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MANUFACTURE OF CELLULOSE ACETATE

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This invention relates to improvements in the manufacture of cellulose derivatives, and especially to the manufacture of fatty acid esters of cellulose wherein wood pulp in dried consolidated form, such as bone dry wood pulps in sheet form is used as the source of cellulose, and wherein a polyalkylene oxide polymerization product is applied to the pulp before it is dried.

This application is a continuation-in-part of our application Serial No. 225,928, filed May 11, 1951, Patent No. 2,692,877.

In the preparation of refined wood pulp suitable for use in the manufacture of cellulose fatty acid esters, the purified fibers are first obtained in the form of a slurry in water. In this undried state the refined wood pulp fibers are potentially very reactive, for example, where the water of the undried fibers is suitably displaced by organic solvents. Dried fibers obtained by such water displacement methods react readily in the nonaqueous processes used for the manufacture of cellulose fatty acid esters. However, as a practicable matter in the commercial production of refined wood pulp for such purposes it is necessary to form the pulp fibers into a consolidated form, such as sheets and to remove the last portions of water by the application of heat, whereby the pulp may be readily transferred to other processing plants or shipped to distant points for conversion into the desired derivatives. In such form the pulp is said to be substantially dry. As used herein, "substantially dry" refers to pulp either dried bone dry or containing that small water content which hygroscopic pulp takes up from the air. Roughly this will refer to pulp containing from zero to ten percent of moisture. Substantially dry pulp may be used in nonaqueous conversion processes for making cellulose esters without first applying costly nonaqueous solvent exchange processes for removing water, but it has been found where heat is used to remove the residual water from the consolidated pulp fibers that a certain inactivation of the fibers takes place which is not present when the pulp from a water slurry is dewatered and the last of the water is displaced by treatment with organic solvents.

It has now been discovered that such inactivation is diminished or minimized by applying to the refined wood pulp minute amounts of a polyalkylene oxide polymerization product while the dry consolidated form of pulp, such as dry sheets of wood pulp are being formed from the wet fiber slurry. Accordingly, the processes of the present invention comprise the acylation of formed substantially dry wood pulp which carries a small amount of a straight chain polymerization product in which residues of ethylene oxide are joined and the terminal members of the chains are hydrogen, RO—, and RS— which will be hereinafter described, the polymerization product being applied to the wet pulp before it is dried.

In a convenient form of the invention the refined wood fibers are formed into a sheet and the polyalkylene oxide product is incorporated into the pulp sheet prior to the final drying of the pulp at an elevated temperature on a sheet forming machine. The pulp sheets are cut into convenient sizes for acylation. It is sufficient where the polyalkylene oxide polymerization product is applied at least

to the surface of the formed pulp but greater distribution in the formed dried pulp or throughout the same is suitable. Only a small amount of any of a large variety of such agents applied to a pulp sheet during its formation and drying is effective in preventing loss of reactivity. The use of such prepared and formed pulp is especially advantageous in the manufacture of cellulose acetate in nonaqueous medium.

The agents used for treating the pulp sheets to be acylated are thus polymerization products of alkylene oxides, especially of the 1,2-alkylene oxides. They are nonionic surface-active agents when dissolved in water and contain a multiplicity of alkenoxy groups. Whether or not these agents exert a surface-active effect in the substantially nonaqueous acylation reaction mixture is not known.

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 with the hydrophilic group or groups resting in the water and the lipophilic group or groups sticking out of the water.

The preferred compounds for use in our invention fall generally into two main sub-classes. The compounds in the first sub-class consist of 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 in water (and be effective in our acylation process) even though the compounds do not have at least one long chain hydrocarbon radical, as is characteristic of conventional surface-active materials.

The most suitable starting materials for preparing the compounds used in our invention are the first two members of the 1–2 alkylene oxides. The 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 degree 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 general all the compounds of the second subclass are mixed ethers or mixed thio ethers containing a poly-

alkylene oxide radical which is coupled through an oxygen or sulfur atom to a lipophilic group, R, said group R having substantially a hydrocarbon character and thus substantially the lipophilic effect of a hydrocarbon radical but not being limited to hydrocarbon radicals.

In one preferred form, the group R is either a high aliphatic hydrocarbon radical, a substituted aryl 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 or chain or cyclic aliphatic groups containing other elements than carbon and hydrogen are, however, not excluded. In this regard very satisfactory results have been obtained using as lipophilic groups the radicals of long chain, water-insoluble polypropylene oxides. Where R contains atoms other than carbon and hydrogen, it is obvious that the groups must be such that the radical is not decomposed when the compound comes in contact with the acidic acylation mixture. We have found that polypropenoxy radicals are satisfactorily stable in this regard.

There is practical upper limits for the number of carbon atoms in any lipophilic surface-activity 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.

