Patented June 17, 1947

2,422,572

UNITED STATES PATENT OFFICE

2,422,572

DRESSING FIBROUS AND TEXTILE MATERIALS

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No Drawing. Application December 22, 1942, Serial No. 469,839. In Great Britain September 7, 1937

39 Claims. (Cl. 117—166)

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This invention relates in general to a process of treating textiles and in particular to a process for coating, pad-dyeing and printing textile fabrics. The invention also includes the production of degraded cellulose derivatives (e. g. ethers) for use in treating textiles, and a solution or dispersion of such degraded cellulose derivatives, for dressing textiles.

In his 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, 2,095,524, 2,165,392, 2,231,927, 2,265,914 to 2,265,919 and in British Patent 374,964 (corresponding to French Patent 715,551, delivered September 29, 1931), the present inventor has described many types of cellulose ethers which are soluble in alkali solution, but insoluble in water.

In these patents he further showed that these "alkali soluble, water-insoluble" cellulose ethers can be successfully used 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.

Furthermore, in his U. S. Patents 1,858,097, 1,910,440, 2,021,861, 2,163,607, 2,165,393, 2,265,914, 2,265,915, 2,265,917, 2,265,918, 2,296,856 and in British Patents 367,920, 459,122, 462,283, 462,456 (and cognate specifications), 462,712, 474,223 and 503,830, he described xanthates of suitable cellulose ethers, including xanthates of alkali-soluble cellulose ethers, and processes for making such xanthated ethers and methods for treating fibrous material therewith. These xanthated ethers are included in the expression "xanthates of those ethers of cellulose in which the content of hydroxyl hydrogen substituted 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

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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 softness and textile appearance. This is due in part to the fact that all the ethers made heretofore are "film-forming" and have high viscosities, so that they invariably impart a stiffness to the treated material which is undesirable for some purposes. The term "finishing" will hereinafter be used to cover this entire group of treatments.

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

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

The reference in the previous paragraph, to textile materials of artificial origin is intended to embrace not only natural fibres but also viscose rayon, cellulose acetate or other cellulose ester threads and fabrics, "nitro-silk" (or threads of 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, e. g. "nylon." 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 effect even in the 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 up to 10% or even up to 30 or 50 percent, 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 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 short of becoming soluble in water, there are obtained alkali-soluble cellulose ethers which are unusually valuable materials for finishing fibrous materials as herein defined. When such degraded cellulose ethers are applied in the form of their solutions or pastes in dilute caustic alkali solution to fibrous materials, the ethers do not substantially impair the soft feel of the fibrous materials to which they are applied, and the finishes thus obtained are in most cases relatively fast to commercial laundering. In addition they do not substantially change the textile appearance of the fibrous materials to which they are applied. Such treatment also does not substantially stiffen the fibrous materials so treated. While the invention herein will be described in connection with the treatment of water insoluble alkali soluble cellulose ethers, the invention is also applicable to the treatment of other oxy-organo compounds of cellulose, including in particular, cellulose ether-esters, cellulose esters and cellulose thiourethanes having the stated solubility in caustic alkali solution, and which are insoluble in water.

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 a small amount of degradation of the cellulose molecule produced, but heretofore the factors in such prior processes have been such 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) 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 a controlled and definite extent (short of producing water solubility), so that the ethers are no longer capable of producing coherent usable films. Moreover, in order to produce finished textiles that are laundry-fast, it will be readily understood that the finish on the textiles must be composed of material which is insoluble in water.

From the foregoing it can be gathered that

one object of the invention is to prepare and utilize cellulose ethers which are soluble in dilute caustic alkali solution but not 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 and utilize 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 cellulosic fibller 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, water-insoluble cellulose ethers as herein defined, the present invention comprises treating a film-forming alkali-soluble water-insoluble cellulose ether with one or more degrading agents which are capable of depriving the cellulose ether of its capacity to form coherent 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 coherent films suitable for practical use.

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.

As initial materials in the present invention there may be used any film-forming cellulose ethers which contain not more than one alcohol radical, for example one alkyl group or hydroxyalkyl group, or 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 degree of etherification, such ethers being described for example in British Patent No. 374,964 and also in the prior literature, those ethers containing over about 14 (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. The oxy-organo derivatives of cellulose (e. g. cellulose ethers, esters, ether-esters, and 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)."

There may also be used as the initial cellulose ether (for degrading), any of the film-forming alkali-soluble, water-insoluble cellulose ethers described in U. S. Patents 2,265,919, 2,231,927, 2,265,916, 1,858,097, 1,910,440, 2,100,010, 2,265,914, 2,265,915, 2,163,607 or 2,296,856, or in British Patents 367,920, 462,283 or 503,830, or 374,964.

