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CELLULOSIC STRUCTURE

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This invention relates to cellulosic structures, especially those of pellicular nature. More particularly, it relates to a method for producing flexible and durable cellulosic pellicles by treating the same with softening agents comprising polymerized alkylene oxide, and the products resulting from such treatment.

This application is related to my copending application Serial No. 392,116, filed of even date herewith.

In the manufacture of cellulosic pellicles of the type precipitated from aqueous solutions such as regenerated cellulose pellicles, including sheets or films, caps, bands, continuous tubing, artificial straw and the like, it has long been customary to incorporate into the cellulosic pellicles a softening agent in order to maintain them in a flexible condition. Such cellulosic pellicles when freed from a softening agent are known to be quite brittle, and while a softener-free pellicle may find certain uses, a softened and, therefore, flexible sheet or film is much more generally useful. Heretofore, as softeners for the cellulosic pellicles, the art has applied such substances as ethylene glycol, propylene glycol, diethylene glycol, formamide, glycerol, and the like, but of these it is found the most important is glycerol which has hitherto known no equal as a softening agent for producing flexible, transparent and durable cellulosic pellicles such as those of regenerated cellulose.

However, glycerol and other softening materials used heretofore for the softening of regenerated cellulose products possess two serious disadvantages, namely, volatility and a tendency to transfer or migrate to other materials in contact with the softened regenerated cellulose. It is generally true that if the concentration of softener is too high, the cellulosic pellicle will be unduly limp and sticky, whereas if the concentration is too low, the article will be brittle and lack durability. An effort is, therefore, made at the time of manufacture to incorporate substantially the correct amount of softener to obtain the physical properties desired in the final film. However, in the case of a pellicle with a large area exposed to the atmosphere for long periods of time, even those softening agents which have a very low but appreciable vapor pressure will in time escape to a sufficient degree to lower the concentration of softener in the film below that at which satisfactory softening action is obtained. A reduction of only a few per cent in the softener content may result in the deleterious reduction of flexibility and durability and in

addition result in certain shrinkage and distortion of the pellicle making it unfit for use.

Difficulties arising from a decrease in softener content may also be brought about in quite a different manner than the escape of the softener through volatilization. It has been observed that regenerated cellulose products, which are in contact with other cellulosic bodies have a tendency to lose their softening agent when this agent is of the volatile or migrating type represented by those materials referred to above and, in fact, most of the softening agents heretofore known. As an example, cellulosic products such as paper, cotton, and linen fabrics, etc., wrapped in thin pellicles of regenerated cellulose softened with glycerol are found after a short time to extract a large portion of the glycerol from the pellicle used as a wrapping tissue leaving the latter brittle and distorted. This is a serious restriction in the use of these materials for wrapping a large number of products which may otherwise advantageously be wrapped in such transparent tissue.

Similarly, it has been proposed to cover wooden forms in the shape of bobbins, spindles, and guiding members with a sleeve of regenerated cellulose shrunk into close contact with the surface of the wooden form. Where such forms are subsequently wrapped with fabric or yarn, the glycerol or other softener soon makes its escape on the one side to the wooden core and on the other side to the cellulosic materials wrapped or placed over the core. As a result, the cellulosic sleeve soon shrinks and cracks and must be replaced.

Certain softeners which have been suggested in the past to produce special effects are, in general, unsatisfactory for commercial production of film because of water insolubility. While it is true that it is possible to introduce softening materials into regenerated cellulose products by special methods, the method ordinarily employed in the production of the regenerated cellulose product requires water solubility of the treating material; the use of special methods for the introduction of water insoluble materials leads to prohibitive costs in the manufacture of the cellulosic product.

It is, therefore, an object of this invention to provide a new and useful method for producing softened cellulosic materials possessing desirable physical properties.

It is a further object to provide cellulosic materials having a softening agent associated therewith, which softening agent will not tend to es-

cape through volatilization or through transfer to other cellulosic bodies.

Other objects of the invention will appear hereinafter.

The objects of this invention can be accomplished, in general, by treating a water-sensitive cellulosic pellicle, such as a regenerated cellulose pellicle, with an aqueous solution or dispersion of a polymer of an alkylene oxide, which may contain modifying groups, said polymer to have a molecular weight in the range of 400 to 5,000 and to be soluble in water at a temperature of 25° C. to the extent of at least 4%.

For convenience, the invention will be described in terms of regenerated cellulose pellicles, particularly sheets or films, ribbons and tubing. Nevertheless, the invention is broadly applicable to water sensitive cellulosic pellicles.

