ether is immersed in, or otherwise mixed with, an excess of sulphuric acid of 3 to 4 per cent strength and left in the sulphuric acid for a few minutes, whereupon the excess of the sulphuric acid is removed by pressing or centrifuging until the press cake or residue of the centrifuging retains 1 per cent of actual sulphuric acid (i. e. approximately 25 to 40 per cent of the dilute acid calculated on the original weight of the cellulose ether). Whereupon, it is comminuted or otherwise finely divided and either allowed to remain in the air at room temperature or with or without intermediate drying at or only slightly above room temperature, or heated in a closed vessel at 30 to 100° C., until the cellulose ether becomes sufficiently converted. In the former instance (cold), the pressed and comminuted material must remain in the air for about 1 to 2 months, whereas in the latter case (with heating) the heating must be conducted for several hours until the desired result is attained.

Or, for instance, the treatment is conducted as in the foregoing two modifications, but with the difference that the concentration of the sulphuric acid is only 1.2 to 1.5 per cent.

In the above treatments, the acid solution may be applied hot or warm or cold.

In the foregoing methods, instead of the acids, also aqueous solutions of acid salts, for example of bisulphates or bisulphites can be used, and also such salts of inorganic acids as exert acid action by way of hydrolysis in their aqueous solutions, for example aluminum sulphate or magnesium chloride or zinc chloride or alkali chlorides or the like.

Particularly, when they are conducted at a raised temperature, in the foregoing three methods, instead of the mineral acids, organic acids by themselves or in mixture with mineral acids may be used, for example formic acid, acetic acid, oxalic acid or an hydroxy-acid, for example glycollic acid, lactic acid, tartaric acid, citric acid or the like. When the organic acids are used by themselves, the concentrations must be higher than the concentrations of the mineral acids. In some cases it is possible to attain the desired result according to the present invention by treating the cellulose ether with a concentrated organic acid, for example with glacial acetic acid, preferably in the heat.

Fourth method.—This method consists in treating a cellulose ether of the aforementioned types, preferably with stirring or otherwise agitating, with strong sulphuric acid of a concentration which is incapable of dissolving the cellulose ether or a substantial part thereof.

Thus, for instance, a cellulose ether of the aforementioned types is immersed in, or otherwise mixed with a sulphuric acid of 55 to 60 per cent strength at or below room temperature and treated therewith at room temperature or at a temperature below room temperature until the cellulose ether becomes sufficiently converted. According to the type of the cellulose ether and/or according to the desired degree of degradation, the duration of the treatment is, for instance, between about 6 and 12 hours.

Fifth method.—This method consists in treating, preferably with stirring or otherwise agitating, a cellulose ether of the aforementioned types at room temperature or at a temperature not substantially exceeding room temperature with strong hydrochloric acid e. g. of 33 to 34 per cent strength until the cellulose ether becomes sufficiently converted. In general, the desired result according to the present invention is attained

after a comparatively long treatment, for example after 12 to 24 hours or longer.

Sixth method.—This method consists in treating a cellulose ether of the aforementioned types at a temperature not substantially exceeding room temperature or at a temperature below room temperature with gaseous hydrochloric acid in presence of a small or moderate amount of water until the cellulose ether becomes sufficiently converted. The water may be introduced either by using the gaseous hydrochloric acid in the moist state (which is the case when the gaseous hydrochloric acid is not dried before coming in contact with the cellulose ether) or by using a parent cellulose ether containing moisture or by moistening the parent cellulose ether.

This method can also be carried out at a raised temperature, for example at 40 to 100° C., for example in such a manner that the cellulose is first saturated with the gaseous hydrochloric acid and then transferred to a closed vessel, for example a pressure vessel and heated to 40 to 100° C., until the cellulose ether becomes sufficiently converted.

Seventh method.—This method consists in treating a cellulose ether of the aforementioned types in presence of alkali, for example in presence of a caustic soda solution of 18 to 20 per cent strength with a small proportion (for example 0.2 to 2 per cent) of chlorine until the cellulose ether becomes sufficiently converted.

Eighth method.—This method consists in treating a cellulose ether of the aforementioned types with chlorine or bromine in presence of water, which may be introduced as described in the sixth method, until the cellulose ether becomes sufficiently converted. (In presence of water the chlorine exerts a hydrolyzing or degrading and oxidizing action on the cellulose ether).

Ninth method.—This method consists in treating a cellulose ether of the aforementioned types with a strong organic acid, for example glacial acetic acid, containing chlorine or bromine, at a raised temperature preferably at a temperature of 30 to 80° C., until the cellulose ether becomes sufficiently converted.

In all the nine methods described above, after the treatment is completed, the product must be washed with water or alcohol or the like until free from acid, and free from the other reagents used.

Regardless of whether the hydrolyzing or degrading or hydrolyzing or degrading and oxidizing agents, particularly acids, are used in the concentrated or more or less diluted state, care must be taken that the treatment is carried out under such conditions as to ensure the production of a cellulose ether which is substantially wholly soluble or partially or incompletely soluble in caustic alkali solution or at least substantially wholly dispersible or partially or incompletely dispersible therein, and which is insoluble or only partially soluble in water and which is "incapable of forming coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or which is incapable of yielding films suitable for practical use" (i. e. until said ether "becomes sufficiently converted"). To avoid great losses in substance, it is further recommendable not to drive the treatment so far as to cause formation of considerable amounts for example amounts substantially exceeding 50 per cent of the weight of the initial cellulose ether) of products which are too deeply degraded, i. e. water-soluble, for example formation of the corresponding ethers of glucose.

Since the paramount factors giving the desired result (sufficient conversion), are either the time of the treatment or the temperature of the treatment or both, to obtain the desired result, it is necessary to adapt the time of the treatment to the temperature and vice versa. And these factors are both influenced by the concentration and degree of activity of the acid or other reagent or reagents used for the conversion.