In other words, not only such film-forming cellulose ethers of the aforementioned types as can be prepared by the processes and methods described in the patents given above, but also film-forming cellulose ethers of the aforementioned types can be used herein, however prepared, can be modified (degraded) and be used in the present invention.

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 means of converting the film-forming cellulose ethers into non-film forming ethers is the treatment of the film-forming cellulose ethers with such agents or mixtures of agents as exert a hydrolyzing and/or degrading and/or oxidizing action on the film-forming cellulose ethers, the conditions, particularly the temperature and/or duration of the treatment being such as to deprive the cellulose ethers of the aforementioned types of their capacity to form coherent films. Such result will be hereinafter referred to, for brevity, as being "sufficiently degraded."

The cellulose ethers degraded to the extent indicated in the preceding paragraph, will hereinafter be termed "water-insoluble alkali-soluble, non-film-forming 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 salt capable of generating acid, 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 preferably 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 carrying the present invention into effect, they may be applied to the cellulose ethers of the aforementioned types in concentrated solutions or preferably 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.

Treating the film-forming cellulose ethers with dilute acids is simpler and easier to control than

by treating such ethers with concentrated acids.

The conversion of the film-forming cellulose ethers into the aforementioned non-film-forming types (i. e. the degrading treatment) 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 film-forming cellulose ether 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.

Second method.—This method consists in treating a film-forming cellulose ether with an excess of a dilute mineral acid as in the first method, but at a raised temperature, with or without pressure.

Third method.—This method consists in impregnating or otherwise mixing a film-forming cellulose ether with an excess of a dilute mineral acid of the types described in the first method at room temperature, removing the excess of the acid by pressing, centrifuging or the like (but without washing), 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.

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, 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, by themselves or in mixture with mineral acids may be used. 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, optionally in the heat.

Fourth method.—This method consists in treating the film-forming cellulose ether 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.

Fifth method.—This method consists in treating, preferably with stirring or otherwise agitating, a film-forming cellulose ether, 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 film-forming cellulose ether, at a temperature not substantially exceeding room temperature or at a temperature below room temper-

ature 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 film-forming cellulose ether, in the presence of alkali, for example in the 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 or bromine until the cellulose ether becomes sufficiently converted.

Eighth method.—This method consists in treating a film-forming cellulose ether with chlorine or bromine in the 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 film-forming cellulose ether 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 and oxidizing 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 in refrigerated aqueous caustic alkali solution or at least substantially dispersible therein, which is insoluble or only soluble in a minor proportion in water and which is "incapable of forming coherent films" as above described, (i. e. until the ether "becomes sufficiently converted").

The degrading should be stopped before too much (say 30–50%) of the weight of the initial cellulose ether of the degraded product becomes water-soluble.

Since the paramount factors giving the desired result (sufficient conversion), are either the time of the treatment or the temperature of the treatmen 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 for the endpoint 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% 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 cellulose ether under treatment gives a solution or dispersion or paste or magma or mass, which spread on the glass plate and coagulated, 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, or is disintegrated during washing or during drying.

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) substances can be used as degrading agents, 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 a 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 the degraded non-film-forming cellulose ethers 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), preferably 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 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 the oxygen of the air or chemically produced oxygen can be used.

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

For the production of finishes as herein defined, the process comprises applying to a fibrous material a solution of a degraded cellulose ether in an aqueous caustic alkali solution, then squeezing out excess of said solution, then treating the so-treated textile with a setting or coagulating bath, then washing 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, thiouretanes, etc., can be used. The term "oxy-organo derivative of cellulose" being hereinafter used to cover such group of substances. The caustic alkali solution can conveniently be a 6–10% NaOH solution in water. One or several of the degraded cellulose oxy-organo bodies may be used. The solution may be made at room temperature, if the cellulose derivative used will dissolve at such temperature, but preferably the degraded cellulose derivative is one that will dissolve only 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., guanadine, 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 degraded cellulose ether, other colloids such as alkali soluble cellulose derivatives, e. g., ethers, or viscose or starch or dextrine or any compatible sizing, for dressing textiles, can be used. The fibrous material to be finished 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 setting or coagulating bath may be any of those commonly used in the production of regenerated articles 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 inventor has further found that, when cellulose ethers of the very lowest degree of etherification, i. e. cellulose ethers which cannot be dissolved in caustic alkali solution (even by freezing) and are insoluble both in water and 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 further embraces the discovery that, on being xanthated, e. g. treated with carbon bisulphide in presence of caustic alkali, the cellulose ethers degraded according to the present invention yield xanthates which, when applied to fibrous materials of any kind yield 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 it possible for the first time to convert yarn or fabric which has a certain fullness, density, thickness and weight into a yarn or

fabric which has a greater and even far greater fullness, density, thickness and weight, and which yarn and fabric in regard to the softness of their feel, their lack of stiffness, their appearance and their dyeing properties are not substantially different from the yarn or fabric before treatment according to the present invention and which yarn and fabric are substantially fast to commercial laundering and sufficiently resistant to wear.