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

TABLE I.—TYPES OF POLYALKYLENE OXIDE POLYMERIZATION PRODUCTS

Type	Description
First Subclass:	
1	Polyethylene oxides.
2	Polypropylene oxide having a specific viscosity of around 0.065–0.138 measured in a 4% benzene solution by weight at 18° C.
Second Subclass:	
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 ethers containing a polyethylene oxide radical and an aryl radical substituted by at least one radical selected from the class consisting of an alkyl radical with more than two carbon atoms, an acyl radical with more than two carbon atoms and a cyclo alkyl radical. (For brevity herein referred to as "mixed ethers of substituted phenols.")
5	Mixed thio ethers having attached to the sulfur atom a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms.
6	Mixed ethers containing a polyethylene oxide radical and a cycloaliphatic hydrocarbon radical derived from abietic acid and selected from the groups consisting of the dihydroabietyl, dehydroabietyl, tetrahydroabietyl, and abietyl radicals.
7	Water-soluble polypropylene oxide-polyethylene oxide polymerization products. (These mixed polyalkylene oxides for brevity are hereinafter termed "polypropenoxy-polyethenoxy polymers.") Suitable polypropenoxy-polyethenoxy polymers include the following sub-types later described in detail: *a.* Bispolyethenoxy Polypropylene Oxides. *b.* Halopolypropenoxy Polyethylene Oxides. *c.* Alkoxy (or phenoxy) Polypropenoxy Polyethylene Oxides. *d.* Bispolypropenoxy Polyethylene Oxides.

More detailed descriptions of examples of types of suitable polyalkylene oxide polymerization products (for convenience classified as in Table I) follows:

Type 1.—In the case of polyethylene oxides, polymerized products having the formula $(C_2H_4O)_nH_2O$ (or its expanded form $HO(C_2H_4O)_{n-1}(CH_2CH_2OH)$ 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 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 relatively simple polyethylene oxides such as tetraethylene glycol may be used with some effect in the invention. In practice however, we find that the best results are obtained when using polyethylene oxide having a relatively high degree of polymerization and having an average molecular weight of at least 1000. Especially good results have been obtained with polyethylene oxides having freezing points from 24° C. to 51° C. Good results have also been obtained using paste-like products prepared by blending a solid polyethylene oxide of high average molecular weight with liquid polyethylene oxides of low average molecular weight. A suitable product of this type is the paste-like blend formed from equal parts of a liquid polyethylene oxide with average molecular weight of 300 and a solid polyethylene oxide of average molecular weight of 1540. All of these products are soluble in water and may be applied to the pulp in water solution.

The term "polyethylene oxide" as used herein includes not only straight, single chain polymers, but also polyethenoxy polymers having more than a single polyethenoxy chain and including highly branched structures. Suitable polyethylene oxides containing a multiplicity of polyethenoxy chains may be formed by polymerizing ethylene oxide in the presence of a small proportion of a polyhydric alcohol of relatively small molecular weight to provide terminal groups. The resulting polyethylene oxide compounds on a weight basis will consist largely of ethenoxy groups but will contain the number of ethenoxy chains equivalent to the number of hydroxyl groups in the polyhydric alcohol used in effecting polymerization. The alkali required to effect polymerization with the alcohols may be sodium combined with at least a part of the hydroxyl groups in the polyhydric alcohol in the form of sodium alcoholate groups (conveniently by addition of sodium to a liquid ammonia solution of the polyhydric alcohol and evaporation). By using respectively the polyhydric alcohols, ethylene glycol, glycerol, pentraerythritol and sorbitol, the resulting multi-chain, water-soluble polyethylene oxides will have respectively 2, 3, 4 and 6 polyethenoxy chains, each attached to the nucleus at one end and having a hydroxyl group at the free end.

Compounds of this type found especialy suitable include the three chain, polyethenoxy polymers formed from one mol of glycerol and 120 moles ethylene oxide and the six chain, polyethenoxy polymer from one mol of sorbitol and 100 moles of ethylene oxide.

Type 2.—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. 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 $(CH_3C_2H_3O)_nH_2O$. Polypropylene oxides fall-

ing within the designated specific viscosity range of 0.065–0.138 are substantially soluble or dispersible in water and may be applied in water solution.

Type 3.—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. 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 water. 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 pulp prior to drying, 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 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 the completeness of acylation, a particularly preferred class of mixed ethers of aliphatic alcohols is one consisting of compounds containing a polyethylene oxide radical with from 8 to 50 ethenoxy groups and an aliphatic hydrocarbon radical (especially a normal primary aliphatic hydrocarbon radical) with from 8–20 carbon atoms.

Type 4.—Another class of mixed ethers which is especially effective for use in the invention is one consisting of mixed ethers of substituted phenols. Structurally these mixed ethers have the formula:

$$R{-}O(\underset{\substack{|\\R_1}}{C}HCH_2O)_xH$$

where R is an aryl radical substituted by at least one aliphatic alkyl or acyl radical having more than two carbon atoms or by at least one cycloalkyl radical, where R_1 is hydrogen or methyl, and where x is a whole number greater than 1.

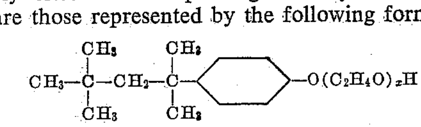
The mixed ethers of substituted phenols are at least dispersible in water and preferably substantially soluble in water. For reasons of dispersibility the polyalkylene oxide radicals in the mixed ethers are derived from the first two members of the 1–2 alkylene oxides. These members are ethylene oxide and propylene oxide, or in other words, the 1–2 alkylene oxides having up to 3 carbon atoms.

In view of its higher solubilizing effect, a polyethylene oxide chain is the preferred form for the polyalkylene oxide radical. Preferably the polyethylene oxide chain will have from 8–50 ethenoxy residues. Practically it is believed there is no upper limit for the number of ethenoxy groups in the polyethylene oxide radical. Materials with a polyethylene oxide group containing even about 160 ethenoxy groups may be satisfactorily used.