To find out the exact or approximate time at which the endpoint of the treatment, i. e. the exact time at which the desired result according to the present invention is attained, it is recommendable to make one or more preliminary experiments in which during the reaction after different times of the treatment a sample of the cellulose ether under treatment is withdrawn, washed with water, and then contacted with a solvent or dispersion medium for the alkali-soluble cellulose ether, particularly with a caustic soda solution of 7 to 10 per cent at room temperature or at a lower temperature, for example at 0° C., or below 0° C., for example at minus 5 to minus 10° C. The thus obtained complete or incomplete or partial solution or dispersion or paste or swollen mass or magma is then tested for film-forming properties, e. g., by being spread on a glass plate and immersed in a coagulating bath, for example in dilute acid, for example in sulphuric acid, of 10 per cent strength that may or may not contain sodium sulphate or magnesium sulphate or in a solution of a salt, for example in a strong solution of ammonium sulphate or ammonium chloride. If it is desired to obtain a cellulose ether which is incapable of forming a coherent film, then the endpoint is reached as soon as the solution or dispersion or paste or magma or mass spread on the glass plate does not form a film, for instance when it disintegrates in the coagulating bath or forms therein only crumbles or a pasty or sticky mass.

When, however, it is desired to obtain a cellulose ether which forms a film that will disintegrate in the coagulating bath or in the washing water into which it is introduced therefrom or on being dried, the endpoint is reached when the solution or dispersion or paste or magma, spread on the glass plate forms a film in the coagulating bath, which however disintegrates; for instance falls into larger or smaller pieces when left in the coagulating bath or in the water into which it is introduced therefrom for a shorter or longer time or which bursts or breaks into larger or smaller pieces on being dried after washing. If it is desired to carry on the treatment only so far as to obtain a cellulose ether which yields a coherent film which has so inferior low dynamometric properties as to render it unsuitable for any practical use, the endpoint is reached when the film dried after washing has so poor dynamometric properties, particularly wet tenacity that it is unsuitable for any practical use.

In some cases, particularly, when a far-going degradation is aimed at, the physical condition of the washed and preferably dried product may serve as a guiding line with regard to the question whether or not the desired endpoint is reached. For example, if after a certain time of treatment the cellulose ether has become more or less friable, for instance if it can be easily

pulverized or easily crushed or ground, the treatment can be regarded as completed.

When the endpoint or endpoints of the treatment of a certain type of cellulose ether with a certain degrading or hydrolyzing agent, for example acid, of a certain concentration and at a certain temperature are determined by one or more preliminary experiments as described above, no further preliminary experiments are necessary if it is desired to produce a degradation product of a cellulose ether of the aforementioned types having the desired properties by means of the very same treatment with the very same materials and at the same temperature.

Since also other substances or mixtures of substances or other materials and also some physical means (for example heating with or without pressure in absence or presence of organic or inorganic substances, such as water or glycerine or oils or liquid or solid hydrocarbons, salts, etc., until the cellulose ether becomes incapable of forming coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or until the cellulose ether becomes incapable of giving films suitable for practical use) which in chemistry are known as hydrolyzing or as degrading or as hydrolyzing and degrading agents, can also be used in the present invention for the treatment of the cellulose ethers of the aforementioned types, it must be expressly stated that it is not intended to limit that modification of the carrying out of the present invention in practice in which the cellulose ethers of the aforementioned types are treated with hydrolyzing or degrading or hydrolyzing and degrading media to the treatment of the said cellulose ethers with hydrolyzing or degrading or hydrolyzing and degrading agent containing one or more acid substances such as acids or acid salts.

Where it is desired to produce degraded cellulose ethers which are incapable of forming coherent films or films which do not disintegrate in the coagulating bath or in the washing water into which they are introduced therefrom or on being dried or cellulose ethers being incapable of giving films suitable for any practical use, by oxidation, practically all known oxidizing agents can be used to obtain cellulose ethers which have the aforesaid properties characteristic of the present invention, a few oxidizing agents being, by way of examples to which the present invention is not limited, set forth in the following lines.

(1) Chloride of lime (bleaching powder), is preferably used in a solution of 2 to 15° Bé. at room temperature or at a raised temperature, for example of 30 to 100° C., with or without subsequent treatment with carbonic acid for which treatment air or carbonic acid produced chemically or chimney gases or lime-kiln gases, may be used.

(2) Hypochlorous acid or a hypochlorite of an alkali metal, such as sodium hypochlorite, preferably in solution, at room temperature or at a raised temperature or at a temperature below room temperature. If hypochlorous acid is used, it may be caused to act on the cellulose ether in the direct or in the indirect manner, for example by conducting an electric current through a suspension of the cellulose ether in an aqueous solution of potassium chloride, which is neutral at the beginning of the treatment.

(3) A solution of chlorine or bromine in water at room temperature or at a raised temperature or at a temperature below room temperature.

(4) Chlorine in presence of sunlight and water at room temperature or at a raised temperature or at a temperature below room temperature.

(5) Potassium permanganate or other permanganate, at room temperature or at a raised temperature or at a temperature below room temperature, preferably in solution, for example of 1.5 to 4 per cent strength in the absence or presence of an alkali, such as caustic soda.

(6) Nitric acid at room temperature or at a raised temperature or at a temperature below room temperature.

(7) Chromic acid, for example in the form of potassium bichromate and sulphuric acid.

(8) Strong caustic soda solution (for example of 20 to 50 per cent) hot and in presence of oxygen. For this purpose air or concentrated (e. g. chemically produced) oxygen can be used.

(9) Hydrogen peroxide or an alkali peroxide in a concentrated or dilute solution, at or above or below room temperature can be used. In some cases, ozone can be used.