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 may be in a conglutinated or non-conglutinated condition, and which also are soft to the touch, sufficiently fast to laundering and which, if in a conglutinated condition, 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.

It is possible, according to the present invention, to produce 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 substantially superior to the textile materials 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 cellulose or non-cellulosic nature, for instance, cellulose precipitated from cellulose solutions (including viscose, and solutions of cellulose in cuprammonia, urea, thiourea, cyanates or others), starch, dextrine, 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. When used as fillers, the cellulose ethers prepared according to the present process are superior to the mineral fillers (such as china clay, zinc white, talc (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 substantially stiffen the textile finishes compared with 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 the treated material. 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 and their density.

Owing to their physical nature, particularly their softness and flexibility, the degraded cellulose ethers are easier fixable on and in the textile material, than the hard and rigid mineral or organic fillers used hitherto. The resistance to mechanical 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 with far smaller proportions (by weight) of the present degraded cellulose ethers used as fillers, than the proportions of the hitherto used mineral or organic fillers necessary for the preparation of finishes exhibiting the same covering power.

Since the lack of fillers capable of giving 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 degraded as herein described, supply another desideratum in the art of finishing fibrous materials, when used in their solid state as fillers for finishing materials.

When the present alkali-soluble water-insoluble degraded cellulose ethers are not used as fillers but are used in compatible admixture with another finishing material as herein defined, they contribute towards its binding effect, to its fastness towards laundering and resistance to wear.

When a mineral filler is added to the solution comprising the compatible admixture of the degraded cellulose ether and the known finishing material present, the degraded cellulose ether cooperates with the other colloidal finishing agent 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.

The application of the solutions or dispersions of the cellulose ethers prepared as above, to the fibrous materials may be accomplished by wholly or partially coating, impregnating, padding or printing or otherwise covering or imbuing a fibrous material as herein defined with the solution or dispersion, 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 of applying solutions of alkali-soluble cellulose ethers (which are not considerably degraded) to fibrous materials, are described and illustrated by many examples. The degraded cellulose ethers prepared according to the present invention may be applied (e. g. in solution) to fibrous materials by any of the methods shown in said prior patents.

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 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 of alkali-soluble cellulose ethers), may be added to the solutions or dispersions of the degraded cellulose ethers, prior to or during their application thereof to the fibrous or textile materials.

As stated above, valuable products which i. e. are also suitable for finishing as herein defined, can be obtained when the cellulose ethers degraded 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 carrying out of the modification of the present invention in which the degraded cellulose ethers are used as fillers is very simple. It consists in adding the degraded cellulose ether in the solid moist or dry state, and preferably finely divided to a solution or dispersion of a colloidal or binding substance, which may be of cellulosic or non-cellulosic nature, and which is suitable for the production of finishes as herein defined. Besides the cellulose ether in the solid state, also other fillers, such as china clay, talc, zinc white, lithopone, barium sulphate, etc., may be used.

In order to more completely explain the present invention, the following specific examples are given. 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. Parts are given by weight.

Example I, A to C

The parent cellulosic material may be a simple or mixed cellulose ether or a cellulose ester or a cellulose thiourethane, 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 derivative (ether or ester or thiourethane) are immersed in, or otherwise mixed with a large excess, say 20,000 to 30,000 parts of hydrochloric acid of 0.5 per cent strength at room temperature in a suitable open or closed vessel made from acid-resistant material, optionally 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 or thiourethane, 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 either dried and dissolved in caustic soda solution or dissolved therein in the undried, i. e. moist state. In the latter case the water content in the moist product is to be taken into account when calculating the strength of the caustic soda solution to be used in the dissolving step.

The washed and dried product is mixed with so much caustic soda solution of 9 per cent strength at 15 to 18° C., as to yield a suspension or solution (according to the starting cellulose derivative subjected to the hydrolyzation), containing 7 per cent of the degraded cellulose ether, which suspension or solution respectively is free from, or contains a small amount of undissolved constituents. Or the still wet degraded cellulose derivative is similarly treated with a proportionately stronger NaOH solution.

According to the appearance of the suspension or incomplete solution, 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 few minutes usually being sufficient.

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, with one or (optionally with intermediate drying) more coatings (impregnations) of the solution thus produced, and the coated or impregnated or filled material, in the wet state or after intermediate drying, is introduced into any coagulating bath known in the viscose art. This may be the so-called Müller bath, for instance a bath containing per 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.

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

It is to be understood that the dressed textile 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 derivative.

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 derivative.

Instead of hydrochloric acid solution of 0.5% strength, given in this example, hydrochloric acid solutions of other concentrations, e. g., 0.05% 0.1%, 0.2%, 1% or 2%, can be used.