While the mixed ethers of substituted phenols are preferably substantially water-soluble, it is possible to obtain the advantages of the invention in part using compounds of only slight solubility. As previously suggested for the mixed ethers of aliphatic alcohols, compounds may be used which are only sufficiently soluble to form emulsions, and the formation of such emulsions may be assisted with dispersing agents.

The preferred mixed ethers of substituted phenols for use in the invention are mixed ethers containing a polyethylene oxide radical sufficiently long to impart water solubility to the compound, and an alkaryl radical in which the aryl group is substituted by at least one alkyl radical with more than two carbon atoms. The preferred class of materials is one consisting of mixed ethers containing a polyethylene oxide radical and an alkyl phenyl hydrocarbon radical having at least one substituted alkyl radical with 3–30 and especially from 7–20 carbon atoms. For best results the polyethylene oxide radical will have from 8–50 ethenoxy residues.

As previously stated, the preferred mixed ethers are those containing predominately a mono-alkyl phenyl radical. Examples of such mixed ethers which are particularly effective in improving the acylation of wood pulp are those represented by the following formula:



where x is an integer between 8 and 50. In practice the product will usually be a mixture having varying chain lengths for the polyethylene oxide radical but with the average or predominating chain length within the preferred range of 8–50 ethenoxy units.

Type 5.—Still another group of mixed ethers which may be effectively used in the invention is one consisting of compounds 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.

Type 6.—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. 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

is one consisting of compounds containing a polyethylene oxide radical with from 8 to 50 ethenoxy groups, and a normal primary aliphatic hydrocarbon radical with from 12 to 18 carbon atoms.

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 8 to 50 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.

Type 7.—Very suitable in the practice of the invention are mixed polyalkylene oxides comprising polypropylene oxide-polyethylene oxide polymers containing at least one relatively lipophilic polypropylene oxide radical and at least one hydrophilic polyethylene oxide radical.

These polypropenoxy-polyethenoxy polymers differ from conventional surface active materials in that they do not have a long chain hydrocarbon radical, but rather the lipophilic effect is derived from a multiplicity of short hydrocarbon chains of three carbon atoms connected to each other through ether oxygens. Also in comparison with conventional nonionic surfactants derived from ethylene oxide, these compounds have relatively long polyethylene oxide chains. There is thus in each a substantial hydrophilic attraction due to the combined effects of a great many weakly hydrophilic ether oxygen atoms in the polyethylene oxide radicals.

The polypropenoxy-polyethenoxy polymers used are only subject to the limitations that they are water-soluble polypropylene oxide-polyethylene oxide polymerization products containing at least one lipophilic polypropylene oxide radical and at least one hydrophilic polyethylene oxide radical and that generally the length of the polypropylene oxide chain (or where there are several chains the sum of the lengths of the several polypropylene oxide chains) is such that it would represent substantially water-insoluble polypropylene oxide if they were not substituted by the one or more polyethylene oxide chains, which render them water soluble. The following are four subtypes of these compounds (sub-types (*a*), (*b*), (*c*) and (*d*) of type 7 of the classification of Table I) which may be readily prepared or obtained and which are especially effective in the invention:

Sub-type (a).—Bispolyethenoxy polypropylene oxides.—These compounds may be represented by the general formula

$$HO(CH_2CH_2O)_w(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_x(CH_2CH_2O)_yH$$

Suitable compounds are derived from polypropylene oxide having a specific viscosity of at least 0.129 in 4% benzene solution at 25° C., so that they are at least substantially water insoluble (or as calculated have an average chain length of at least 13 propenoxy groups), and which have two terminal hydroxyl groups, by substitution of the hydrogens in both terminal hydroxyl groups by polyethylene oxide chains. These compositions consist of mixtures of compounds in which the end polyethenoxy chains, *w* and *v* may be of equal or unequal length, but which tend to be approximately equal in length. With a polypropenoxy chain of the minimum length to correspond to a substantially water-insoluble polypropylene oxide as represented by a specific viscosity of 0.129 or a calculated average length of 13 propenoxy groups, it will in general require a content of at least 20% ethylene oxide to render the final compound water soluble but a range of 40–70% ethylene oxide is preferred. Where, however, much longer polypropylene oxide chains are used as representaed by polypropylene oxide with specific viscosities in a range of 0.257 to 0.584, much larger contents of ethylene oxide may be desirable, in some cases of the order of 80–90%.

Sub-type (b).—Halopolypropenoxy polyethylene oxides.—These compounds may be represented by the general formula

$$A-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_z(CH_2CH_2O)_yH$$

where A is a halogen atom, such as chlorine or bromine. Suitable compounds are derived from a long chain polypropylene oxide having a specific viscosity of at least 0.129 at 25° C. and having one terminal halogen group and one terminal hydroxyl group, by substitution of the hydrogen in the terminal hydroxyl group by a polyethylene oxide chain. In general, for water solubility, the length of the polyethylene oxide chain will be of the same order as the sum of the lengths of the two polyethylene oxide chains in polymers of sub-type (*a*). An example of a suitable halopolypropenoxy polyethylene oxide for the preparation of these compounds is a long chain water-insoluble polypropylene oxide having one chlorine atom as a terminal group and one hydroxyl group as a terminal group which may be prepared by polymerizing polypropylene oxide in the presence of a small amount of stannic chloride.

