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RAW COTTON FOR CONVERSION INTO
RAYON

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This invention relates to the production of cellulosic products and has for its object the provision of certain improvements in the production of cellulosic products from cotton, and particularly cotton linters. The invention is of special advantage in the production of regenerated cellulose products, and particularly by the viscose process, from cotton. A further object of the invention is the provision, as a new article of manufacture, of an improved cellulosic product consisting mainly of cotton.

Cotton, and more particularly cotton linters, is extensively used in the production of various cellulosic products such as nitrocellulose, cellulose acetate, cellulose ethers, rayon and other synthetic fibers, cellophane and similar cellulosic films or sheets, etc. Cotton is available as a source of cellulose in the raw state and as chemical cotton in loose form or in sheet form. In neither case is the cotton subjected to any textile operation to form it into threads or fabric; and in the appended claims the term "cotton in the raw state" is used to designate raw cotton or raw cotton which has been subjected to chemical treatment to purify and bleach it, as hereinafter referred to, but which has not been subjected to any textile operation to form it into threads or fabric. The invention aims to incorporate in such cotton, or its derivatives such as the alkali cellulose, one or more added compounds of the invention to improve one or more of the steps in the formation of the cellulosic products.

In the production of viscose the sheets formed of cotton linters are usually steeped in a caustic soda solution to form alkali cellulose and the alkali cellulose, after pressing and while still in sheet form, is shredded to prepare the cotton fibers for the xanthating reaction with carbon bisulfide. The resulting sodium cellulose xanthate is dissolved in dilute caustic soda to form the solution commonly known as viscose, which, opacified if desired, is filtered and spun into filaments.

We have discovered that the incorporation in cotton, advantageously in cotton linters, of certain compounds in minute quantities, imparts to the cellulose, properties that make it more amenable to various processing steps in the production of rayon by the viscose process, resulting in increased efficiency and a decrease in the cost of the operation. The invention accordingly involves the incorporation in the cotton of a small quantity of a polyalkylene oxide polymerization product and the utilization of the cotton so treated for the production of viscose rayon. The invention provides as an article of manufacture an improved product comprising cotton, especially cotton linters, having one or more of said compounds incorporated therein. The cotton having incorporated therein a polyalkylene oxide polymerization product is especially amenable to

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processing into viscose and gives improvements in various of the steps leading up to and including the spinning operation. For example, when viscose rayon is delustered by incorporating a suitable opacifying agent in the spinning solution, usually an oil or a pigment such as titanium dioxide, it is necessary in order to get a uniform emulsification or dispersion of the agent throughout the body of the viscose solution to use an emulsifying or opacifying agent. Even with the aid of emulsifying agents, it has in the past been very difficult to obtain satisfactory emulsification when using cotton linters. In fact, in order to obtain satisfactory emulsification, it has previously been frequently necessary to blend cotton linters with good pulp. A particular sub-class of the polyalkylene oxide polymerization products, herein termed "mixed ethers of aliphatic alcohols," produce an exceptionally good emulsifying and dispersing effect which is quite remarkable in view of the small quantities used. The emulsification is characterized not only by the fineness of the average particle size, but also by a remarkable uniformity of particle size. This, together with a high degree of stability, ensures the resulting viscose being substantially free of even small amounts of large globules which weaken the filaments on spinning. In addition to the advantages mentioned, the use of the compounds of our invention also gives an improvement in the spinning performance, especially by obtaining less incrustation of spinneret holes.

The compounds of our invention are polymerization products of alkylene oxides, especially of the 1-2 alkylene oxides. More particularly, our compounds are surface-active materials at least dispersible in water, stable in solution of alkali metal hydroxide, and which contain a multiplicity of alkenoxy groups.