For the production of finishes, the practice of the invention consists in applying to a fibrous material a solution of a xanthate of degraded cellulose ether in an aqueous caustic alkali solution, then squeezing out excess of said solution, and then treating with a setting bath, then washing, desulphurizing and drying. Instead of a solution, a magma, suspension, dispersion or paste can be used. Instead of a degraded cellulose ether, other degraded cellulose derivatives, such as esters, thiourethanes, etc., can be used. The fibrous material may be loose fibres, yarns, threads, fleeces, fabrics, paper or the like, of natural (vegetable or animal) or artificial or synthetic origin (e. g. cotton, wool, linen, flax, hemp, ramie, jute, rayon etc.). The caustic alkali solution can conveniently be a 6–10% NaOH solution in water. Milder solutions, e. g. 3 to 5% NaOH can be used for dissolving the xanthate. One or several of the degraded cellulose oxy-organo bodies may be xanthated, and the mixed xanthate solutions can be used. The solution may be made at room temperature, if the xanthated cellulose derivative used will dissolve at such temperature, or the xanthate can be dissolved at a much lower temperature, e. g., −15 to +5° C. In place of some or all of the caustic alkali, a solution of a strong organic base, e. g., guanidine, or a quaternary base or a derivative thereof, or an ammonia derivative of carbon dioxide (e. g. urea, cyanamid, thiourea, dicyanamid) or a solution of a thiocyanate, can be used as the solvent or dispersion medium. With the solution etc., of the xanthate of the degraded cellulose ether derivative, other colloids such as alkali soluble cellulose derivatives, e. g., ethers, or viscose or starch or dextrine or any compatible sizing can be used.

The setting bath may be any of those commonly used in the production of artificial threads from viscose.

Thus, for instance, coagulating or precipitating baths containing an acid or an acid salt or one of these with a neutral salt of a monovalent or divalent or trivalent metal or a solution of one or more neutral salts, for example a solution of ammonium chloride or of ammonium sulphate, or of an alkali metal chloride or the like, which baths may or may not contain an organic substance, for instance glucose or glycerine, may be

successfully used in the present invention as coagulating or precipitating baths.

Also water or solutions of normal alkali carbonates or alkali bicarbonates or carbonated water can be used in the present invention as coagulating or precipitating baths. These baths offer the possibility of recovering at least part of the caustic alkali contained in the solution of the cellulose ether prepared according to the present invention and in the case of the alkali carbonates also at least part of the coagulating agent.

The application of the solutions or dispersions or pastes or magmas or suspensions of the xanthates of cellulose ethers prepared according to the present invention to fibrous materials as herein defined, such as the production of coatings, layers and impregnations of any kind, dressing on fabrics, textile printing, book-cloth, tracing cloth, sizing of yarn, paper-sizing, paper-like surfacing etc., and the subsequent coagulation or precipitation may be accomplished by wholly or partially impregnating, printing or otherwise covering or imbuing a fibrous material as herein defined with the solution or partial or incomplete solution or dispersion or partial or incomplete dispersion or paste or magma or suspension and, with or without intermediate drying, treating the material with a coagulating bath, either by introducing the material into the coagulating bath or by spraying the coagulating liquid on the material, or by conducting the material through a mist of the coagulating liquid or by any other method of applying a liquid to a fibrous material as herein defined, particularly to a textile material as herein defined.

In U. S. Patents Nos. 1,722,928, 1,682,293, 2,265,917, 2,265,918, 2,231,927, 2,265,916 and 2,224,874 and in British Patents 374,964, 459,122, 462,712, 462,456 (including cognate specifications) and 474,223, processes and methods of applying solutions of alkali-soluble cellulose ethers (which are not considerably degraded) to fibrous materials as herein defined in general and to textile materials as herein defined in particular are described and illustrated by examples so thoroughly that, instead of repeating the working formulas given therein, it is sufficient to refer to the said other cases which will serve as useful descriptions of examples for the application of the xanthates of the degraded cellulose ethers prepared according to the present invention to fibrous materials as herein defined in general and to textile materials as herein defined in particular. The xanthates of the degraded cellulose ethers (e. g. in solution), can be applied by the processes shown in the said prior cases.

Any suitable softening agent, such as glycerine or a glycol or a sugar, such as glucose or a soap or Turkey-red oil, or a drying or non-drying oil, or a halogen derivative of a di- or polyvalent alcohol, particularly a halohydrin, such as a dichlorohydrin or a monochlorohydrin or ethylene chlorohydrin, in short, in so far as it is compatible with the xanthated cellulose ethers prepared according to the present invention, any substance known in the art of alkali-soluble cellulose ethers or in the viscose art as additions to viscose or to solutions or alkali-soluble cellulose ethers may be added to the solutions or partial or incomplete solutions or dispersions or partial or incomplete dispersions or pastes or magmas or suspensions of the xanthated cellulose ethers prepared according to the present invention prior to their application to fibrous materials as herein defined.

As stated above, valuable products which are also suitable for finishing as herein defined, can be obtained when the cellulose ethers prepared according to the present invention are xanthated, for example according to the processes described in U. S. Patents Nos. 2,021,861, 1,858,097, 1,910,440, 2,265,914, 2,265,915, 2,163,607, 2,265,917, 2,296,856, 2,265,918 and 2,296,857, and British Patents 367,920, 459,122, 462,283, 462,456 (and cognated cases), 462,712, 472,888 and 472,933.

The xanthates of the cellulose ethers prepared according to the present invention can be produced by acting on the cellulose ethers with carbon bisulphide in presence of alkali. The carbon bisulphide may be caused to act either upon the cellulose ethers in the solid form in presence of caustic alkali solution, for example, upon a moist alkali compound of a cellulose ether or upon a mixture of a cellulose ether with caustic alkali solution or upon a suspension of a cellulose ether in caustic alkali solution or upon a solution of a cellulose ether in caustic alkali solution.

The methods of producing xanthates of cellulose ethers and the working up of such xanthates into finishes as herein defined are described in the aforesaid patents and applications described and illustrated by examples in so exhaustive a manner that, instead of repeating the said working formulas, it is wholly sufficient to refer to the respective parts of the said cases which will serve as useful descriptions of, and examples for, the conversion into their xanthates of the alkali-soluble cellulose ethers prepared according to the present invention and the working up of such xanthates into finishes as herein defined.

Any suitable softening agents, such as glycerine or a glycol or a sugar, such as glucose or a soap or Turkey-red oil, or a drying or non-drying oil, or a halogen derivative of a di- or polyvalent alcohol, particularly a halohydrin, such as a dichlorohydrin or a monochlorohydrin or ethylene chlorohydrin may be added to the solutions of the xanthates of the cellulose ethers produced according to the present invention.