Sub-type (c).—Alkoxy (or phenoxy) polypropenoxy polyethylene oxides.—These compounds may be represented by the general formula

$$RO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_z(CH_2CH_2O)_yH$$

where R is an alkyl group with 1–7 carbon atoms or a phenyl group. Suitable compounds are derived from a polypropylene oxide of sufficient length to be substantially water insoluble as characterized by having a specific viscosity of at least 0.129 in 4% benzene solution and having as one terminal group a small hydrocarbon group attached through an ether oxygen, the small hydrocarbon group being in itself of insufficient magnitude to influence surface activity, and one terminal hydroxyl group. From these water-insoluble polypropylene oxides the water-soluble polymers are derived by substitutions of the hydrogen in the terminal hydroxyl group by a polyethylene oxide chain. In general, to impart water solubility, the polyethylene oxide chain will be of the same order of magnitude as in the polymers of sub-type (*b*). As examples of especially suitable water-insoluble alkoxy polypropylene oxides are polypropylene oxides prepared by polymerizing propylene oxide in the presence of a small amount of the monomethyl ether of propylene glycol (containing combined sodium up to the theoretical for the formation of a sodium alcoholate group) or in the presence of small amounts of sodium methylate.

Sub-type (d).—Bispolypropenoxy polyethylene oxides.—These compounds may be represented by the general formula

$$HO(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_n(CH_2CH_2O)_y(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_zH$$

Suitable compounds are derived from a polyethylene oxide of chain length of the order of those in Examples 2 and 3 (or of the order of the sum of the two polyethylene oxide chains of the compounds of sub-type (*a*) where there are two polyethylene oxide chains) and having two terminal hydroxyl groups, the hydrogen of which are substituted by polypropylene oxide radicals. These compositions consist of mixtures of compounds in which the end polypropenoxy chains, *n* and *z* may be of equal or unequal length, but which tend to be of equal length. The polypropylene oxide chains are of sufficient length so that if they did not have a polyethylene oxide chain between them their combined length would represent a water-insoluble polypropylene oxide. That is, the two polypropylene oxide chains

if not separated by a polyethylene oxide chain would represent a polypropylene oxide having a specific viscosity of at least 0.129 in 4% benzene solution or a calculated average chain length of at least 13 propenoxy units. The compounds in general will contain at least 20% ethylene oxide to render them water soluble but a range of 40% to 70% ethylene oxide is preferred.

The following examples are illustrative of methods of preparing types of polypropenoxy-polyethenoxy polymers (for convenience as classified in Table I) for use in practicing the invention:

Preparation of type 7a compounds (bispolyethenoxy polypropylene oxides)

A long chain, water-insoluble polypropylene oxide having two terminal hydroxyl groups is prepared by polymerizing propylene oxide in the presence of a small amount of propylene glycol in which up to 1 mol of combined sodium has been introduced. The combined sodium may be readily introduced by dissolving the propylene glycol in liquid ammonia and mixing with a further amount of liquid ammonia in which is dissolved the required amount of sodium and then evaporating off the ammonia under substantially anhydrous conditions. While this method serves for giving a readily characterizable product, for practical purposes it will frequently be preferable to polymerize propylene oxide in the presence of a small amount of aqueous caustic soda (suitably 50% caustic soda). In this case the water and sodium hydroxide serve to produce the terminal groups and regulate the length of the chain inversely to the amount in which they are present. In any event, following the polymerization, a small portion of the product is treated for removal of sodium by washing, extracting with benzene and drying, and is then characterized by determining the specific viscosity in 4% benzene solution. The main portion of the product, still containing combined sodium, is now reacted by heating with required amount of ethylene oxide, most generally at a temperature in the range of 60–100° C., until the pressure falls to zero. For use in the treatment of pulp, extensive purification is not necessary but the alkali in the product should be neutralized with any of the common acids and most suitably by mixing a small amount of glacial acetic acid with the molten product.

Preparation of type 7b compounds (halopropenoxy polyethylene oxides)

Very suitable members of this sub-type are the chloropolypropenoxy polyethylene oxides. For the preparation of these compounds, a long chain water-insoluble polypropylene oxide having a chlorine atom as one terminal group and a hydroxyl group as the other terminal group is prepared by polymerizing propylene oxide in the presence of a small amount of stannic chloride. The amount of stannic chloride regulates the length of the chain inversely proportional to the amount in which it is present. The polymerization may conveniently be carried out in the general manner described in U. S. Patent 2,362,217 of Paul Henry Schlosser and Kenneth Russell Gray and suitable proportions of stannic chloride are from about 2.5 cc. down to about ½ cc. per 50 grams propylene oxide. Both for use in the further preparation of the nonionic surfactants and for characterization, the product should be de-tinned. This may readily be accomplished by boiling the tin-containing material wiith water, whereupon the tin separates out as a white precipitate, presumably stannic hydroxide. The tin-free product may then be extracted in benzene, dried with sodium sulfate, filtered, and the benzene evaporated off.

A small portion of the tin-free chloropolypropylene oxide is removed and characterized by determining the specific viscosity in 4% benzene solution at 25° C. In the main portion of the product, sodium is incorporated in amounts up to the theoretical amount to convert the terminal hydroxyl group to a sodium alcoholate group. This may be conveniently accomplished by dissolving the polypropylene oxide in ether and mixing with liquid ammonia containing the required amount of sodium, and after allowing the ammonia to boil off, distilling off the ether. The sodium-containing chloropolypropylene oxide is then reacted in an autoclave with the required amount of ethylene oxide, conveniently at a temperature up to 60–100° C., until the pressure falls to zero. The alkali in the water-soluble polymer is neutralized in a manner similar to that described for type 7a.