Surface-active compounds are compounds containing one or more lipophilic (oil or fat attracting, water repulsing) groups together with a hydrophilic group or a plurality of hydrophilic groups. Further, the lipophilic group or groups must be of sufficient magnitude to impart to a portion of the molecule a substantial repulsive action towards water. The hydrophilic group or plurality of hydrophilic groups must possess a sufficient hydrophilic character so that the molecule is water-soluble or at least soluble to the extent that it is readily dispersible in a finely divided form in water.

The surface-active property of molecules thus arises as the result of their containing at least one hydrophilic (water attracting) group and at least one lipophilic (fat or oil attracting and hence water repulsing) group. By virtue of the compounds containing a hydrophilic group, they are at least to a certain extent, soluble in water.

However, by virtue of their containing a lipophilic group, they tend to be repulsed by the water. Thus, they tend to concentrate largely on the surface of the water or interface layer where they can take up a compromise position with the hydrophilic group or groups resting in the water and the lipophilic group or groups sticking out of the water.

The preferred compounds of our invention fall generally into two main sub-classes. The compounds in the first sub-class have a polyalkylene oxide radical, preferably though not necessarily relative short (e. g., 5-20 alkenoxy residues), which is coupled through an oxygen or sulphur atom to a lipophilic group, R, said group R having substantially a hydrocarbon character but not being limited to hydrocarbon radicals.

In the preferred forms the group R is either a higher aliphatic hydrocarbon radical or a cycloaliphatic hydrocarbon radical selected from the group consisting of the dihydroabietyl, dehydroabietyl, tetrahydroabietyl and abietyl radicals. Other lipophilic groups such as aralkyl groups, alkaryl groups, or chain or cyclic aliphatic groups containing a small proportion of other elements than carbon and hydrogen are, however, not excluded. Where R contains atoms other than carbon and hydrogen, it is obvious that the groupings must be such that the radical is not decomposed when the compound comes in contact with caustic soda solutions in the viscose process.

In regard to the use of higher aliphatic hydrocarbon radicals as lipophilic surface-active inducing groups, either straight chain, branched chain, saturated or unsaturated radicals may be used. Suitable aliphatic hydrocarbon groups will include those having more than 7 carbon atoms. There is a practical upper limit for these or any other type of lipophilic surface-active inducing radical in that the compounds must be soluble or at least dispersible in water.

In all these compounds there is no single strongly water attracting group, but there is nevertheless a substantial hydrophilic attraction through the sum of the effects of a multiplicity of weakly hydrophilic ether linkages in the polyalkylene oxide radical.

In general all the compounds in the first sub-class are mixed ethers and mixed thio ethers containing a polyalkylene oxide radical and a hydrocarbon radical or a radical which has substantially a hydrocarbon character and thus substantially the lipophilic effect of a hydrocarbon radical. The second sub-class consists of the alkylene oxides polymerized in the presence of small quantities of NaOH, water or other materials which provide terminal groups of negligible size in comparison with the chain itself. Where the alkylene oxide is polymerized thus substantially alone to a sufficiently high degree the molecule will have definite surface-active properties (and be effective in our process) even though the compounds do not conform to the conventional requirements of surface-active materials for orientation at an interface.

The most suitable compounds for preparing the compounds of our invention are the first two members of the 1-2 alkylene oxides. These members are ethylene oxide and propylene oxide, or, in other words, the 1-2 alkylene oxides having up to 3 carbon atoms.

When the alkylene oxides are polymerized alone, a considerable degree of molecular complexity is required in order for the products to be appreciably surface-active. This required de-

gree of molecular complexity in the case of the polyethylene oxides may be characterized by the specification of a minimum melting point and in the case of the polypropylene oxides may be characterized by the specification of a minimum specific viscosity measured under stated conditions. In the case of the polypropylene oxides there is also an upper limit for the degree of polymerization in that the compounds must be soluble or at least readily dispersible in water. This upper limit for the degree of polymerization may also be characterized by the specification of a specific viscosity—in this case a maximum value.