In the manufacture of regenerated cellulose sheets or films, as for example by the viscose process, the viscose dispersion is extruded through a fine slot into a coagulating and/or regenerating bath from which it is finally obtained in the form of a continuous cellulosic sheet, which is customarily led in a continuous manner through a series of purifying, bleaching and washing operations, as described in Brandenberger, U. S. Patent No. 1,548,864. In certain cases, the viscose solution is extruded and processed in the form of a tube by well-known methods of operation. Just prior to the drying operation, which is also usually continuous, coordinating with the extruding operation, the film is passed through a bath containing a softening agent in such concentration that after the excess liquid has been removed from the surface of the sheet by suitable squeeze rolls and the excess moisture removed by passage through the drier, the web can be wound up in a continuous fashion and will contain an appropriate, predetermined amount of softening agent.

The commercially available regenerated cellulose film contains approximately 4% to 8% moisture, depending upon the softener content and the relative humidity of the atmosphere. Depending upon the use of the film, the softening agent contained therein, usually glycerol, may vary from about 8% to 25%, based on the combined weight of the cellulose and softening agent in the sheet.

The total amount of softener in the film is controlled primarily by the total amount of softening agent in the treating bath, however, film thickness, rate of passage through the bath, temperature of the bath, etc., may also contribute to a certain extent. The regenerated cellulose pellicle, when reaching the treating bath is in a highly swollen and hydrated condition and usually the cellulose of the pellicle is associated with 300% or more of water, based upon the weight of the cellulose. This highly swollen and wet pellicle, usually referred to as the gel sheet, is impregnated with the treating bath. Because of the large amount of water associated with the cellulose, it is apparent that the removal of this water during the drying operation will concentrate the softening agent with respect to the cellulose content of the pellicle.

It has now been discovered that polymers of alkylene oxide having a molecular weight in the range of 400 to 5,000 and which exhibit a solubility in water at 25° C. of at least 4% are eminently suited for the purposes of this invention. In some instances, the polymers may contain modifying groups as hereinafter specified.

The polyalkylene oxide used in the process of this invention may be prepared by any of the known methods, for example by heating the monomeric oxide in the presence of a catalyst (e. g., an alkaline catalyst), if necessary under pressure, until a substantial proportion of polymer is formed, and removing the unchanged monomer. Staudinger, *Die Hochmolekularen Organischen Verbindungen*, 1932, page 287 et seq.) The products, depending on their molecular weight, are solid, semi-solid, or even fluid materials, which are soluble in both water and certain organic solvents such as benzene. These products are generally believed to be composed of a plurality of alkylene groups linked together in linear configuration through ether linkages, and to bear hydroxyl groups at the ends of the polymeric chain. Thus, polyethylene oxide is represented by $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$ (Staudinger loc. cit.). These polymers are sometimes called polyethylene glycols.

Commercially prepared polyalkylene oxides, such as the materials produced by the Carbide and Chemicals Corporation under the trade name "Carbowax" are satisfactory for the process of this invention.

The molecular weight of the polyethylene oxide used is a critical factor and it is therefore necessary to use products having a molecular weight not substantially in excess of 5,000 since higher molecular weight products become less soluble and less easily dispersible in the cellulosic material. It is also necessary, for satisfactory results, that the molecular weight of the polymers be above 400 since those of lower molecular weight are, to some extent, volatile and tend to migrate or transfer out of the regenerated cellulose product to other cellulosic materials with which the same may be in contact.

Although the polymeric alkylene oxides themselves are to be preferred in the practice of this invention, a number of materials composed of a polymeric alkylene oxide having certain constituents attached to one end of the molecule, for example, such as methyl cellosolve (beta methoxy ethanol) or castor oil, are useful in the practice of this invention.

It has been pointed out by Flory, JACS, volume 62, page 1561 (1940), that ethylene oxide reacts with ethylene glycol to form diethylene glycol and higher glycols by successive additions of ethylene oxide on a chain basis. In a similar manner, the ethylene oxide will form reaction products with castor oil and other materials having hydroxyl groups.

The following examples are given to illustrate the preferred methods of carrying out the present invention. The parts and percentages referred to are parts and percentages by weight.

Example I

A sheet of gel regenerated cellulose in which the final dry thickness will be about .0009 inch is immersed in or drawn through an aqueous bath containing 7% polyethylene oxide having an average molecular weight of 1,500, maintained at a temperature of 30° C. The sheet remains in contact with this bath sufficiently long to thoroughly impregnate the gel structure with the solution, after which it emerges from the bath. Excess liquid is removed from the surface of the sheet by means of squeeze rolls, doctor knives, etc. and the sheet dried on the conventional roll drier. After drying, the sheet is found to contain 13% polyethylene oxide, based on the weight

of the cellulose, and approximately 6% water. The sheet so produced is transparent, flexible and durable, and the flexibility of the sheet is not substantially impaired when used in wrapping of paper or fabric goods.