Preparation of type 7c compounds (alkoxy (or phenoxy) polypropylene oxides)

Very suitable members of this class, both from the standpoint of effectiveness and from the standpoint of economics, are the methoxy polypropenoxy polyethylene oxides. For the preparation of these compounds, a long chain water-insoluble polypropylene oxide having as one terminal group a methoxy group and as the other terminal group a hydroxyl group is prepared by polymerizing propylene oxide in the presence of a small amount of the monomethyl-ether of propylene glycol in which up to 1 mol of combined sodium is introduced. Alternatively, this type of propylene oxide may be prepared by polymerizing propylene oxide in the presence of small amounts of methyl alcohol containing sodium methylate. In general, the lower the proportion of the monomethyl ether of propylene glycol containing sodium or the lower the proportion of methyl alcohol-sodium methylate, the higher will be the molecular weight. Where the monomethyl ether of propylene glycol is used to provide the terminal groups, sodium may be conveniently introduced by dissolving the monomethyl ether in ammonia and mixing it with sodium in ammonia, preferably using less than the theoretical amount of sodium. The monomethyl ether containing sodium is isolated by removing the ammonia under strictly anhydrous conditions and is used without delay in that it is not stable on long standing. The preparation of the water-soluble polymer involves reacting it with the required amount of ethylene oxide in an autoclave until the pressure falls to zero.

Preparation of type 7d compounds (bispolypropenoxy polyethylene oxides)

Ethylene oxide may be polymerized in an autoclave by heating in the presence of a small amount of concentrated aqueous sodium hydroxide or in the presence of a small amount of ethylene glycol containing combined sodium. Where ethylene glycol containing combined sodium is used, the sodium may be introduced practically by heating the glycol with considerably less than the theoretical amount of sodium. Alternatively, larger amounts of sodium, up to the theoretical amount may be introduced by dissolving the glycol in ammonia, adding a further proportion of ammonia containing dissolved sodium, and evaporating off the ammonia. This higher proportion of sodium will in general permit a more rapid polymerization. In general, the smaller the amount of aqueous sodium hydroxide or the smaller amount of ethylene glycol containing combined sodium, the longer will be the length of the polyethylene oxide chain formed. The polyethylene oxide thus prepared will have two terminal hydroxyl groups and should have an average chain length of at least 24 ethenoxy units and more preferably a chain length of at least 36 ethenoxy units. From a small proportion of the polyethylene oxide product, sodium is removed for characterization purposes. To remove sodium, a portion of the product is neutralized with hydrochloric acid, dissolved in benzene, and dried by adding sodium sulfate. The sodium chloride and hydrated sodium sulfate are then filtered off and the benzene evaporated.

The sodium-free product is then characterized by determining the freezing point. The main portion of the polyethylene oxide still containing combined sodium is placed in an autoclave and reacted with a proper proportion of polypropylene oxide, suitably at a temperature

in the range of 100–140° C., until the pressure falls substantially to zero. Alternatively, as a starting material for the reaction with propylene oxide, a commercial polyethylene oxide, such as is sold under the name of Carbowax may be used. Such products are already characterized by the manufacturer, both in regard to freezing point and average molecular weight. The sodium necessary for reaction with propylene oxide may be introduced into such polyethylene oxide by dissolving it in ammonia and adding a solution of sodium in liquid ammonia and evaporating off the ammonia. Amounts of sodium up to the theoretical to convert both hydroxyl groups to sodium alcoholate groups may be used. As a simpler means of introducing sodium, suitable for large scale operation, the Carbowax may be melted and heated with a small proportion of sodium which melts and after breaking into small globules will completely react. In this manner, it is not possible generally to introduce a large molar proportion of sodium but this merely means that the subsequent reaction with the propylene oxide will be somewhat slower at a given temperature than when high proportions of sodium are introduced by the liquid ammonia method. A very suitable commercial polyethylene oxide for this purpose is Carbowax 1540 which is a polyethylene oxide containing two hydroxyl groups and which is considered to have an average molecular weight of 1540 which would represent about 35 ethenoxy groups.

For the preparation of the materials on a large scale, the procedure will be similar to that outlined for the preparation of the compounds of types 7*a* to 7*d*, except that it will usually be preferable to introduce ethylene oxide in gaseous form at a relatively low pressure from an external source during the course of the reaction. In this way, the possibility of uncontrolled reaction may be avoided, and, if desired, somewhat higher reaction temperatures may be used.

Four compounds which were prepared by the methods described and which were found to have especially suitable properties in the invention are the following:

1. Chloropolypropenoxy polyethylene oxide in which the chloropolypropylene oxide having a specific viscosity of 0.257 in 4% benzene solutions at 25° C. is substituted by 1 polyethylenoxy chain equivalent in weight to 90% of the total weight. The chlorine content of the chloropolypropylene oxide used was 1.48% corresponding to a molecular weight of about 2400.

2. Methoxypolypropenoxy polyethylene oxide in which methoxy polypropylene oxide having a specific viscosity of 0.137 in 4% benzene solution at 25° C. is substituted by 1 polyethylene oxide chain equivalent in weight to 60% of the total weight. This is believed to represent an average composition of about 14.5 propenoxy units and about 29 ethenoxy units.