In the case of the combinations of the polyalkylene oxide radicals with groups having a hydrocarbon character; i. e., in the cases of the mixed ethers and mixed thio ethers we believe that the best results will generally be obtained by employing ethylene oxide rather than propylene oxide. This is because ethenoxy groups have a higher solubilizing effect than propenoxy groups. Where, however, the alkylene oxide is polymerized alone; i. e., where there is no single strongly lipophilic group but rather only a multiplicity of short alkylene groups within the polyalkylene oxide, we find in general that propylene oxide gives better results than ethylene oxide. In general polypropylene oxide is more effective for the purposes of the invention than polyethylene oxide and may also be used in smaller concentrations.

While the agents of our invention are only subject to the limitation that they are surface-active materials which are at least dispersible in water and stable in solutions of alkali metal hydroxide and which contain a multiplicity of alkenoxy groups, examples are given below of five types of these agents that may be readily prepared or obtained and which are especially effective.

1. Polyethylene oxide having a freezing point of at least 34° C.
2. Polypropylene oxide having a specific viscosity of around 0.065-0.138 measured in a 4% benzene solution by weight at 18° C.
3. Mixed ethers containing a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms. (For brevity herein referred to as "mixed ethers of aliphatic alcohols.")

4. Mixed thio ethers containing a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms.
5. Mixed ethers containing a polyethylene oxide radical and a cycloaliphatic hydrocarbon radical derived from abietic acid and selected from the group consisting of the dihydroabietyl, dehydroabietyl, tetrahydroabietyl, and abietyl radicals.

All five types listed above are effective in improving the spinning operations. Group 3, the mixed ethers of aliphatic alcohols, are also very effective in improving the emulsification of mineral oils in the viscose. By use of very small amounts of these mixed ethers of aliphatic alcohols, emulsions may be obtained which are characterized by exceptional fineness and uniformity of particle size and by exceptional stability in regard to maintaining these properties.

In the class of polyethylene oxides, polymerized products having the formula $(C_2H_4O)_n \cdot H_2O$ (or its expanded form $HO(C_2H_4O)_n-CH_2CH_2OH$) are preferred, and the term polyethylene oxide is intended to include any product which consists substantially of C_2H_4O groups, irrespective of any small terminal group or groups it may contain other than hydroxyl. With a long polyethylene

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oxide chain, substitution of any other small groups for the hydroxyl groups has a relatively small effect, and the resulting substitution product will still yield at least in part the advantages of the invention. Thus, the term polyethylene oxide is intended to include products having a relatively long polyethylene oxide chain making up the greater part of the molecule and either one or two terminal groups consisting of halogen or any hydrocarbon group containing not more than seven carbon atoms and linked to the polyethylene oxide through either oxygen or sulfur. We have found that those polyethylene oxides, having a freezing point of at least 34° C. are suitable for the purposes of the invention. Especially good results have been obtained with polyethylene oxides having a freezing point of 46–51° C. The polyethylene oxides are soluble in water and may be applied to the cotton as a solution or incorporated in any solution in which the cotton is treated.

We have found that those polypropylene oxides are operative which have a specific viscosity of around 0.065–0.138 measured in a 4% benzene solution by weight at 18° C. Best results, however, are obtained when the polypropylene oxides fall within a more restricted specific viscosity range of 0.083–0.138. The polypropylene oxides may be prepared by polymerizing propylene oxide with water in the presence of a suitable catalyst, such as sodium hydroxide, or by carrying out the polymerization under anhydrous conditions in the presence of a catalyst, such as stannic chloride. Products prepared in the presence of sodium hydroxide and water, which are the preferred polypropylene oxides for use in our invention, are believed to have the empirical formula $(\text{CH}_3\text{CH}_2\text{H}_3\text{O})_n \cdot \text{H}_2\text{O}$. Polypropylene oxides falling within the designated specific viscosity range of 0.065–0.138 are substantially soluble or dispersible in water and may be applied in solution form or incorporated in any solution contacting the cotton or one of its derivatives.