Example II

A sheet prepared as in Example I, is passed through a bath containing 11% polyethylene oxide ("Carbowax" with an average molecular weight of 4,000), excess solution removed from the surface of the web, and the same dried in the conventional type of roll drier. Films so produced were found to have a softener content of 17% based on the weight of the cellulose, and a moisture content of 6%. This film was transparent, highly flexible and durable, and maintained its flexibility when in contact with cellulosic materials such as paper and fabrics.

Example III

A sheet produced as in Example I is passed through a bath containing 7% of the reaction product of 4 parts of ethylene oxide polymer and 3 parts of glycerol (parts by weight). Excess solution was removed from the surface of the sheet and the same dried in the usual manner. The final product contained 13% of the softening agent and was highly flexible, transparent and durable.

Example IV

A sheet prepared as in Example I is passed through a bath containing 11% of a condensation product of ethanol formamide and ethylene oxide, said condensation product containing one mol of ethanol formamide per mol of polymer and having an average molecular weight of 469. Excess solution is removed from the surface of the sheet and dried in the conventional manner. The sheet so produced contains 17% of the softening agent and is highly flexible, durable and transparent.

Example V

A sheet produced as in Example I is passed through a bath containing 7% of the reaction product of glycerol and ethylene oxide polymer having an average molecular weight of 461. Excess solution was removed from the surface of the sheet and the same dried in the usual manner. The final product contained 13% of the softening agent and was highly flexible, transparent and durable.

Example VI

A sheet prepared as in Example I is passed through a bath containing 14% of the reaction product of ethanol hydroxy acetamide and ethylene oxide, said reaction product having an average molecular weight of 1071. The sheet so produced is found to contain 17% of the softening agent, based upon the cellulose, and is highly durable, flexible and transparent.

Example VII

A sheet produced as in Example I is treated with a bath comprising 7% of the reaction product of tetrahydro furfuryl alcohol and ethylene oxide, said products having an average molecular weight of approximately 721. The product after removal of excess liquid and drying contains approximately 13% of the softening agent together with 6% moisture, based upon the cellulose. It is highly transparent, flexible and durable.

Example VIII

A sheet produced as in Example I is passed through a bath containing 11% of the reaction product of cetyl alcohol and ethylene oxide, said reaction product having an average molecular weight of approximately 480. After removal of excess liquid and drying, the sheet is found to contain approximately 17% of the softening agent and is highly flexible, durable and transparent.

Example IX

A regenerated cellulose pellicle in the form of a tube is coagulated, regenerated and purified in a manner similar to that described in Example I with reference to the production of a regenerated cellulose sheet. The tube is then passed through a bath containing 11% of the reaction product of methyl cellosolve (beta methoxy ethanol) and ethylene oxide polymer, said reaction product having an average molecular weight of approximately 783. Excess liquid is removed from the surface of the tube, the same cut into short lengths and applied to the mouth and neck of a liquor bottle as a secondary closure. Upon evaporation of the moisture, the band shrinks into intimate contact with the neck of the bottle serving to protect the cork or other primary closure and the upper portion of the neck of the bottle. This cellulosic band is in contact with the paper liquor stamp with which such bottles are provided. It is found that even after long periods of storage the softening material does not transfer from the cellulosic band to the paper of the tax stamp and hence the cellulosic band is not embrittled or otherwise deleteriously affected so as to cause its premature removal from the bottle. Longer sections of tubing prepared in this manner may be very satisfactorily shrunk onto wooden cores used as bobbins and forms for the winding of textile yarns.

As a base, the invention contemplates the use of any non-fibrous, water-sensitive cellulosic structure, particularly of pellicular nature such as a sheet or film, artificial straw, caps, bands, or continuous tubes, such as may be obtained by the coagulation and/or regeneration from an aqueous alkaline cellulosic dispersion in an acid coagulating bath in accordance with the procedure customary to the art. Thus, the invention comprehends the use of regenerated cellulose pellicles such as may be obtained from viscose or cuprammonium cellulose, glycol cellulose, cellulose glycolic acid, lowly esterified or lowly etherified cellulose derivatives where there is only one ether or ester group associated with several cellulose units, and other cellulosic structures of similar character.