The carrying out in practice of that modification of the present invention, in which the cellulose ether xanthates produced according to the present invention are used with fillers, is very simple. It consists in mixing a cellulose ether xanthate prepared according to the present invention in the solid moist or preferably in the dissolved condition, or as a paste, and which may also contain one or more of the colloidal or binding substances set forth further above in the general description, with one or more of the degraded cellulose derivatives (ethers) etc., without being xanthated. Besides the cellulose ether in the solid state, also one or more other fillers, such as china clay, talc, zinc white, lithopone, or barium sulphate, (and coloring bodies, pigments) may be added. The solution or paste is then padded, back-filled, printed, etc., on textiles, then coagulated, washed, desulphurized and dried.

In order to explain the nature of the present invention, the following specific examples are set forth. It is to be understood that the invention is not limited to these examples, to the precise proportions of ingredients, the times and temperatures and sequences of steps set forth; the parts are by weight:

Example I, A to C

The parent cellulosic material may be a simple or mixed cellulose ether or a cellulose ester,

prepared for instance according to the disclosure of any one of the U. S. Patents Nos. 1,589,606, 1,683,682, 1,683,831, 1,722,927, 1,722,928, 1,682,292, 1,682,294, 1,682,293, 2,095,524, 2,265,917, 2,265,918, 2,265,919, 2,231,927, 2,265,916, 1,858,097, 1,910,440, or 2,100,010 or 2,265,914 or 2,163,607 or 2,296,856 or British Patents 367,920, 374,964, 459,122, 462,283, 462,456 (and cognate cases), 474,223 or 503,830. 1,000 parts of such cellulose ether or ester are immersed in, or otherwise mixed with, 20,000 to 30,000 parts of hydrochloric acid of 0.5 per cent strength at room temperature in a suitable vessel, for instance an open or closed vessel made from acid-resistant metal or in a vessel provided with reflux-cooling. The mixture is heated to 50 to 100° C., for 30 minutes to 4 hours. After that time, the heating is discontinued and the reaction mass is washed in a suitable washing apparatus, for instance on a straining cloth or in a centrifuge or the like until free from acid. This product is a degraded cellulose ether or ester, of a very advanced stage of degradation, but is not so far degraded as to be water soluble. (Water soluble degradation products are not used because unsuitable). The washed product is pressed, and if desired is dried.

The degraded cellulose ether is then xanthated. This operation can be carried out in several different manners.

(*a*) 100 parts of the dried degraded cellulose derivative (or an amount of the moist degraded product containing 100 parts of the degraded cellulose derivative) are mixed with so much water and caustic soda as to give 2,000 parts of 18% NaOH solution, at room temperature, the mass is then mixed or agitated 1 to 3 hours in a vessel provided with a stirrer and having a lid that can be tightly closed, then 30 to 60 parts of CS_2 are added, the lid then tightly closed and the mass agitated for 1 to 2 hours, at room temperature, or until the degraded cellulose derivative has been completely xanthated.

(*b*) After well mixing with 18% caustic soda solution, for 1 to 3 hours to two hours, the mass is filtered and pressed down to 300–400 parts, then shredded, at room temperature, then placed in a tumbling box having a tight fitting lid. Then 40 to 60 parts of carbon bisulphide are added, the box tightly closed, then agitated for 6 to 10 hours at 18–20° C., (room temperature). The excess of carbon bisulphide is blown off for 15–20 minutes, and the sulphided mass is then dissolved in so much water and caustic soda as to yield a solution containing 5 to 7% of the degraded cellulose derivative and 8% of caustic soda..

(*c*) The amounts of carbon bisulphide can be varied considerably, e. g., from 10% to 100%, based on the actual amount of the degraded cellulose derivatives. The amount of caustic soda can be substantially less than the amounts given above, e. g. down to one-half the indicated quantities. The amount of caustic soda solution to be mixed with the xanthate, can be substantially reduced, to give a paste or magma instead of a solution.

The xanthated product is mixed with so much caustic soda solution of appropriate strength at 15° to 18° C., to yield with the water present a 9% NaOH solution, containing 7% of the degraded cellulose ether, in the form of its xanthate.

According to the appearance of the suspension or incomplete solution of the xanthated product, it is cooled down with stirring sufficiently to effect solution of the degraded cellulose ether. This may require cooling to plus 5° C., or to 0° C., or to minus 5° C., to minus 10° C., and maintaining the low temperature and agitation until solution occurs.

A fabric, such as a woven cotton fabric is provided by means of a suitable machine, for example a back-filling machine or a padding machine or a spreading machine, or by printing or stenciling, with one or (optionally with intermediate drying) more coatings of the xanthate solution or paste thus produced, and the coated or impregnated or filled material, in the wet state or after intermediate drying, is introduced into any precipitating bath known in the viscose art, such as the so-called Müller bath, for instance a bath containing par litre 160 grams of sulphuric acid monohydrate and 320 grams of sodium sulphate, or 100 grams of sulphuric acid monohydrate and 160 grams of sodium sulphate, or into a bath composed of 64 parts of water, 10 parts of sulphuric acid, 9 parts of glucose, 12 parts of sodium sulphate, 12 parts of ammonium sulphate and 1 to 3 parts of zinc sulphate, or into sulphuric acid of 10 to 20 per cent strength, or into a bath composed of 11 parts of sodium sulphate, 14 parts of magnesium sulphate, 9 parts of glucose, 1 to 3 parts of zinc sulphate and 65 to 63 parts of water, or into a bath consisting of sodium carbonate solution of 20 to 28 per cent strength. The temperature of the bath may be 45 to 50 C.

However, not only the so-called Müller bath or any modification thereof come into consideration as coagulating baths in the present process, but all baths known in the viscose art regardless of whether or not, in addition to the purely coagulating constituents, such as acids and/or acid or neutral salts, they contain any other inorganic or organic (liquid, oily, crystalline or colloidal) substance or substances.

The fabric is washed, desulphurized, dried and finished in the manner common in textile finishing.

It is to be understood that the material may be bleached (if desired or necessary) in any known manner before or after it has been dried.