The mixed ethers of aliphatic alcohols will contain a polyethylene oxide radical and an aliphatic hydrocarbon radical having more than 7 carbon atoms. For use in our invention the mixed ethers of aliphatic alcohols are preferably substantially soluble in water. Such compounds will generally contain a polyethylene oxide radical, having at least half as many ethenoxy groups as there are carbon atoms in the hydrocarbon radical. Practically, it is believed there is no upper limit for the number of ethenoxy groups in the polyethylene oxide radical and we may use, for example, materials with a polyethylene oxide group containing up to 157 ethenoxy groups. While the mixed ethers used in our invention are preferably substantially water-soluble, it is possible to obtain the advantages of the invention in part using compounds of only slight solubility. Thus mixed ethers containing the simplest possible polyethylene oxide radical composed of two ethenoxy groups; i. e., a diethylene glycol ether group, may be used. Even though such products do not have a great solubility, they still possess a sufficient tendency to emulsify so that they may be dispersed in a finely divided state in the viscose yielding in part the advantages of the invention. If, however, a high degree of "solubility" in water is desired with such agents, as, for example, in the preparation of concentrated stock solutions for application to the cotton or in the viscose process, it may be advantageous to combine them with dispersing agents. Such additional dispers-

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ing agents should preferably be of a nonionic nature, for example, a mixed ether of an aliphatic alcohol containing a higher proportion of ethenoxy groups. In a preferable form of our invention, however, sufficient ethenoxy groups will be present in the polyethylene oxide radical so that the products will be substantially water-soluble or dispersible without the aid of any additional dispersing agents.

Further, from the standpoint of improving emulsification, the most preferred class of mixed ethers of aliphatic alcohols are those compounds containing a polyethylene oxide radical with from 9 to 20 ethenoxy groups and an aliphatic hydrocarbon radical (especially a normal primary aliphatic hydrocarbon radical) with from 12–18 carbon atoms. Such compounds are also particularly effective in suppressing or minimizing the formation of incrustations in spinneret orifices during spinning.

The mixed ethers of aliphatic alcohols may be prepared by any of the known methods for reacting ethylene oxide with a fatty alcohol. They may be prepared by etherifying the fatty alcohols with polyethylene glycols, as, for example, by reacting the sodium salt of the fatty alcohol with a halogen hydrin of the polyethylene glyco.

We prefer, however, to react ethylene oxide at moderate temperatures with aliphatic fatty alcohols containing more than 7 carbon atoms, incorporating an alkali as catalyst with the alcohol.

Compounds effective for use in the invention which are identifiable by the approximate formula of the predominating compound in the product are as follows: lauryl- $\text{O}(\text{C}_2\text{H}_4\text{O})_{12}\text{H}$, stearyl- $\text{O}(\text{C}_2\text{H}_4\text{O})_{16}\text{H}$, oleyl- $\text{O}(\text{C}_2\text{H}_4\text{O})_{14}\text{H}$, lauryl- $\text{O}(\text{C}_2\text{H}_4\text{O})_{157}\text{H}$, and oleyl- $\text{O}(\text{C}_2\text{H}_4\text{O})_{157}\text{H}$.