All of the examples given have been set forth in terms of a sheet or film of gel regenerated cellulose (gel regenerated cellulose is a water swollen regenerated cellulose which never has been dried). Obviously this is the more practical way of practicing the invention since the softening agent is customarily incorporated into the sheet or film while the latter is in the gel state in and during the normal course of manufacture. Obviously, if one desires to impregnate an already dried regenerated cellulose film with a softener of the character described, it is possible to rewet the dried film so as to render it highly swollen whereupon it may be treated with treating baths similar to those described, but of

composition suitable to obtaining the final product desired.

In general, the softening materials comprehended by this invention are those that are formed by the polymerization or chain reaction of an alkylene oxide such, for example, as ethylene oxide, propylene oxide, butylene oxide, etc. said chain formations to extend to products with a molecular weight lying in the range of 400 to 5,000. The products of interest in this invention are those having a water solubility at a temperature of 25° C. of at least 4% in order that they may be introduced in a satisfactory manner into the regenerated cellulose or other water sensitive cellulosic structure.

If desired, a polymeric alkylene oxide material may be modified by incorporation of certain other organic radicals having an active hydrogen, for example, aliphatic acids, amines, hydroxylated materials such as glycerol, ethyl cellosolve (beta ethoxy ethanol), etc. In general, the softening material will be formed by reacting the modifying group with ethylene or other alkylene oxide until the molecular weight of the resulting product lies in the range of 400 plus the molecular weight of the modifying group to 5,000 plus the molecular weight of the modifying group. Modifying groups of especial interest to this invention are as follows: adipic acid, castor oil, aniline, glycerol, methyl cellosolve (beta methoxy ethanol), N-isobutyl acetamide, bis-N,N'-ethyl ethanol urea, N-butyl-N-beta-hydroxy ethyl lactamide, bis-N,N'-ethanol oxamide, glycerol furfural, glycerol formal, 2,2-diethyl-1,3-propanediol.

It is also to be understood that various mixtures of the newly described softening agents may be employed with single softeners of the prior art or with mixtures of the latter, depending upon the type of final film desired and the purposes for which the film is to be used. Other softening agents suitable for incorporation with the softeners of the invention are as follows: tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, ethanollactamide, isopropanolglycolamide, ethanollformamide-ethylene oxide reaction product of an apparent molecular weight of 152, aniline-ethylene oxide reaction product of an apparent molecular weight of 244, etc.

If a colored cellulosic pellicle is desired, it may be obtained in any of the ways commonly known in the art, including the passage of the sheet or film through a bath containing a suitable dyestuff. If desired, the dyestuff may be added to the bath used for introducing the softening agent. In the same way, after the film has been treated with the softening agent, it may be subjected to any of the customary after treatments such as sizing or coating or the like, which may be cus-

tomarily given to cellulosic pellicles of the type described, in just the same manner that a glycerol softened regenerated cellulose film, for example, may be treated.

5 The term "durability" as used in the present specification refers to resistance to shock or rough handling. Thus, for example, bags may be fabricated from the pellicle and filled with some standard material such as a certain weight of dried beans, and the package sealed, whereupon the durability may be measured, by dropping the package under standard conditions and noting the resistance to breakage of the wrapper.

15 The outstanding advantage of the softening agents of this invention over those described in the prior art is the permanence with which they remain in a non-fibrous cellulosic structure. Since they are of very low volatility, they are not lost by volatilization such as a number of well known softeners, for example, glycol and glycerol. Furthermore, they do not migrate or transfer out of the transparent cellulosic structure to other cellulosic structures with which the same may be in contact. This last named property permits use of these materials in the form of thin pellicles as wrappings with cellulosic materials, for example, fabrics, textiles, paper, etc., and permits their long and continued contact with the contents of the package without losing the softening agent and consequently with the retention of the flexibility and durability of the original wrapping tissue. As another example, caps and bands used as secondary closures for containers may be applied to the mouths and necks of bottles over paper labels and still exhibit no tendency to embrittlement, splitting and cracking after long periods of storage. Similar cellulosic tubing may be employed as durable and lasting protective coverings for wooden cores and bobbins, etc.

40 Since it is obvious that many changes and modifications can be made in the above described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the details described herein except as set forth in the appended claims.

I claim:

50 1. A flexible, durable, regenerated cellulose pellicle, said pellicle containing, as a softener therefor, an alkylene oxide polymer having a molecular weight between 400 and 5,000 and having a solubility of at least 4% in water at a temperature of 25° C.

55 2. A flexible, durable, regenerated cellulose pellicle, said pellicle containing, as a softener therefor, an ethylene oxide polymer having a molecular weight between 400 and 5,000 and having a solubility of at least 4% in water at a temperature of 25° C.

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