Example II, A to C

The process is conducted as in Example I, A to C except that, to the solution of the degraded cellulose derivative, is added powdered talc, china clay or similar mineral filler, in an amount 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 III, A to C

The process is conducted as in any one of the Examples I, A to C, to II, A to C, but 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 derivative) are incorporated with the solution of the degraded cellulose body.

Example IV

1,000 parts of a simple or mixed cellulose ether or cellulose ester (prepared for example according to one of the processes described in the patents enumerated in Example I, A, 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.

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

Example V

1,000 parts of a simple or mixed cellulose ether or cellulose ester (prepared, for example, according to any suitable one of the processes described in the patents enumerated in Example I, A) 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.

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

Example VI

Mode of procedure as in Example V, 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 VII

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.

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

Example VIII

Mode of procedure as in Example VII, 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 IX

The process is conducted as in Examples VII or VIII, 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 VII.

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 the freezing point (e. g. −10 to +5° C.), as well as those which dissolve therein only at or near the freezing point (i. e. −10 to +5° C.), a very 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 principally 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 substantially 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.

This product is a hydroxyl alkyl ether of cellulose and although it cannot be stated that no degrading whatever has taken place, the ether can be defined as "a substantially undegraded cellulose ether," and this term will be used hereinafter in that sense.

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., during 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 not over one-tenth of that of the substantially undegraded ether (i e. the "standard 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 below one-tenth of that of the standard (substantially undegraded) 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 a solution viscosity of below 0.002 times that of the 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 term "fibrous material" used in the specification and claims is, wherever the context permits, intended to include any material consisting of, or containing fibres, such as loose fibres, whether vegetable or animal or artificial or mixed, of any kind and in any form, or textile materials

as herein defined or paper at any stage of its preparation, paper pulp included.

The expression "textile material" in the specification and claims includes, wherever the context permits, any spun or woven textile fibres, whether animal or vegetable (for example, silk, flax, linen, hemp, ramie, jute, wool and particularly cotton) as well as artificial fibres of any kind (for example, artificial silk or artificial cotton or artificial wool or staple fibre, any one of them in the form of yarn or fabrics or knitted goods consisting of or containing artificial fibres) in the form of pure fabrics or pure knitted goods or in the form of mixed fabrics or mixed knitted goods or in the form of pure or mixed yarn in skeins, cops, or warps.

In the specification and claims hereof, the term "finish" is, wherever the context permits, intended to include impregnating, coating, dressing, filling, weighting, sizing, printing, stencilling, in short every type of finish produced by coating or treating the whole or part of the surface of, or incorporating with, or introducing into, the totality or part of the fibrous materials as herein defined in general or textile materials as herein defined, in particular one or more organic materials that may or may not contain one or more inorganic materials.

The expression "finishing" is, wherever the context permits, intended to include any process or method or operation capable of producing a finish as herein defined.

The expression "finishing material" used in the specification and claims is, wherever the context permits, intended to include any organic material by itself or in conjunction with one or more inorganic materials suitable for the production of any finish as herein defined.

The expressions "applying" and "application" as used in this specification includes, wherever the context permits, any manner of application, whether manual or mechanical, such as is customary in dressing, sizing, filling, weighting, impregnating, finishing, coating, printing or stencilling fibrous materials as defined above, whether yarn or fabrics.

The expression "filler" used in the specification and claims is, wherever the context permits, intended to include an organic or inorganic substance which is added in the solid form to a finishing material as herein defined and which is insoluble in the finishing material or in its solutions or dispersions or pastes or magmas or suspensions and which is evenly or unevenly distributed in the finishing material and in the finish as herein defined.

The term "cellulose" used in the description and claims is, wherever the context permits, intended to include cellulose, its conversion and oxidation products, such as cellulose hydrate, hydrocellulose, oxycellulose, acid cellulose and the like, in short, any body of the cellulose group which has been proposed as starting material for the preparation of cellulose derivatives or cellulose compounds of any kind.

In the specification and claims, wherever the context permits, the expressions "alkali-soluble cellulose ether," "cellulose ether which is soluble or partially soluble or incompletely soluble in caustic alkali solution" and "cellulose ether which is at least partially soluble in caustic alkali solution" are intended to include such simple and mixed cellulose ethers and such cellulose ether-esters as can be completely or partially or incompletely dissolved in caustic alkali solution at room temperature and/or at a lower temperature, for example at a temperature between room temperature and 0° C., or lower and such simple or mixed cellulose ethers and such cellulose ether-esters as cannot be completely or incompletely or partially dissolved in caustic alkali solution at room temperature, but as can be dissolved or dispersed or incompletely or partially dissolved or dispersed in caustic alkali solution by cooling their mixtures with, or suspensions or incomplete solutions in, caustic alkali solution to a temperature between room temperature and 0° C., or to 0° C., or to a temperature below 0° C., for example to minus 5° C., or to minus 10° C., or lower, and such simple or mixed cellulose ethers and such cellulose ether-esters as cannot be completely or incompletely or partially dissolved in caustic alkali solution at room temperature or at a temperature between room temperature and 0° C., or even at 0° C., but as can be dissolved or dispersed or incompletely or partially dissolved or dispersed in caustic alkali solution by cooling their mixtures with, or suspensions or incomplete solutions in, caustic alkali solution to a temperature below 0° C., e. g. to temperatures at which freezing or formation of crystals occurs, for example minus 5° or minus 10° C., or minus 15 to 20° C., or more, included.