It is obvious that the aliphatic alcohols used for making the mixed ethers may be prepared by any desired method; for example, synthetic aliphatic alcohols containing more than 7 carbon atoms and built up from smaller molecules may be used. Such compounds are usually essentially branched chain molecules. We frequently, however, use fatty alcohols prepared by catalytic reduction by hydrogen of vegetable or animal oils according to well-known practices, which are substantially straight chain compounds. It is, however, not necessary to use pure aliphatic alcohols. Indeed, higher molecular weight alcohols prepared by hydrogenation of fats and oils are generally, if not always, offered in commercial quantities in the form of mixtures of different alcohols. Thus, in place of pure lauryl alcohol, technical lauryl alcohol such as is commonly sold under the trade name of "Lorol" may be used. "Lorol" is considered to be essentially a mixture of C_{10} , C_{12} , C_{14} , and C_{18} carbon length chains with the C_{12} chain predominating. Actually, however, when using such a mixture in which lauryl alcohol predominates, the result is almost identical as if pure lauryl alcohol itself were used. Also, instead of using pure stearyl or oleyl alcohols, technical products may be used. In condensing such technical mixtures of fatty alcohols with ethylene oxide, it is quite satisfactory to base the desired molar ratio of ethylene oxide on the assumption that the entire weight of fatty alcohol has the same molecular weight as the predominating fatty alcohol in the mixture. This may be done since small variations in the ratio of ethenoxy in the products do not produce very great differences in the properties. Furthermore, even when using pure fatty alcohols, it is not necessary to use exact stoichi-

metrical proportions of ethylene oxide. Thus, for example, if pure lauryl alcohol were treated with 12.5 mols of ethylene oxide, mixtures of mixed-ethers would be obtained in which chains of 12 and 13 ethenoxy groups would predominate.

Still another group of mixed ethers which may be effectively used in the invention are those formed by reacting ethylene oxide with a rosin alcohol which as used herein means an alcohol derived by reduction of rosin or abietic acid and consisting of dihydroabietyl, dehydroabietyl, tetrahydroabietyl or abietyl alcohol. More particularly the compounds are mixed ethers containing a polyethylene oxide radical and a cycloaliphatic hydrocarbon radical derived from abietic acid and selected from the group consisting of the dihydroabietyl, dehydroabietyl, tetrahydroabietyl, and abietyl radicals.

Suitable compounds at least water-dispersible will be mixed ethers containing a polyethylene oxide radical with at least three ethenoxy residues and a cycloaliphatic hydrocarbon radical selected from the group consisting of dihydroabietyl, dehydroabietyl, tetrahydroabietyl, and abietyl radicals.

It is not necessary to use pure rosin alcohols. Very effective materials may be prepared by condensing ethylene oxide with the mixture of rosin alcohols, commonly sold under the name "Hydroabietyl Alcohol," and which consists chiefly of a mixture of dihydroabietyl, dehydroabietyl, tetrahydroabietyl and abietyl alcohols. Examples of specific products are products obtained by condensing approximately 3, 4, 6, 12, 20 and 160 mols of ethylene oxide respectively per average molecular weight of the rosin alcohol mixture known as hydroabietyl alcohol. The condensation is brought about by any of the normal methods for reacting ethylene oxide with an alcohol, preferably incorporating an alkali as catalyst with the alcohol. Suitable methods include either adding a small proportion of 48% NaOH or dissolving metallic sodium in the heated rosin alcohol.

The mixed ethers are generally applied to the cotton as water solutions or dispersions.

The mixed thio ethers used in the invention contain a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms. While we prefer to use those that are substantially soluble in water, it is possible to obtain the advantages of the invention in part using compounds of only slight solubility. Thus, mixed thio ethers, containing even the simplest possible polyethylene oxide radical composed of two ethenoxy groups, may be used. Even though such products do not have a great solubility, they still possess a sufficient tendency to emulsify so that they may be dispersed in a finely divided state in the viscose yielding in part the advantages of the invention. If, however, a high degree of "solubility" in water is desired with such agents, as, for example, in the preparation of concentrated stock solutions for application to the cotton or in the viscose process, it may be advantageous to combine them with dispersing agents. Such additional dispersing agents should preferably be of a nonionic nature; for example, a mixed thio ether containing a higher proportion of ethenoxy groups. In a preferred form of mixed thio ethers, however, sufficient ethenoxy groups will be present in the polyethylene oxide radical so that the products will be substantially water-soluble without the aid of any additional dispersing agents.

