Patented Oct. 26, 1954

2,692,877

UNITED STATES PATENT OFFICE

2,692,877

ACETYLATION OF WOOD PULP

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No Drawing. Application May 11, 1951, Serial No. 225,928

8 Claims. (Cl. 260—229)

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This invention relates to the production of cellulosic derivatives from wood pulp and has for its object the provision of certain improvements in the production of such derivatives. The invention aims particularly to improve the acylation of wood pulp in sheet form and contemplates the use in acylation processes of substantially dry refined wood pulp in sheet form having incorporated therein a polyalkylene oxide polymerization product.

In one of its important aspects, the invention involves the use of substantially dry refined wood pulp in the preparation of fatty acid esters of cellulose, and has for a particular object the use of pulp having incorporated therein polyalkylene oxide polymerization products prior to final drying at an elevated temperature, whereby inactivation of the pulp as regards production of the cellulosic ester is greatly reduced.

As used in this specification, "substantially dry" refers to pulp either dried bone dry or containing that small moisture content which the hygroscopic pulp takes up from the air. Roughly this will refer to pulp containing from zero to ten per cent moisture.

In the preparation of refined wood pulp, 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 and if the water in the wet fibers is first displaced by organic solvents, the fibers react readily in such non-aqueous processes as the manufacture of cellulose acetate.

For practical reasons, however, it is generally necessary to form the pulp fibers into a dry pulp sheet, using heat to remove the last portions of the water. In such dry sheet form, the pulp may be readily shipped to distant factories for conversion into various derivatives. Also, in such relatively dry form, the pulp may be used in non-aqueous conversion processes without the need for expensive displacement of water by organic solvents.

However, in the formation of the pulp sheet and the drying at elevated temperature, the pulp fibers undergo various degrees of inactivation as regards use in the cellulose acylation processes, as for example the cellulose acetate process.

We have discovered that inactivation effects in the acylation of dry sheet pulp may be minimized by using pulp to which has been added minute amounts of polyalkylene oxide polymerization products during the production of the dry pulp sheet from the wet fiber slurry.

In accordance with the invention the acylation is carried out with refined wood pulp in which has been incorporated prior to final drying a small quantity of a polyalkylene oxide polymerization product. In the preferred form of the invention, the agents are incorporated in the pulp prior to completion of drying the pulp at an elevated temperature on the sheet forming machine. For minimizing inactivity in the acetylation and other esterification processes carried out in non-aqueous solution, for satisfactory benefit it is necessary that at least the surfaces of the sheet be completely treated prior to final drying at elevated temperature.

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The agents which we discovered for use in the invention are very effective in preventing loss of reactivity of the fibers during the formation of the dry pulp sheet and accordingly can be used in very small quantities.

The treated pulp containing the polyalkylene oxide polymerization products may be used with particular advantages in the production of cellulose acetate.

The compounds used in the improved acylation process of our invention are polymerization products of alkylene oxides, especially of the 1-2 alkylene oxides. More particularly, our compounds are non-ionic surface-active materials when dissolved in water, and which contain a multiplicity of alkenoxy groups.

The compounds used in the process of the invention are thus surface-active when used in water solution to treat the pulp fibers. Whether or not they actually exert a surface-active effect in the substantially non-aqueous medium of the 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 subclass 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 polyalkylene oxide radical, preferably though not necessarily relatively short (e. g., 8–50 alkenoxy residues), 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 the preferred forms, the group R is either a higher 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 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 groups must be such that the radical is not decomposed when the compound comes in contact with the acidic acylation mixture. There is a practical upper limit 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 six 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 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.
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.

In the class 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 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 pulp as a water solution.

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 falling within the designated specific

viscosity range of 0.065–°.138 are substantially soluble or dispersible in water and may be applied in water solution.

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 non-ionic 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.

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:

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

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 examples of mixed ethers which may be used in the invention are mixed ethers of polyethylene oxide and the following phenols:

Alkyl phenols

p-n-Butyl phenol, p-tertiary butyl phenol, p-$\alpha,\alpha,\gamma,\gamma$-tetramethyl butyl phenol, decyl phenol, dodecyl phenol, cetyl phenol, octadecyl phenol, (2-ethyl hexyl) phenol, oleyl phenol, such polyalkyl phenols as di- and trioctyl phenols, amyl cresol, dodecyl cresol; substituted naphthols such as isopropyl naphthol, isobutyl naphthol, dodecyl naphthol.

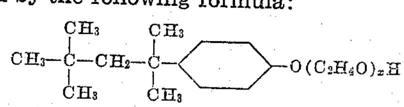
Cycloalkyl phenols

p-Cyclohexyl phenol, cyclohexyl - cyclohexyl phenol, bornyl phenol.

Acyl Phenols

Butyryl, valeryl, dodecyl, stearoyl phenols and the corresponding cresols, naphthols and xylenols.

As previously stated, the preferred mixed ethers are those containing predominantly a monoalkyl 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.

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, dehydro-

abietyl, 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 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.

The aforementioned water-soluble non-ionic surface-active agents are either available or can be produced according to operations described in U. S. Patents 2,451,558 and 2,481,693, issued to Paul Henery Schlosser and Kenneth Russell Gray.

Descriptions of the treatment of pulp with other sub-classes 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.

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 that 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.