Wherever the context permits, the term "alkali cellulose" means alkali cellulose prepared in the usual manner, namely by steeping cellulose in caustic alkali solution and removing the excess of the latter by pressing, or by mixing cellulose with such an amount of caustic alkali solution or with such amounts of caustic alkali and water as are desired to be present in the final alkali cellulose.

The expression "etherification" used in the specification and claims covers alkylation or aralkylation or hydroxyalkylation or production of hydroxy-acid derivatives (ethers), "ether" covers simple alkyl or aralkyl and hydroxy-alkyl or hydroxy-acid ethers and also mixed ethers, for example the mixed ethers hereinbefore set forth, "etherifying agents" covers alkylating and aralkylating and hydroxy-alkylating agents and halogen fatty acids.

The term "hydroxy-alkyl" is intended to include the introduction of halogenated or non-halogenated hydroxy-alkyl radicals, or di- or polyvalent alcohols in conjunction with one or more oxygen atoms or hydroxyl groups.

Wherever the context permits, the terms "alkyl, "alkylate," "alkylating agent," "alkylation" are intended to include unsubstituted or substituted (for example aralkyl groups) alkyl groups, alkylating with alkylating agents that contain unsubstituted or substituted (for example aralkyl groups) alkyl groups, alkylating agents that contain unsubstituted or substituted (for example aralkyl groups) alkyl groups, alkylation with alkylating agents that contain unsubstituted or substituted (for example aralkyl groups) alkyl groups.

The term "hydroxy-alkylating agents" is, wherever the context permits, intended to include halogen derivatives of di- or polyhydric alcohols, particularly halohydrins, such as monohalohydrine and alkylene oxides.

In the specification and claims the expression "halogen fatty acids" or "monohalogen fatty acid" includes, wherever the context permits, monochlor-, monobrom- and mono-iodo-fatty acids themselves, their derivatives (such as esters) and their salts, as well as substances and

mixtures of substances which yield monohalogen fatty acids or their derivatives.

In the appended claims, the term "liquid dispersing agent" is used in a broad sense to include liquid media in which the hydrolyzed, oxidized or degraded cellulosic bodies can be colloidally dispersed and/or partly or wholly dissolved.

In the appended claims, the term "oxy-organo derivative of cellulose" is intended to cover both ethers and esters, i. e. bodies in which a hydroxyl hydrogen atom of the cellulose molecule has been substituted by an organic radical (substituted or unsubstituted).

It has been demonstrated that the alkaline solution of the degraded cellulose ethers, with or without mineral fillers, can be kept for long periods, at atmospheric temperatures. Accordingly it is entirely feasible for a factory to prepare such solutions, and to ship these to a textile dressing plant.

While caustic soda solutions of 7 to 9% concentration, and containing 7 to 12% of the degraded cellulose ether, are referred to above, it is to be understood that more dilute or more concentrated solutions can be used, e. g. NaOH solutions of 4 to 15% containing about 3 to 20% of the degraded cellulose ether. Generally it is advisable to use as low a concentration of the caustic alkali as will dissolve the desired amount of the degraded cellulose ether.

This application is a continuation-in-part of copending application Serial No. 228,715 filed September 6, 1938. The herein described process of treating textiles with the xanthated degraded cellulose ethers and the making of such xanthated products are claimed in another application Serial No. 469,841 filed concurrently herewith.

What is claimed is:

1. A process of finishing a textile material which comprises applying thereto a dispersion in an aqueous caustic alkali solution, of a degraded cellulose derivative which is at least partially soluble in such caustic alkali solution, but insoluble in water, and in aqueous alcohol, and which degraded cellulose derivative has a solution viscosity less than one-tenth of that of the corresponding substantially undegraded film-forming cellulose derivative having the same ratio of the same substituent radical, under like conditions, and coagulating said degraded cellulose derivative on said textile material in the form of discrete particles, the cellulose derivative being one selected from the group consisting of cellulose ethers, cellulose esters, cellulose ether-esters and cellulose thiourethanes, said degraded cellulose derivative being so far degraded as to be incapable of forming a coherent film which does not disintegrate when a thin layer of the alkaline solution thereof is subjected to the series of steps, coagulating, washing and drying.