Furthermore, the preferred class of mixed thio ethers are those containing a polyethylene oxide radical with from 9 to 20 ethenoxy groups and a normal primary aliphatic hydrocarbon radical with from 12 to 18 carbon atoms. Such compounds are particularly effective in suppressing or minimizing formation of incrustations in the spinneret orifices during spinning.

The mixed thio ethers may be prepared by reacting ethylene oxide at moderately elevated temperatures with aliphatic mercaptans containing more than 7 carbon atoms under conditions in which at least part of the mercaptan may be considered to be present as alkali mercaptide. This may be accomplished by reacting ethylene oxide with a mercaptan in which has been incorporated a small amount of strong aqueous caustic soda. Rapid reaction with the ethylene oxide may, however, be obtained by transforming the aliphatic mercaptan into a mercaptide containing the theoretical amount of sodium. This may readily be accomplished by addition of a solution of the theoretical amount of sodium in liquid ammonia to an ether solution of the mercaptan, or by addition of liquid ammonia to an ether solution of the mercaptan followed by subsequent addition of metallic sodium. The solvents are then evaporated off, taking care that the product does not take up any appreciable amount of moisture.

A mixed thio ether which is particularly effective is predominantly a compound represented by the probable formula $C_{12}H_{25}S(C_2H_4O)_{12}H$. In the preparation of this product, mixtures of mercaptans prepared from technical lauryl alcohol, which is a mixture in which C_{12} predominates, may be used, and in basing the amount of ethylene oxide, it suffices to consider the whole material as having the molecular weight of lauryl mercaptan. Furthermore, the exact twelve ethenoxy units shown are not essential and could range according to the description given above for the most preferred compounds, from 9 to 20 residues. Also, other mercaptan mixtures prepared from fats and oils or from petroleum products are suitable and practical for conversion to thio ethers for use in the invention.

In accordance with the method of the invention, we may incorporate the compound in the cotton using a solution or dispersion of the compound. Chemical cotton is subjected to a purification and bleaching treatment. The purified and bleached cotton in loose form is then formed into sheets on a paper machine of conventional design. The sheet is passed over drying rolls and then cut into sheets of the desired size.

The compounds may be incorporated either in the loose cotton or in the sheets in any suitable stage as by spraying the cotton with an aqueous solution or dispersion of the compound, or by immersing in a solution or dispersion. In any case, there is produced a cotton product having the compound incorporated therein. When the compound is incorporated in the cotton, as by the manufacturer thereof, the cotton comes to the rayon manufacturer in a form calculated to secure the full advantages of the invention in the preparation and processing of the cotton into rayon by the viscose process.

In order to effect the contemplated improvements, the amount of the compound used is relatively small, ranging from 0.01-0.20% on the bone dry weight of the cotton used. In most cases the preferred amounts for improving spinning will generally be about 0.08-0.10. Polyethylene oxides, however, are somewhat less active than most

of the compounds and accordingly for effecting substantial improvements will usually be added in amounts approaching 0.20%.

As heretofore described, the mixed ethers of aliphatic alcohols also bring about important improvements in emulsification in that they give emulsions characterized not only by extraordinary fineness of particle size, but also by exceptional uniformity of particle size and by exceptional stability in regard to maintaining the particle size. The amount of the mixed ethers of aliphatic alcohols required for securing the maximum improvement in emulsification is generally somewhat less than the amount required for securing the contemplated improvement in suppressing or minimizing crater formation during spinning. Thus the maximum improvement in emulsification will generally be brought about by from 0.025-0.05% of the mixed ether and the amount used for this purpose will commonly be about 0.03%. In order to secure the additional benefit of substantially suppressing or minimizing crater formation, the mixed ether should be present in amount of 0.08-0.10% or higher. By using such amounts of the order of 0.08-0.10% the emulsions are substantially as fine and uniform as when using the optimum of 0.025-0.05%. Emulsions prepared, however, in the presence of the higher amount of mixed ether may under certain circumstances have a slight tendency to partially separate as a cream or scum during the various viscose processing steps or during the aging period. Accordingly, when both emulsification and suppression of cratering are of paramount concern, we prefer to add only 0.025-0.05% of the mixed ether but to still obtain the contemplated improvement in cratering or an even greater improvement by adding an additional small amount of a cation-active amino compound as described in our copending application, Serial No. 530,740. In such cases the amount of the mixed ether will preferably be about 0.03% and the amount of cation-active amino compound will preferably be about 0.05% though it may be added in amounts up to 0.20%.