B. Mode of procedure as in A, but with the difference that, instead of 7 per cent., the suspension or solution in caustic soda solution of 9 per cent strength contains 9 per cent of the degraded cellulose ether, in the form of its xanthate.

C. Mode of procedure as in A, but with the difference that, instead of 7 per cent., the suspension or solution in caustic soda solution of 9 per cent strength contains 12 per cent of the degraded cellulose ether, in the form of its xanthate.

Example II, A to C

The process is conducted as in Example I, A to C, but with the difference that, instead of the hydrochloric acid of 0.5 per cent strength, a hydrochloric acid of 0.05 per cent strength is used, for degrading.

Example III, A to C

The process is conducted as in Example I, A to C, but with the exception that, instead of the hydrochloric acid of 0.5 per cent strength, a hydrochloric acid 0.1 per cent strength is used.

Example IV, A to C

The process is conducted as in Example I, A to C, but with the exception that, instead of the hydrochloric acid of 0.5 per cent strength, a hydrochloric acid of 0.2 per cent strength is used.

Example V, A to C

The process is conducted as in Example I, A to C, but with the difference that, instead of the hydrochloric acid of 0.5 per cent strength, a hydrochloric acid of 1 per cent strength is used.

Example VI, A to C

The process is conducted as in Example I, A to C, but with the difference that, instead of the hydrochloric acid of 0.5 per cent strength, a hydrochloric acid of 2 per cent strength is used.

Example VII, A to C

The process is carried out as in any one of the Examples I, A to C to VI, A to C, but with the difference that, instead of hydrochloric acid, sulphuric acid is used in the corresponding concentrations.

Example VIII, A to C

The process is conducted as in any one of the Examples I, A to C to VII, A to C, but with the exception that, to the solution of the degraded cellulose derivative xanthate, is added powdered talc, china clay or similar mineral filler, the amount of which may be from one to two times the amount of the degraded cellulosic body. The resulting slurry is then applied to the textile and then subjected to the coagulating, washing, etc., steps.

Example IX, A to C

The process is conducted as in any one of the Examples I, A to C, to VII, A to C, but with the difference that, prior to its being applied to the textile material, 100 to 200 per cent of a softening agent (based on the amount of the degraded cellulose), are incorporated with the solution of the xanthate of the degraded cellulosic body.

Example X

1,000 parts of a simple or mixed cellulose ether or cellulose ester (prepared for example according to any one of the processes described in the patents enumerated in Example I, A or according to any other process or method which is suitable for the preparation of suitable simple or mixed cellulose ethers or cellulose esters), are mixed or kneaded at 18 to 20° C., for 6 to 12 hours in a suitable apparatus, for example a Werner-Pfleiderer shredder or a kneading machine with 5,000 to 10,000 parts of sulphuric acid of 55 to 60 per cent strength added at 15° C. After that time, the reaction mass is washed with water, (hot or cold), for example on a straining cloth or in a centrifuge or the like until free from sulphuric acid, and xanthated.

The product thus obtained is dissolved in dilute caustic soda solution, and the solution applied to textile materials as described in Example I, A to C.

Example XI, A to C

1,000 parts of a simple or mixed cellulose ether or cellulose ester (prepared, for example, according to any one of the processes described in the patents enumerated in Example I, A or according to any other process or method which is suitable for the preparation thereof) are mixed in a suitable vessel with 20,000 to 30,000 parts of a solution of chloride of lime (bleaching powder) of 4° Bé. to 10 Bé. until the mixture is homogeneous and allowed to stand at room temperature for 12 to 24 hours. After that time, the mass is washed in a suitable washing apparatus, for instance on a straining cloth or in a centrifuge until free from chlorine, then, acidified with a weak organic acid, for example acetic acid of 3 to 5 per cent strength and then freed from the acetic acid by washing it again.

After the washing step the product may be dried and in the dried or moist state xanthated and dissolved in caustic soda solution and the solution applied to a textile material as described in Example I, A to C.

Example XII, A to C

Mode of procedure as in Example XI, A to C, but with the difference that, instead of being washed immediately after the treatment with the solution of chloride of lime of 4 to 10° Bé, the product is, after removal of the excess of the solution of chloride of lime by straining or centrifuging, exposed to the action of air at room temperature for 12 to 24 hours, then washed, acidified and re-washed.

Example XIII, A to C

1,000 parts of a simple or mixed cellulose ether or cellulose ester prepared, for example, according to any one of the processes described in the patents enumerated in Example I, A or according to any other suitable process, are steeped in a solution containing 140 parts of potassium permanganate in 20,000 parts of water which have been mixed with 760 parts of a caustic soda solution of 4.5 per cent strength, the mixture is well stirred and then with frequent stirring allowed to stand at 18 to 20° C., for 4 hours. Afterwards, the mixture is placed on a straining cloth or another suitable washing appliance, for example a filter press, and washed with water until free from alkali. After having removed the excess of water by pressing or centrifuging, the residue is mixed with 2300 to 2400 parts of caustic soda solution of 18 per cent strength, and the mixture slowly heated to 50° C., with constant stirring and allowed to stand at 18 to 20° C. for 12 to 36 hours. After that time, and if desired after previous dilution with water, the mixture is acidified with dilute sulphuric acid or with any other suitable acid and then decolorized in known manner. This, for instance, may be performed by passing gaseous SO_2 into the mixture or by adding sodium bisulphite in the solid or dissolved state to the mixture until the mixture becomes colorless. The product of the reaction is then washed and, if desired, dried in a suitable manner, then xanthated.

The product thus obtained is then dissolved and the solution applied to a textile material as described in Example I, A to C.

Example XIV, A to C

Mode of procedure as in Example XIII, A to C, but with the exception that no caustic soda solution is added to the potassium permanganate and that, instead of at room temperature, the oxidation is carried out at 90 to 100° C., the duration being 1 hour.

Example XV, A to C

The process is conducted as in Example XIII, A to C or XIV, A to C, but with the difference that the treatment of the reaction product with the caustic soda solution at 50° C., is omitted, and that the washed product, if desired after appropriate dilution, for instance with water, is decolorized with sulphurous acid as described in Example XIII.