3. Bispolyethenoxy polypropylene oxide in which polypropylene oxide having a specific viscosity of 0.155 in 4% benzene solution at 25° C. is substituted at both ends by polyethylene oxide chains which together are equivalent in weight to 60% of the total weight. The polypropylene oxide used had a molecular weight of about 1025 and the polymer prepared has an average composition calculated to represent 17.5 propenoxy units and about 35 polyethenoxy units. Other specific compounds of this type which were effective had ethenoxy contents of 55% and 80%.

Good results were also obtained with a polymer prepared from polypropylene oxide having a specific viscosity of 0.539 in 4% benzene solution at 25° C. and ethylene oxide in amount to represent 60% of the total weight.

Other very effective polymers used were prepared from polypropylene oxides within the molecular weight range of 1500–1800 by reacting them with ethylene oxide equivalent to 40–50% of the weight of the final polymer.

4. Bispolypropenoxy polyethylene oxide in which polyethylene oxide having an average of about 36 ethenoxy units is substituted at both ends by polypropylene oxide chains which together have an average of about 17 propenoxy units.

Treatment of pulp with the aforementioned polypropenoxypolyethenoxy polymers (the type 7 compounds of Table I) is described in pending application Serial No. 289,883, filed May 24, 1952, of Paul Henry Schlosser, Reid Logan Mitchell and Kenneth Russell Gray.

Descriptions of the treatment of pulp with other types of the polyalkylene oxide polymerization products may be found in the following U. S. patents issued to Paul Henry Schlosser and Kenneth Russell Gray: 2,393,817, 2,362,217, 2,451,558, 2,392,103 and 2,423,469. The water-soluble non-ionic surface-active agents are either available or can be produced according to operations described in said U. S. Patents 2,451,558 and 2,481,693.

In general for improving the acetylation and similar acylation reactions, the polyalkylene oxide polymerization products may be incorporated in the wood pulp at any stage in the production of dry sheet pulp from the wet fiber slurry. For treating the pulp, the compounds may be incorporated either in the bulk pulp before sheet formation or in the sheet at any stage prior to completion of the drying as by spraying the pulp with an aqueous solution or dispersion. A most practical and convenient method of securing the incorporation of the polyalkylene oxide polymerization compounds prior to completion of drying is to incorporate the compound in the refined wood pulp while it is on the sheet forming machine by means of sprays or a rotating roll. Such application may be made to the wet pulp web subsequent to removal of the mechanically removable water by pressing, or later at any stage while it is passing through the hot dryer rolls prior to completion of drying.

When pulp is dried in a conventional manner on hot dryer rolls, inactivation of the fibers toward esterification is greatest on the surface of the sheets. The inactivation probably results from minute changes in physical structure of the fibers, as for example in hydrogen bonding, caused by loss of the last portions of water under conditions of high temperature. It is the function of the added compounds of the invention to prevent or minimize these physical changes and thus prevent or minimize inactivation. Thus, if desired, the treatment of the pulp sheet with the additives of the invention may be accomplished by spray or a rotating roll in such a manner that the additives are largely incorporated near one or both surfaces of the sheet. Thus application is made largely to those fibers which would otherwise have the greatest tendency toward inactivation. In any event there is produced a substantially dry sheet of pulp containing a polyalkylene oxide polymerization product incorporated prior to completion of drying.

While the invention will be most usually applied in the drying of the pulp on the sheet forming machine as described above, it may also be applied to the reactivation of the pulp fibers in a sheet which has been already dried at an elevated temperature. In such case the dried sheet pulp will have at least one or both surfaces treated with a water solution of polyalkylene oxide polymerization product, as by spraying, or the dried pulp will be completely treated by dipping. The sheet thus treated with a water solution of a mixed ether will be redried using such heat as may be practically required. In such method of application, it is believed that the reactivation is brought about at least in part by the rewetting of the sheet with the water and that one function of the polyalkylene oxide polymerization products is to prevent or minimize loss during the second drying of the improved activity obtained by the rewetting operation in the same manner as above explained. Generally, however, where possible it will be economically preferable to carry out the treatment with the mixed ethers during the original drying on the sheet forming machine so that rewetting and redrying will be unnecessary.

The effective proportion of the polyalkylene oxide polymerization products incorporated in the wood pulp during the production of dry pulp from a wet slurry or in any reactivation treatment is from 0.015% to 0.5% based on the weight of bone dry pulp. Above this range in general no additional advantages are obtained and there are disadvantages in that the pulp sheet will tend to become undesirably soft and dusty and the added compound will undesirably contaminate the end product from the pulp. The quantities which would be preferred in practice for treating pulp intended for acetylation or other acylation processes will, however, frequently be considerably less than 0.5% and will depend both on the method of application and the economics. If essentially only the surfaces of the sheet are treated, less agent will be required for effecting a given amount of improvement than if the whole sheet is treated. This is because only those fibers would be treated which would have the greatest tendency to become unreactive.

EXAMPLE I

We find that use of sheet wood pulp dried in the presence of the agents gives marked improvement in acetylation as compared with pulp dried in a conventional manner in the absence of these additives. The inactivating effect of conventional drying and drying at an elevated temperature, and the improvements resulting from the application of the invention may be demonstrated by the following convenient and rapid laboratory test for comparing the acetylation reactivity of samples of sheeted wood pulp fibers:

Small specimens of the pulps to be examined are dipped in distilled water containing the required amount of polymer and dried in a circulating oven at a controlled elevated temperature to dry them under comparable conditions. An accurately weighed sample of 0.5 gram of each pulp is torn into small bits and placed in a 35 ml. vial. A flattened glass rod is placed in the vial through a hole in the cap and the vial and sample set in a water bath at 20° C.