2. A process as in claim 1, in which the degraded cellulose derivative has a solution viscosity between about 0.002 and 0.01 times that of the corresponding substantially undegraded cellulose derivative under like conditions.

3. A process as in claim 1, in which the degraded cellulose derivative is a hydroxy-alkyl ether of cellulose.

4. A process as in claim 1, in which the dispersion of degraded cellulose derivative includes a coloring agent and the textile material is padded therewith.

5. A process as in claim 1, in which the dispersion of the degraded cellulose derivative is printed upon the textile material.

6. A process which comprises degrading an alcohol insoluble, alkali soluble, water insoluble oxy-organo derivative of cellulose which initially is capable of yielding a strong flexible film by introducing a thin uniform layer of a solution thereof in dilute caustic alkali solution into an acid coagulating bath, washing and drying, and which cellulose derivative initially has a high solution viscosity, which process comprises subjecting such cellulose derivative to the action of a degrading agent until the solution viscosity of the so treated cellulose derivative has fallen to below one-tenth of that of a substantially undegraded oxy-organo derivative of cellulose having the same ratio of the same substituent organic radical, and discontinuing the action of such degrading agent while the major part at least of said oxy-organo derivative of cellulose is still insoluble in water and in alcohol but capable of being dissolved in dilute caustic alkali solution, thereafter dissolving such degraded product in caustic alkali solution of about 3% to about 14% concentration, impregnating a textile material therewith, coagulating the degraded oxy-organo derivative of cellulose in the form of discrete particles on and in said textile material.

7. A process of dressing a textile material which comprises impregnating a textile material with a dispersion in a caustic alkali solution of a water insoluble degraded oxy-organo derivative of cellulose, which has been so far degraded that its solution viscosity is substantially below one-tenth of that of a substantially undegraded oxy-organo derivative of cellulose which contains the same ratio of the same substituent organic radical, and thereafter coagulating the degraded oxy-organo derivative of cellulose in the form of discrete particles on and in said textile material.

8. A process of dressing a textile material which comprises impregnating a textile material with a dispersion in a caustic alkali solution of a degraded oxy-organo compound of cellulose, which latter is substantially identical with the degraded product produced by the process of claim 22, and coagulating the degraded oxy-organo compound of cellulose, in the form of discrete particles on and in said textile material.

9. A process as set forth in claim 6, in which the degrading agent is a dilute mineral acid.

10. A process as in claim 6, in which the degrading agent has oxidizing properties.

11. A process of treating a textile material which comprises mixing with a caustic alkali solution, a degraded cellulose ether which 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 20 to 30 times its weight of hydrochloric acid solution of 0.05% to 2% strength and heating the mixture to 50° to 100° C., for between half an hour and four hours, finishing the textile material with the mixture so produced, and thereafter treating the so dressed textile material with a coagulating agent.

12. A process which comprises applying to a textile material, an alkaline solution of a degraded cellulose ether which is insoluble in water and capable of being dissolved by a NaOH solu-

tion of about 3% to about 14% concentration, and then subjecting the textile material with the solution carried thereby, to the action of a coagulating agent for said degraded cellulose ether, said degraded cellulose ether having a degree of degradation substantially equal to that of a water insoluble product produced by heating a substantially undegraded water insoluble alkali soluble cellulose ether with 20 to 30 times its weight of hydrochloric acid solution of 0.5% strength for a period between a half hour and four hours at 50° to 100° C., and then washing until acid-free.

13. Textile material carrying, intimately bonded thereto, a dressing consisting of discrete particles of a degraded water insoluble alkali soluble oxy-organo derivative of cellulose, said degraded derivative of cellulose being so far degraded that it cannot be made into a coherent film by the process of introducing a thin sheet of an alkaline solution of the cellulose derivative into an acid setting bath, washing the product and drying the same, and said degraded cellulose derivative being one selected from the group consisting of cellulose ethers, cellulose esters, cellulose ether-esters and cellulose thiourethanes, such degraded cellulose derivative being insoluble in water but at least partially soluble in dilute caustic alkali solution.

14. A product as in claim 13, which also carries a coloring matter.

15. A product as in claim 13 in which the degraded cellulose derivative is a degraded hydroxyalkyl cellulose ether.

16. A product as in claim 13 in which the degraded cellulose derivative is so far degraded that its solution viscosity is between 0.01 and 0.002 times that of the corresponding substantially undegraded cellulose derivative containing the same ratio of the same substituent groups, under like conditions.

17. As an agent for treating textile materials, the herein described liquid which comprises a dispersion in an aqueous caustic alkali solution, of a degraded cellulose derivative which contains a cellulose residue and which is degraded to the extent specified in claim 1.