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 treated with a solution of the treating agent or with distilled water and dried in a circulating oven at a selected controlled elevated temperature to dry them under comparable conditions. An accurately weighed sample of 0.5 gram of this 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 to a clear solution. The time required for this solution to take place, the relative clarity and residual undissolved fibers, and the relative appearance during the reaction time will indicate whether any of the samples is more or less reactive than the standard.

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 nonionic agents.

The compounds applied, drying temperatures, and test observations are shown in the following Table II. The compounds are classified according to the six types described in this specification (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 temperature, ° C. after additive treatment	Acetylation results	
			Dissolving time, hours	Insoluble residue at 7 hours
	Pulp Sample 1—Machined dried hemlock pulp:			
	Completely untreated in the laboratory			
	Water only		8–10	Many fibers.
1	Polyethylene oxide, freezing point 49.5° C	50	7	Few small fibers.
2	Polypropylene oxide, sp. viscosity 0.131 [2]	50	6	Do.
4	Pentadecaethenoxy ether of dibutyl phenol	50	6	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:	50	6½	Do.
	Water only			
3	Dodecaethenoxy ether of lauryl alcohol	50	6½	Many large fibers.
3	Nonadecaethenoxy ether of oleyl alcohol	50	5	None.
3	Commercial polyethenoxy ether of lauryl alcohol (BRIJ 35)	50	5½	Few small fibers.
	Pulp Sample 3—Machine dried pine pulp:	50	5	Very few fibers.
	Water only			
3	Commercial agent—BRIJ 35	50	6	Many large fibers.
	Pulp Sample 4—Machined dried hemlock pulp:	50	5	Few small fibers.
	Water only			
	---do	25	4½	None.
1	Commercial polyethylene oxide, mol weight about 1,000 (CARBOWAX).	85	10–12	Opaque mass.
2	Commercial polypropylene oxide, mol weight about 2,025	85	8	Slightly hazy.
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	Do.
	Pulp Sample 5—Hemlock pulp not previously dried:	85	8	Very slightly hazy.
	Water only			
	---do	25	5½	None.
1	Commercial polyethylene oxide, mol weight about 1,000 (CARBOWAX).	85	10–12	Opaque mass.
		85	8	Slightly hazy.

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

We claim:

1. In the process of manufacturing cellulose acetate from sheets of wood pulp which are dried at temperatures which render untreated pulp partially inactive toward acetylation, the improvement which comprises applying the acetylation agent to sheets of wood pulp which contain from about 0.02% to 0.50% by weight of the dry pulp of a water-soluble nonionic surface-active agent applied to said pulp prior to drying, said surface-active agent being one in which the hydrophilic attraction is due to ether oxygen atoms in a chain containing a multiplicity of ethenoxy groups and its lipophilic action is due to a hydrocarbon group containing more than 7 carbon atoms.

2. In the process of manufacturing cellulose acetate from sheets of wood pulp which are dried at temperatures which render untreated pulp partially inactive toward acetylation, the improvement which comprises applying the acetylating agent to sheets of wood pulp which contain about 0.02 to about 0.50% by weight of the dry pulp of a water-soluble polyalkylene oxide product in which the lipophilic action is due to a hydrocarbon group containing more than 7 carbon atoms.

3. The process in accordance with claim 2 in which the surface-active agent is a mixed ether having attached to the ether oxygen a polyethylene oxide radical and an aliphatic hydrocarbon radical containing more than 7 carbon atoms.

4. The process in accordance with claim 2 in which the surface-active agent is a polyalkylene oxide product represented by the formula

$$R-O-(CH(R_1)-CH_2O)_x-H$$

where R is an aryl radical substituted by at least one of the group consisting of alkyl having more than two carbons, acyl having more than two carbons and cycloalkyl; and R_1 is one of the group consisting of hydrogen and methyl; and x is an integer greater than 1.

5. The process in accordance with claim 2 in which the surface-active agent is a water-soluble mixed thio ether having attached to the sulfur atom a polyethylene oxide radical and the radical of an aliphatic hydrocarbon containing more than 7 carbon atoms.

6. The process in accordance with claim 1 in which the surface-active agent is a polyalkylene oxide product which is a water-soluble mixed ether having attached to the ether oxygen a polyethylene oxide radical and a cycloaliphatic radical of the group consisting of dihydroabietyl, dehydroabietyl, tetrahydroabietyl and abietyl.

7. The process in accordance with claim 2 in which the surface-active agent is a polyalkylene oxide product represented by the formula

$$R-A-(CH(R_1)-CH_2O)_x-H$$

where R is a hydrocarbon group selected from an alkyl group with at least 7 carbon atoms, an alkaryl group in which there is at least one alkyl radical having more than two carbon atoms, and an acylaryl group in which there is at least one acyl group having more than two carbon atoms; A is a linking atom selected from the group consisting of oxygen and sulfur and R_1 is one of the group consisting of hydrogen and methyl and x is an integer greater than 1.

8. 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 dried formed wood pulp which carries at least on its surface about 0.02% to about 0.50% by weight of the dry pulp of a water-soluble open chain polyalkylene oxide containing a multiplicity of alkenoxy groups; said chain having terminal groups, one of said terminal groups being —H and the other one of the class consisting of alkoxy having more than 7 carbon atoms, RS— in which R is an alkyl with more than 7 carbon atoms, R'O— where R' is alkaryl in which there is at least one alkyl group with more than two carbon atoms, and R''O— where R'' is acylaryl in which there is at least one acyl group having more than two carbon atoms.

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