The acetylating mixture is prepared by mixing 2.500 gms. H_2SO_4, 88.0 ml. acetic anhydride, and 175.0 ml. acetic acid. This mixture is unstable and should be freshly prepared every two days.

To the sample vial in the water bath 15 ml. of the acetylating mixture are added from a pipette. The pulp and acid are mixed with the glass rod, which remains in the vial. The vials are stored in the water bath and the mixing repeated every 15–20 minutes. It is important to include a standard sample with each group of unknowns and to handle and agitate all samples alike.

As the pulp samples are acetylated by the mixture they dissolve continuously. The time required for substantial solution to take place and the relative clarity and residual undissolved fibers at the time of observation will indicate whether any of the samples is more or less reactive than the standard. An observation of color is also made.

Acetate type wood pulps made and dried on commercial machines at four different times were tested by the above procedure after treatment with solutions of various polyalkylene oxide polymerization products of the six types described in Table I above. The sheet pulp samples were dipped into water solutions of the agents until they had absorbed about 0.4% thereof (by weight, dry basis), then redried at elevated temperatures. Control samples, treated only with water and dried at elevated temperatures and also at room temperature, show the effects of both the drying action and the added non-ionic agents.

The compounds applied, drying temperatures, and test observations are shown in the following Table II. The compounds are classified according to the 7 types described in this sepecification (Table I).

A portion of sample 1 was tested without any laboratory treatment whatever, and indicates the inactivity of conventional machine dried sheet pulp. The effect of the initial drying is further shown by sample 5, removed from commercial production before machine drying and dried at two temperatures in the laboratory.

TABLE II.—ACETYLATION REACTIVITY OF ACETATE WOOD PULPS TREATED WITH POLYALKYLENE OXIDE POLYMERIZATION PRODUCTS

Type [1]	Additive Used—Name or Description	Drying Temp., °C., after Additive Treatment	Acetylation Results	
			Dissolving Time, hrs.	Insoluble Residue at 7 hours
	Pulp Sample 1.—Machine Dried Hemlock Pulp			
	Completely untreated in the laboratory	----------	8-10	Many fibers.
	Water only	50	7	Few small fibers.
1	Polyethylene oxide, freezing point 49.5° C	50	6	Do.
2	Polypropylene oxide, sp. viscosity 0.131 [1]	50	6	Do.
4	Pentadecaethenoxy ether of dibutyl phenol	50	6½	Do.
5	Octaethenoxy ether of lauryl mercaptan	50	6½	Do.
6	Polyethenoxy (160 groups) ether of hydroabietyl alcohol	50	6½	Do.
	Pulp Sample 2.—Machine Dried Hemlock Pulp			
	Water only	50	6½	Many large fibers.
3	Dodecaethenoxy ether of lauryl alcohol	50	5	None.
3	Nonadecaethenoxy ether of oleyl alcohol	50	5½	Few small fibers.
3	Commercial polyethenoxy ether of lauryl alcohol (Brij 35)	50	5	Very few fibers.
	Pulp Sample 3.—Machine Dried Pine Pulp			
	Water only	50	6	Many large fibers.
3	Commercial agent—Brij 35	50	5	Few small fibers.
	Pulp Sample 4.—Machine Dried Hemlock Pulp			
	Water only	25	4½	None.
	Water only	85	10-12	Opaque mass.
1	Commercial polyethylene oxide, mol wt. about 1000 (Carbowax)	85	8	Slightly hazy.
2	Commercial polypropylene oxide, mol wt. about 2025	85	8	Do.
4	Commercial tridecaethenoxy ether of tetradecyl phenol	85	8	Do.
5	Dodecaethenoxy ether of octadecyl mercaptan	85	8	Do.
6	Dodecaethenoxy ether of hydroabietyl alcohol	85	8	Very slightly hazy.
	Pulp Sample 5.—Hemlock Pulp not Previously Dried			
	Water only	25	5½	None.
	Water only	85	10-12	Opaque mass.
1	Commercial polyethylene oxide, mol wt. about 1000 (Carbowax)	85	8	Slightly hazy.

[1] Description of additive types is given under corresponding number in Table I.
[2] Measured in 4% solution by wt. in benzene at 18° C.

Example II

A machine dried acetate pulp rewetted with distilled water and dried at 50° C. required to 6.5 hours to be dissolved in the acetylation test described in Example I and even then the solution contained some residual fibers. When another sample of the same pulp was treated in water solution with 0.4% of a chlorpropenoxy polyethylene oxide and likewise dried at 50° C., it dissolved in four hours to give a solution free from residual fibers.

We claim:

1. In the process of manufacturing cellulose acetate from formed wood pulp which is dried at temperatures which render untreated pulp partially unreactive toward acylation, the improvement which comprises applying the acylating agent to said wood pulp which carries at least on its surface from 0.02% to 0.5% by weight based on the substantially dry pulp of a water-soluble nonionic surface active agent applied to said pulp prior to drying, said surface active agent being a chain compound composed of a multiplicity of alkenoxy groups deriving its hydrophilic attraction from ether oxygen atoms and which is selected from the group consisting of a multiplicity of ethenoxy groups with one chain terminal group being —H and the other —OH, a multiplicity of propenoxy groups with one chain terminal group being —H and the other —OH, and a mixture of a multiplicity of ethenoxy and propenoxy groups with one terminal group of the chain being —H and the other being of the class consisting of —OH, alkoxy having 1 to 7 carbons, phenoxy, chlorine and bromine.