18. A process for the manufacture of a new degraded cellulose ether having the characteristics that it is at least partially soluble or dispersible in dilute caustic alkali solution and substantially insoluble in water and which is brittle and friable when dry, and incapable of forming from a thin layer of a solution thereof in dilute caustic alkali solution, coherent films which do not disintegrate in an acid coagulating bath or in the washing water whereinto it is introduced from the said coagulating bath or on being dried, and which degraded cellulose ether is incapable of forming films which are suitable for practical use as films, which process comprises treating an alkali soluble water insoluble cellulose ether capable of forming a coherent film and which ether is substantially insoluble in strong alcohol and in dilute alcohol, with a degrading agent capable of degrading the cellulose molecule, and continuing said treatment until a product is formed which has the aforesaid characteristics, and stopping said treatment while a major portion of the ether remains substantially insoluble in water and in strong alcohol and in dilute alcohol and at least partially dispersible in caustic alkali solution.

19. A process for the manufacture of a new degraded cellulose ether having the characteristics that it is at least partially soluble or dispersible in dilute caustic alkali solution and substantially insoluble in water and in alcohol and which is too far degraded to yield coherent films but breaks up into particles by introducing a thin uniform layer of the alkaline solution of such ether into an acid coagulating bath or in the washing water whereinto it is introduced from the said coagulating bath or on being dried, and which degraded ether is too far degraded to be capable of forming films which are suitable for practical use as films, which process comprises treating an alkali soluble water insoluble alcohol insoluble film-forming cellulose ether with a degrading agent, continuing said treatment until a degraded cellulose ether remains which is degraded to the extent stated, and stopping said treatment while a major portion of said degraded ether remains insoluble in water and in alcohol but at least partly soluble in refrigerated caustic alkali solution.

20. A process for the manufacture of a new degraded cellulose ether having the characteristics that it is at least partially soluble or dispersible in dilute caustic alkali solution and substantially insoluble in water and in alcohol and which is incapable of forming coherent films by treating a thin layer of its alkaline solution with an acid setting bath, which do not disintegrate in the said acid bath or in the washing water whereinto it is introduced from the said acid bath or on being dried, and which degraded cellulose ether is incapable of forming films which are suitable for practical use as films, which process comprises treating an alkali soluble water insoluble alcohol insoluble film-forming cellulose ether with a degrading agent, continuing said treatment until degrading of the cellulose ether has so far progressed that the degraded cellulose ether becomes incapable of forming coherent films by treating a thin layer of its alkaline solution with an acid setting bath, which do not disintegrate in the said acid bath or in the washing water whereinto it is introduced from said setting bath or on being dried and which degraded cellulose ether is incapable of forming films which are suitable for practical use as films, and then stopping such treatment while at least the major part of the degraded cellulose ether remains insoluble in water and in alcohol but at least partly soluble in refrigerated caustic soda solution of 3 to 14% concentration.

21. A process as covered in claim 20 in which the degrading agent is a dilute acid.

22. A process for the manufacture of a new degraded oxy-organo compound of cellulose having the characteristics that it is at least partially soluble and dispersible in refrigerated dilute caustic alkali solution and substantially insoluble in water and in alcohol and which is too far degraded to be capable of forming coherent films by bringing a thin layer of its alkaline solution into an acid coagulating bath, which does not disintegrate in the said coagulating bath or in the washing water whereinto it is introduced from said coagulating bath or on being dried, and which degraded oxy-organo compound of cellulose is incapable of forming films which are suitable for practical use as films, which process comprises treating an alkali solubile water insoluble alcohol insoluble oxy-organo compound of cellulose capable of forming a coherent film, with a degrading agent, continuing said treatment until the oxy-organo compound of cellulose becomes so far degraded that it remains insoluble

in water but capable of at least partly dissolving in refrigerated NaOH solution of about 3 to 14% concentration and until degrading of said oxy-organo compound of cellulose has progressed to the extent stated, and then stopping such degrading treatment while the major part at least of the degraded oxy-organo compound of cellulose remains insoluble in water and in alcohol, but capable of at least partly dissolving in refrigerated dilute caustic alkali solution.

23. A process as claimed in claim 18, wherein the degrading agent used for treating the cellulose ether is a substance having acid properties.

24. A process as claimed in claim 18 wherein the degrading agent used for treating the cellulose ether is a substance having an oxidizing action.

25. A process as claimed in claim 18, wherein the cellulose ether used is a mixed ether which is substantially insoluble in water but which can be dissolved in dilute caustic alkali solution under refrigeration.

26. A deeply degraded cellulose ether which is substantially insoluble in water and in dilute acids at all temperatures, and insoluble in organic solvents, and which can readily be dispersed in caustic alkali solution under refrigeration, and of which a substantial part at least will dissolve in caustic alkali solution under refrigeration, and which cellulose ether is too far degraded to produce a coherent film by the steps of subjecting a thin layer of its solution in caustic alkali solution to coagulation, washing and drying, and which cellulose ether in the dry state is friable.