The sizing yarn will be readily understood from the foregoing examples.

It is of course well known that heretofore, in

the manufacture of cellulose ethers of the alkali-soluble varieties including those which will readily dissolve in dilute NaOH solution at or near ordinary room temperature (18° to 25° C.) as well as those which dissolve therein only at or near the freezing point (e. g. —10 to +5° C.), a small amount of degrading of the cellulose or of the ether has occurred. But in such processes, the aim has been to prevent any such degree of degrading as would materially injure the film-forming property of the cellulose ethers and the quality of the products. Thus in U. S. Patent 1,589,606, alkali soluble ethers of cellulose are prepared, and in the etherification step, heat is applied. British Patent 374,964 produces cellulose ethers which dissolve in refrigerated caustic alkali solution, by a process in which no extraneous heat is employed in the etherification operation. Both of these two kinds of cellulose ether are capable of forming strong flexible films. But the process of the British patent gives ethers which, in the form of films, have a much higher degree of flexibility, toughness and tenacity (illustrated by much higher Schopper fold test) than ethers of said U. S. patent. This higher quality of the films produced in the British patent is believed to be due to the fact that the cellulose ethers of this British patent are less degraded than those of the U. S. patent.

The ethers of the said U. S. patent and also those of the British patent, are shown in these patents as being suitable for dressing textiles, but only where stiffened products are desired.

In the present case, the cellulose ethers are deeply degraded, so that they are no longer capable of giving coherent films, or films that do not disintegrate, either in the coagulating bath, or in the washing bath or in the drying step, and at the same time the degrading is not carried sufficiently far to give water soluble products.

Owing to the fact that the cellulose ethers are degraded too far to produce coherent films, they do not substantially increase the stiffness of the textile material under treatment, i. e., they give a soft finish, as compared with the stiff finish of the said prior patents.

The term "degraded" as used in the present specification and the appended claims in connection with the cellulose derivatives (ethers, etc.) treated in accordance with the present invention, is intended to include cellulose ethers degraded to the extent indicated. Such degraded products have a lowered solution viscosity compared with a standard solution of undegraded cellulose ether.

A solution of standard hydroxy ethyl cellulose ether, (film forming ether), was prepared as follows (all parts are by weight).

100 parts of air dry wood pulp were steeped for 45 minutes in a large excess of an aqueous 19% sodium hydroxide solution, at room temperature, and the moist alkali cellulose then pressed to 270 parts by weight. The pressed material was comminuted in a shredding machine at 17° to 18° C., for 50 minutes and allowed to stand at 23° C., for 6 hours and 25 minutes. The aged material was then mixed in the shredder with 16.1 parts of ethylene chlorohydrin for 2 hours and 30 minutes at 19–20° C., without any extraneous heat being applied. The mass was allowed to stand at 23° C., for 21 hours and 30 minutes. The material was purified by washing with water at 75–80° C. After centrifuging and drying, the material contained 7.72% moisture.

In the process of the last preceding paragraph, no substantial amount of degradation takes place, and the ether so produced can be referred to as "substantially undegraded." Due to the fact that the ether so produced is "substantially undegraded" it has a relatively high solution viscosity, and can be used for making films by the conventional method (using the conventional baths used in the regeneration of cellulose from viscose).

A solution was prepared by mixing 7 parts of this substantially undegraded hydroxy ethyl cellulose ether (water-free basis) with 9 parts of solid sodium hydroxide and sufficient water to make a total of 100 parts, chilling to 0° C., with stirring, and finally allowing the solution to warm up to room temperature. At 25° C., the viscosity of this solution was 20.2 times that of pure glycerol. This viscosity was taken as 1.0 as a standard.

A portion of this solution was spread on glass plates to a depth of 0.015 inch. The plates, carrying this film of solution, were placed in 10% sulphuric acid solution at room temperature for five minutes in order to coagulate the ether. The resulting films were removed from the plates, washed acid-free in water, then immersed in a 5% glycerol solution at 58–60° C., for one minute while supported on a frame, and then allowed to dry. The films so prepared were clear, transparent and of good wet and dry strength. The films so produced were of good commercial quality.

The following test example is given by way of illustrating the invention and not in a limiting sense, (the parts are by weight).

100 parts of the standard hydroxy ethyl cellulose prepared as described were mixed with 2,000 parts of 0.5% hydrochloric acid solution at room temperature and heated to 100° C., for 35 minutes and kept at 100° C., for 30 minutes. The material was separated from the acid by filtration, washed free of acid with water at room temperature, and allowed to air-dry until the moisture content was 6.0%.

7 parts of the dried material (water-free basis) were mixed with 9 parts of solid sodium hydroxide and sufficient water to make 100 parts, then chilled to 0° C., with stirring, (to effect solution of the degraded ether), and the solution was allowed to warm up to room temperature.

Portions of this solution were spread on a glass plate to a depth of 0.015 inch. The plate was immersed in 10% sulphuric acid for five minutes to coagulate the degraded ether. When removal of the film from the plate was attempted, the film disintegrated. Small fragments of the film could be removed, but these disintegrated quickly when an attempt was made to wash them in water.

The solution viscosity of the degraded product was tested at 25° C., and found to be 0.0043 as compared with that of the above mentioned substantially undegraded standard hydroxy ethyl cellulose ether taken as unity.

This degraded product was found to be insoluble, (*a*) in water at room temperature and (*b*) in a mixture comprising 50% water and 50% ethyl alcohol at room temperature.

Various modifications of this degrading treatment were tried out (different concentrations of acid, different temperatures of treatment, and different time periods). It was found that if the ether is so far degraded that the solution viscosity is substantially below one-tenth of that of the substantially undegraded ether, the degrading is sufficient to be fairly satisfactory for the present invention, and when the ether is so far degraded that its solution viscosity is substantially

below one-tenth of that of the standard ether, it is so far degraded that coherent films cannot be made by the steps of spreading into a sheet, coagulation, washing and drying, applied to the caustic alkali solution of the degraded ether.