2. The process in accordance with claim 1 in which the surface active agent is a polyethylene oxide.

3. The process in accordance with claim 1 in which the surface active agent is a polypropylene oxide having a specific viscosity of about 0.065 to about 0.138 measured in a 4% by weight benzene solution at 18° C.

4. The process in accordance with claim 1 in which the polyalkylene oxide comprises a polymeric compound of 1–2 alkylene oxides of the group consisting of the compounds represented by the formulas

$$HO(CH_2CH_2O)_w-(\underset{CH_3}{\underset{|}{C}}HCH_2O)_x-(CH_2CH_2O)_vH$$

$$R-(\underset{CH_3}{\underset{|}{C}}H-CH_2O)_x-(CH_2CH_2O)_yH$$

and

$$HO(\underset{CH_3}{\underset{|}{C}}HCH_2O)_n-(CH_2CH_2O)_y-(\underset{CH_3}{\underset{|}{C}}H-CH_2O)_z$$

wherein R is one of the groups consisting of halogen, alkoxy having 1 to 7 carbons and phenoxy; x is at least 13, the sum of n and z is at least 13, the sum of w and v is the same as y, and the number of ethenoxy groups represented by y is such that the polymeric compound contains at least 20% ethylene oxide by weight and is water soluble, said compound being nonionic.

5. The process in accordance with claim 1 in which the polyalkylene oxide comprises a polymeric compound of 1–2 alkylene oxides of the group consisting of the compounds represented by the formulas

$$HO(CH_2CH_2O)_w(\underset{CH_3}{\underset{|}{C}}HCH_2O)_x-(CH_2CH_2O)_vH$$

$$R-(\underset{CH_3}{\underset{|}{C}}H-CH_2O)_x-(CH_2CH_2O)_yH$$

and

$$HO(\underset{CH_3}{\underset{|}{C}}HCH_2O)_n-(CH_2CH_2O)_y-(\underset{CH_3}{\underset{|}{C}}H-CH_2O)_zH$$

wherein R is one of the groups consisting of halogen, alkoxy having 1 to 7 carbons and phenoxy; x is at least 13, the sum of n and z is at least 13, the sum of w and v is the same as y, and the number of ethenoxy groups

represented by y is such that the polymeric compound contains 40% to 70% ethylene oxide by weight and is water soluble, said compound being nonionic.

6. The process in accordance with claim 1 in which the soluble polyalkylene oxide composed of a multiplicity of alkenoxy groups is an open composite chain comprising at least one polypropenoxy chain, at least one polyethenoxy chain and terminal groups, one of said terminal groups being —H and the other being one of the class consisting of HO—, alkoxy having 1 to 7 carbons, phenoxy, chlorine and bromine.

7. In the process of manufacturing cellulose acetate from wood pulp sheets machine dried at temperatures which render untreated pulp partially unreactive toward acetylation, the improvement which comprises applying the acetylating agent to the machine dried wood pulp which carries at least on its surface about 0.02% to 0.50% by weight of the substantially dry pulp of a water soluble surface active agent bispolyethenoxy polypropylene oxide of the general formula

$$HO(CH_2CH_2O)_w(\underset{CH_3}{\underset{|}{C}}HCH_2O)_x(CH_2CH_2O)_vH$$

in which x is at least 13, and w and v are such that the ethenoxy content represents from 20% to 90% of the agent.

8. In the process of manufacturing cellulose acetate from wood pulp sheets machine dried at temperatures which render untreated pulp partially unreactive toward acetylation, the improvement which comprises applying the acetylating agent to the machine dried wood pulp which carries at least on its surface about 0.02% to 0.50% by weight of the substantially dry pulp of a water soluble surface active agent halopolypropenoxy polyethenoxy oxide of the general formula

$$A-(\underset{CH_3}{\underset{|}{C}}HCH_2O)_x(CH_2CH_2O)_yH$$

where A is a halogen of the group consisting of chlorine and bromine and x is at least 13, and y is such that the ethenoxy content varies from 20% to 70% of the agent.

9. In the process of manufacturing cellulose acetate from wood pulp sheets machine dried at temperatures which render untreated pulp partially unreactive toward acetylation, the improvement which comprises applying the acetylating agent to the machine dried wood pulp which carries at least on its surface about 0.02% to 0.50% by weight of the substantially dry pulp of a water soluble surface active agent polypropenoxy polyethylene oxide of the general formula

$$RO-(\underset{CH_3}{\underset{|}{C}}HCH_2O)_x(CH_2CH_2O)_yH$$

where R is a radical of the group consisting of alkyl with 1–7 carbon atoms and phenyl and x is at least 13, and y is such that the ethenoxy content varies from 20% to 70% of the agent.

10. In the process of manufacturing cellulose acetate from wood pulp sheets machine dried at temperatures which render untreated pulp partially unreactive toward acetylation, the improvement which comprises applying the acetylating agent to the machine dried wood pulp which carries at least on its surface about 0.02% to 0.50% by weight of the substantially dry pulp of a water soluble surface active agent bispolypropenoxy polyethylene oxide of the general formula

$$HO(\underset{CH_3}{\underset{|}{C}}HCH_2O)_n(CH_2CH_2O)_y(\underset{CH_3}{\underset{|}{C}}HCH_2O)_zH$$

where the sum of n and z is at least 13, and y is such that

the ethenoxy content varies from 20% to 70% of the agent.

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