So far as the objectives of the invention are concerned, there is little, if any, improvement by increasing the amount of the polyalkylene oxide polymerization products above 0.20% and such higher amounts frequently give rise to certain disadvantages. These disadvantages include the causing of excessive softness in the sheet, resulting in mechanical difficulties in steeping, difficulties in the dissolving operation due to excessive foaming in the viscose solution. Also, there may be considerable difficulty in obtaining a completely deaerated viscose which is necessary for satisfactory spinning. Higher concentrations of the compound may also unduly lower the surface tension of the viscose, thus changing the coagulating conditions so that the viscose cannot be satisfactorily spun by standard methods, causing the filaments to break and the thread to stick to the godet wheels or thread guides.

While it is our preferred practice to incorporate the compound in the cotton, the presence of the compound during the processing steps of spinning and opacifying may be secured in any other appropriate manner. However, we believe it will generally be found more advantageous to incorporate in the cotton, both as a matter of convenience and economy in preparing and processing the viscose, and because a very uniform distribu-

tion of the compound throughout the viscose is easily attained. The next best manner of obtaining very effective results is to spray the agents into the shredder prior to the completion of shredding. With the mixed ethers of aliphatic alcohols the method of adding the agents is of particular importance in regard to imparting anticreaming properties if the viscose is to be subsequently opacified. Whether this is a question of the agents themselves undergoing some change during the xanthation or whether it is merely a question of the uniformity of the distribution in the viscose we do not know. In any event, for the most effective results the agents should be added not later than prior to the completion of shredding and preferably to the cotton prior to use in the viscose process.

We claim:

1. As a new article of manufacture, a cellulosic product consisting of cotton in the raw state as a raw material for conversion into rayon having incorporated therein from 0.01% to 0.2% by weight based on the bone dry weight of the cotton of an added polyalkylene oxide polymerization compound selected from the group consisting of a polyalkylene oxide and a mixed ether having attached to the ether oxygen a polyalkylene oxide radical and a hydrocarbon radical containing more than 7 carbon atoms, said polymerization compound being at least partially dispersible in water and stable in a solution of alkali metal hydroxide.

2. An article of manufacture according to claim 1 in which the polyalkylene oxide compound is a polypropylene oxide having a specific viscosity of 0.065 to 0.138 measured in a 4% benzene solution by weight at 18° C.

3. As a new article of manufacture, a cellulosic product consisting of cotton in the raw state as a raw material for conversion into rayon having incorporated therein from 0.01% to 0.2% by weight based on the bone dry weight of the cotton of an added mixed ether having attached to the ether oxygen a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms, said mixed ether being at least partially dispersible in water and stable in a solution of alkali metal hydroxide.

4. As a new article of manufacture, a cellulosic product consisting of cotton in the raw state as a raw material for conversion into rayon having incorporated therein from 0.01% to 0.2% by weight based on the bone dry weight of the cotton of an added polyethylene oxide having a freezing point of at least 34° C.

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Certificate of Correction

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PAUL HENRY SCHLOSSER ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 16, for the word "good" read *wood*; line 38, for "solution" read *solutions*; column 3, line 13, for "relative" read *relatively*; column 6, line 27, for "glyco" read *glycol*; line 63, for "urging" read *using*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of February, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.