27. As a new product, a deeply degraded oxy-organo compound of cellulose, which is insoluble in water and in alcohol and in acetone and in dilute alcohol and in dilute acetone, but which will at least partly dissolve in dilute caustic alkali solutions under refrigeration, and from a solution of which componud in caustic alkali solution acidification will coagulate said degraded cellulose derivative, such product being too far degraded to form a coherent film by the series of steps of treating a thin uniform layer of the alkali solution thereof with an acid coagulating bath, then washing and then drying, such cellulose derivative in the dry state being friable and brittle.

28. A product as claimed in claim 26, which has a solution viscosity of substantially below one-tenth of that of a substantially undegraded cellulose ether having the same content of the same alcohol radical substituted for hydroxyl hydrogen.

29. A degraded oxy-organo compound of cellulose, which product is soluble in dilute caustic alkali solution, which product has a solution viscosity below one-tenth of that of the substantially undegraded cellulose compounds having the same proportion of the same organic substituent radical, and which product is insoluble in water, insoluble in strong alcohol and insoluble in dilute alcohol, and which product is friable and brittle.

30. A degraded cellulose ether, which product has a solution viscosity below one-tenth of that of the corresponding substantially undegraded cellulose ether, and which product is insoluble in water, insoluble in strong alcohol and insoluble in dilute alcohol, and at least partly soluble in a refrigerated dilute aqueous solution of caustic alkali, which product is friable and brittle.

31. A degraded oxy-organo compound of cellulose, which product has a solution viscosity between 0.002 times and 0.01 times that of the corresponding substantially undegraded cellulose compound, and which product is insoluble in water, insoluble in strong alcohol and insoluble in dilute alcohol, and at least partly soluble in a refrigerated dilute aqueous solution of caustic alkali, which product is friable and brittle.

32. As a novel sizing material for the dressing of textiles, a deeply degraded water insoluble alkali soluble cellulose ether, dissolved in dilute aqueous caustic alkali solution, such degraded cellulose ether, when in the solid state having the properties as set forth in claim 26.

33. A process of degrading a water insoluble, alcohol insoluble cellulose ether of a kind which is capable of being dissolved in a dilute aqueous caustic alkali solution to give a cellulose ether solution from which high quality strong, flexible films can be produced by subjecting a thin layer of an aqueous alkaline solution of such ether to the action of an acid coagulating bath, washing and drying, which process comprises subjecting such a cellulose ether to the action of a reagent capable of degrading cellulose, and continuing such treatment until the treated ether no longer has the property of giving a coherent film by subjecting a thin layer of an alkaline solution thereof to the action of an acid coagulating bath, washing and drying, but stopping such treatment with such reagent while the major part at least of said cellulose ether remains insoluble in water and in alcohol and thereafter washing such degraded cellulose ether with water until substantially free from water soluble constitutents.

34. A process as in claim 33 in which the reagent for producing degradation of the cellulose ether is a dilute mineral acid.

35. A process as in claim 33, in which the degrading agent has oxidizing properties.

36. A process of degrading a cellulose ether which has a high solution viscosity, which ether is insoluble in water and in such organic solvents as are capable of dissolving highly etherified ethers of cellulose and which initial ether is capable of being converted into a strong flexible film by bringing a thin uniform layer of a solution of the ether in dilute aqueous caustic alkali solution into contact with a bath of an acid coagulating solution, washing and drying, which process comprises treating such an ether with a degrading agent until the solution viscosity of the said ether has fallen to below one-tenth of that of a substantially undegraded cellulose ether having the same ratio of the same organic substituent radical, and discontinuing such treatment with the degrading agent before the major part of the said cellulose ether becomes soluble in water and while the said ether remains capable of being dissolved in dilute caustic alkali solution.

37. A process as in claim 36, in which the degrading agent is a dilute mineral acid.

38. A process as in claim 36, in which the degrading agent has oxidizing properties.

39. A deeply degraded cellulose ether which is substantially insoluble in water and in dilute acids at all temperatures, and insoluble in organic solvents, and which can readily be dispersed in caustic alkali solution under refrigeration, and of which a substantial part at least will dissolve in caustic alkali solution under refrigeration, and which cellulose ether is too far degraded to produce a coherent film by the steps of subjecting a thin layer of its solution in caustic alkali solution to coagulation, washing and dry-

ing, and which cellulose ether in the dry state is friable, and which product has the same properties as and is of 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 20 to 30 times its weight of hydrochloric acid solution of 0.05% to 2% strength and heating the mixture to 50° to 100° C., for between half an hour and four hours, and washing out the water soluble constituents from the treated cellulose ether.

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