But for the best results, the degradation of the cellulose ether is preferably carried so far that the solution viscosity of the degraded ether is between 0.002 and 0.01 times that of the substantially undegraded ether.

Degrading to below a solution viscosity of 0.002 times that of the substantially undegraded ether, so long as too great a portion of the ether does not become water soluble, does not appear to do any harm.

The present application is, in major part, a continuation of copending application Serial No. 228,715, filed September 6, 1938. The degrading of the cellulose derivatives, and the product so produced as set forth herein, are claimed in a concurrently filed application Serial No. 469,839, and the use of such degraded cellulose derivatives in the unxanthated condition, for dressing fibrous and/or textile material, and the products thereby produced, are claimed in said application No. 469,839.

What is claimed is:

1. A process of treating a textile material which comprises mixing with a caustic alkali solution, a xanthate of a degraded cellulose ether, which ether in the unxanthated state is insoluble in water but which at least is partially soluble in dilute caustic alkali solution, and which degraded cellulose ether is of substantially the same degree of degradation as the herein described product obtained by mixing a cellulose ether of a low degree of etherification with 20 to 30 times its weight of hydrochloric acid solution of 0.5% strength and heating the mixture to 50° to 100° C., for between half an hour and four hours, dressing the textile material with a fluent composition containing the xanthated product, and thereafter treating the so dressed textile material with a coagulating agent.

2. In the process of dressing a textile material with a xanthate of an alkali soluble, water insoluble cellulose derivative selected from the group consisting of cellulose ethers, cellulose esters, cellulose thiourethanes and mixed cellulose ether-esters, by xanthating such cellulose derivatives, dressing the textile material with a solution of such xanthate in a caustic alkali solution and coagulating the cellulose derivative on said textile material, the step of degrading the cellulose derivative before xanthating, such degrading operation being carried to the extent of reducing the solution viscosity to substantially below one-tenth of the solution viscosity of the substantially undegraded cellulose derivative.

3. A process of treating a textile material which comprises mixing with a caustic alkali solution, a xanthate of a degraded cellulose ether, which ether is insoluble in water but of which at least a substantial part is soluble in dilute caustic alkali solution, and which degraded cellulose ether in the unxanthated state is of approximately the same degree of degradation as the herein described product obtained by mixing a water insoluble alkali soluble cellulose ether of a low degree of etherification with several times its weight of sulphuric acid of 55 to 60% strength, and agitating for 6 to 12 hours at 15° to 20° C., then washing out the acid with water, xanthating the degraded cellulose ether; dressing the textile material with a fluent mixture containing such xanthate and said caustic alkali solution, and thereafter treating the so dressed textile material with a coagulating agent.

4. A process of treating a textile material which comprises mixing with a caustic alkali solution, a xanthate of a degraded cellulose ether, which ether is insoluble in water but of which at least a substantial part is soluble in dilute caustic alkali solution, and which degraded cellulose ether is of approximately the same degree of degradation as the herein described product obtained by mixing a water insoluble alkali soluble cellulose ether of a low degree of etherification with about 20 to 30 times its weight of bleaching powder solution of 4° to 10° Bé., letting stand for 12 to 24 hours, straining off the solution, optionally exposing to the air for 12 to 24 hours, washing out with water, acidifying with a weak organic acid of a strength corresponding to acetic acid of about 3% to 5%, and washing out the acid, xanthating the so degraded cellulose ether, dressing the textile material with a fluent mixture containing a caustic alkali and containing the xanthate so produced, and thereafter treating the so dressed textile material with a coagulating agent.

5. A process of treating a textile material which comprises mixing with a caustic alkali solution, a xanthate of a degraded cellulose ether, which ether is insoluble in water but of which at least a substantial part is soluble in dilute caustic alkali solution, and which degraded cellulose ether is of approximately the same degree of degradation as the herein described product obtained by mixing a water insoluble alkali soluble cellulose ether of a low degree of etherification with a large excess of a 0.7% permanganate solution and maintaining at 90 to 100° C., for an hour, washing, pressing out the excess of water, mixing with about 2.3 to 2.4 parts of caustic soda solution of 18% strength, per one part of the original cellulose ether, optionally heating to 50° C., letting stand at 12–20° C., for 12 to 30 hours, acidifying, reducing the residual manganese compounds and washing with water, xanthating the degraded cellulose ether so produced, dressing the textile material with the mixture so produced, and thereafter treating the so dressed textile material with a coagulating agent.

6. A process of finishing a textile material which comprises applying thereto a dispersion containing a xanthate of a deeply degraded water-insoluble derivative of a cellulosic body, in which derivative, a hydroxyl hydrogen atom of the cellulose molecule is substituted by an organic radical, and which cellulose derivative, in the non-xanthated condition, has been degraded to a solution viscosity between 0.002 and 0.01 times that of the substantially undegraded cellulose derivative, and which non-xanthated degraded derivative is at least partially soluble in dilute caustic alkali solution; and coagulating such degraded cellulose derivative on the textile material.

7. A process of finishing textile materials which comprises applying thereto a solution of a xanthate of a water-insoluble water-resistance degradation product of a cellulose ether in a liquid dispersing medium containing dissolved caustic alkali, which cellulose ether in the non-xanthated condition is at least partially soluble in such alkaline dispersing medium and which cellulose ether has a solution viscosity between 0.002 and 0.01 times that of the substantially undegraded cellulose ether and which degraded

cellulose ether is so far degraded as to be incapable of yielding coherent films which do not disintegrate during the series of steps of coagulation, washing and drying; and coagulating the degraded cellulose ether on the textile material in a form which is substantially fast to laundering, and thereafter washing the so treated textile material in water and drying the same.

8. A process as in claim 7, in which the cellulose ether, before the treatment to degrade the same, is one that is water insoluble but which can dissolve in caustic alkali solution under refrigeration.

9. A process of finishing textiles which comprises the step of applying thereto, a mixture of a xanthate of a water insoluble alkali-dispersible degraded cellulose ether and a dispersing agent, such mixture being selected from the group consisting of complete dispersion, partial dispersion, complete solution, incomplete solution, colloidal suspension, paste and magma and the degree of degradation of the cellulose ether being so great that the degraded ether has a solution viscosity between 0.002 and 0.01 times that of the substantially undegraded cellulose ether.

10. A process of finishing a textile material which comprises treating such textile material with a dispersion in caustic alkali solution, of a xanthate of a deeply degraded water insoluble alkali soluble cellulose derivative selected from the group consisting of cellulose ethers, cellulose esters, cellulose ether-esters and cellulose thiourethanes and thereafter coagulating said degraded cellulose derivative, the solution viscosity of the unxanthated cellulose derivative being between 0.002 times and 0.01 times the solution viscosity of the substantially undegraded cellulose derivative.

11. In the process of dressing a textile material with a xanthate of an alkali soluble, water insoluble cellulose derivative selected from the group consisting of cellulose ethers, cellulose esters, cellulose thiourethanes and mixed cellulose ether-esters, by xanthating such cellulose derivatives, dressing the textile material with a solution of such xanthate in a caustic alkali solution and coagulating the cellulose derivative on said textile material, the step of degrading the cellulose derivative before xanthating, such degrading operation being carried to the extent of reducing the solution viscosity to between 0.002 times and 0.01 times the solution viscosity of the substantially undegraded cellulose derivative.

12. A process for dressing a textile material with a degraded cellulose ether, such degraded ether having the characteristics that it is at least partially soluble in dilute caustic alkali solution and substantially insoluble in water and which is incapable of forming coherent films which do not disintegrate in the coagulating bath or in the washing water whereinto they are introduced from the said coagulating bath or on being dried and which degraded ether is incapable of forming films which are suitable for practical use as films, wherein an alkali soluble, water insoluble cellulose ether is treated with an agent selected from the group consisting of hydrolyzing agents, degrading agents and oxidizing agents, until a product is formed which has a solution viscosity substantially below one-tenth of the solution viscosity of the substantially undegraded cellulose ether, and which still remains substantially insoluble in water and at least partially soluble in caustic alkali solution, and thereafter reacting upon the so degraded cellulose ether with a caustic alkali and carbon disulphate to form a xanthate which is at least partially soluble in dilute caustic alkali solution, dressing a textile material with a solution of the reaction product and thereafter coagulating such degraded cellulose ether in intimate contact with such textile material.

13. A process which comprises forming a xanthate of a degraded cellulose derivative by subjecting a water insoluble alkali soluble cellulose derivative to the action of a degrading agent until the solution viscosity of the degraded cellulose derivative is between 0.002 times and 0.01 times the solution viscosity of the substantially undegraded cellulose derivative, washing out water solubles, xanthating the water insoluble degraded cellulose derivative, thoroughly incorporating the xanthate with a caustic alkali solution, impregnating a textile material with such solution, and coagulating the degraded cellulose derivative.

14, A composition of matter for use in the dressing of fibrous and textile material which comprises a xanthate of a deeply degraded water insoluble cellulose derivative selected from the group consisting of ethers, esters, ether-esters and thiourethanes, such xanthate being carried in a dilute caustic alkali solution, such xanthated product being at least partly soluble in such dilute caustic alkali solution, and such degraded cellulose derivative being so far degraded that its solution viscosity is between 0.002 times and 0.01 times the solution viscosity of the substantially undegraded cellulose derivative.

15. A process which comprises forming a xanthate of a degraded cellulose oxy-organo derivative by subjecting a water insoluble alkali soluble oxy-organo cellulose derivative to the action of a degrading agent until the solution viscosity of the degraded cellulose derivative is between 0.002 times and 0.01 times the solution viscosity of the substantially undegraded cellulose derivative, washing out water solubles, xanthating the water insoluble degraded cellulose derivative, and thoroughly incorporating the xanthate with a caustic alkali solution.

16. A xanthate of a deeply degraded cellulose ether, the extent of degradation of the said ether being such that the solution viscosity of such degraded ether is not substantially greater than one one-hundredth of that of the corresponding substantially undegraded cellulose ether.

17. A process of producing a xanthate of a deeply degraded cellulose ether, which cellulose ether is insoluble in water but of which at least a substantial part is soluble in dilute caustic alkali solution, and which degraded cellulose ether is of approximately the same degree of degradation as the herein described product obtained by mixing a water insoluble alkali soluble cellulose ether of a low degree of etherification with about 20 times its weight of an alkaline 0.7% solution of permanganate for about 4 hours, washing, removing the excess of wash water, mixing with about 2.3 to 2.4 parts of 18% NaOH solution, per one part of the original cellulose ether, optionally heating to 50° C., then letting stand at 18–20° C., for 12 to 36 hours, acidifying, reducing the residual manganese compounds, and washing; which process comprises reacting upon such degraded cellulose ether, with carbon disulphide and caustic alkali, in the presence of water.

18. A process for the manufacture of a xan-

thate of a degraded cellulose ether, such degraded ether having the characteristics that it is at least partially soluble in dilute caustic alkali solution and substantially insoluble in water and which is incapable of forming coherent films which do not disintegrate in the coagulating bath or in the washing water whereinto they are introduced from the said coagulating bath or on being dried and which degraded ether is incapable of forming films which are suitable for practical use as films, wherein an alkali soluble, water insoluble cellulose ether is treated with an agent selected from the group consisting of hydrolyzing agents, degrading agents and oxidizing agents, until a product is formed which has a solution viscosity substantially below one-tenth of the solution viscosity of the substantially undegraded cellulose ether, and which still remains substantially insoluble in water and at least partially soluble in caustic alkali solution and thereafter reacting upon the so degraded cellulose ether with a caustic alkali and carbon disulphide to form a xanthate which is at least partially soluble in dilute caustic alkali solution.

19. A xanthate of a deeply degraded cellulose ether, the extent of degradation of the said ether being such that the solution viscosity of such degraded ether is below one-tenth of that of the corresponding substantially undegraded cellulose ether.

ANTONIE LILIENFELD,
Administratrix C. T. A. of the Estate of Leon Lilienfeld, Deceased.

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