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ARTICLE OF MANUFACTURE AND PROCESS OF PREPARING SAME

James E. Snyder, Kenmore, N. Y., assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to cellulosic structures, especially pellicles, such as may be obtained by the casting and appropriate coagulation and/or regeneration of aqueous cellulosic dispersions. It relates particularly to softening agents for such cellulosic structures, and it relates especially to softeners for regenerated cellulose pellicles.

The invention will be described in its preferred form in terms of its application to regenerated cellulose pellicles, but it is to be understood that it is also applicable to cellulosic structures such as may be obtained by coagulation or precipitation of aqueous cellulosic dispersions. Thus, the invention contemplates, for example, cellulose regenerated from viscose or from cuprammonium solution as well as cellulose derivatives such as glycol cellulose, cellulose glycolic acid or other lowly esterified or etherified cellulose derivatives.

Pellicles of regenerated cellulose are well known and as they are commonly manufactured, they contain from 5–8% of moisture and a certain amount of a substance commonly known as a softener which serves to impart flexibility to the pellicle (especially when the moisture content is low). A pellicle of regenerated cellulose containing no softener and from which the moisture has been removed is very fragile and brittle, the least strain causing it to shatter.

Most of the uses to which pellicles of regenerated cellulose may be put require at least a certain degree of flexibility and durability, and this is particularly true in the case of wrapping tissues of regenerated cellulose where flexibility and resistance to shattering constitute characteristics of prime importance. The mechanism of the softening action is not thoroughly understood, but the best softening action seems to be obtained when the softener is hygroscopic in nature and cooperates with the moisture in the film to impart and maintain flexibility. Thus, the softening agent may of itself exert some softening, or perhaps lubricating action, especially when the moisture content is low.

Under the conditions of manufacture, the softener and moisture content of regenerated cellulose pellicles are carefully controlled and if the conditions such as temperature and air humidity under which the product is used could always be maintained the same as those under which the product is manufactured, then, of course, the problem of softening or flexibilizing the regenerated cellulose sheet would be greatly simplified. As a matter of fact, however, the atmospheric conditions to which the regenerated cellulose sheeting may be subjected during transportation, storage and use are subject to variations and rarely approximate the conditions of manufacture. Thus, for example, during transportation in the summer time, the film may be subjected to relatively high temperatures while in the winter time, the temperatures may be very low. In certain uses, such as the packaging of frozen foods according to the quick freezing art, the foodstuffs may be wrapped in sheets of regenerated cellulose and subjected to a temperature as low as −30° F. for intervals sufficiently long to bring them into proper condition and thereafter the goods are maintained at a low temperature by any convenient means until they are ready for consumption. When the sheets of regenerated cellulose are subjected to low temperatures, the softening agent may tend to lose its softening action. It may become so viscous that it no longer exerts a lubricating action on the cellulosic material, or, indeed, it may crystallize. On the other hand, when the regenerated collulose pellicles are subjected to elevated temperature, the moisture may be driven out and the softener may itself volatilize. Then, again, the sheets may be subjected to atmospheres of high temperatures and/or relatively low humidity, a condition which is frequently characteristic of winter atmospheres indoors and in arid regions in summer. When such pellicles are subjected to low humidities, moisture is lost from the film and consequently the preferable balance between softener and moisture content is lost.

One object of the invention comprises the softening of cellulosic materials so as to retain flexibility and durability.

It is a further object of the invention to provide a coated pellicle of cellulosic material of the type described with a softening agent for the cellulosic material such that the product retains its flexibility and durability under abnormally low atmospheric conditions of temperature and/or humidity during storage, transportation and use.

A further object of the invention comprises the use of softening agents for cellulosic materials of the type described, which may normally be too volatile for practical purposes, characterized in that the softened cellulosic material is provided with a top coat which prevents loss of softener by evaporation.

Other objects of the invention will appear hereinafter.

According to present practice and the prior art, glycerol has been the accepted softener for regenerated cellulose pellicles. The substitutes for glycerol that have been suggested present so

many difficulties and disadvantages that they are quite unsatisfactory for use. Many of them are relatively low boiling and consequently, when a pellicle of regenerated cellulose softened with them is exposed to the atmosphere, the softener itself volatilizes and the film is rendered less flexible and even brittle. On the other hand, those softeners that are not objectionably volatile at ordinary temperatures, no longer exert a softening action at low temperatures, possibly because they become too viscous when subjected to such low temperatures. Additionally, when the humidity is low and the moisture content of the film is thereby decreased, the loss of softening action at low temperatures makes the product even more brittle.

As a consequence, glycerol has been used to soften pellicles of regenerated cellulose and for ordinary conditions has proved satisfactory. Pellicles of regenerated cellulose softened with it, however, if satisfactory under normal conditions become brittle at low temperatures. If attempts are made to increase the amount of glycerol in order to improve the flexibility at low temperatures, it is found that the pellicles then become useless at ordinary temperatures because the amount of glycerol required renders them limp and sticky at ordinary temperatures and humidities. It is obvious, then, that the use of glycerol in large amounts is not in itself a solution to the problem, for, of course, the softened film must be useful not only at low temperatures, but must be useful as well at ordinary or elevated temperatures.

Recently, there have appeared on the market pellicles of regenerated cellulose bearing surface coatings and these pellicles are normally softened by means of glycerol. These materials are useful particularly as wrapping tissues and in their preferred form, the product is moistureproof, being rendered so by virtue of a moistureproofing coating composition which may comprise in one of its preferred forms a cellulose derivative lacquer comprising a moistureproofing agent such as a wax or wax-like material and preferably also, a resin or blending agent and a plasticizer. In another of its preferred forms, the moistureproofing coating composition may comprise a resin and a moistureproofing agent such as a wax or wax-like material, either with or without added blending agent and/or plasticizer.

These coated pellicles find wide use in the wrapping of various materials and they are subjected during the course of their transportation, storage and use, to widely varied atmospheric conditions. The flexibility of the coated product, which is a very important factor, depends very largely on the softening agent which is used for the base film of regenerated cellulose and since glycerol is commonly the softening agent, the coated product will generally have the flexibility and durability characteristics of an uncoated regenerated cellulose film softened with glycerol. As a consequence, these coated pellicles are generally unsatisfactory at low temperatures because of the loss of flexibility. As a matter of fact, they are poorer than uncoated pellicles possibly because the coating interferes with the increase in moisture content which would normally take place at low temperatures and relatively high humidities. This embrittlement of the film at low temperatures offers serious disadvantages in the wrapping of frozen foodstuffs or other materials which must be maintained at low temperatures. It causes serious losses in shipping during winter. It seriously interferes with the operation of high speed wrapping machines for various types of commodities, especially during the winter months when indoor humidities are low.

According to the present invention, it has been found that the disadvantages inherent in coated regenerated cellulose pellicles softened with glycerol can be overcome by using ethylene glycol as a softener for the regenerated cellulose. Ethylene glycol is volatile as compared to glycerol, but it is rendered useful as a softener at normal or slightly elevated temperatures by providing the softened regenerated cellulose pellicle with a suitable topcoat which so inhibits the volatilization of the softener as to make the product useful over a wide range of temperatures and/or relative humidities. When a moistureproofing coating composition is used as the topcoat, the product is substantially unaffected in its flexibility and durability by wide variations in atmospheric humidity.

According to the invention, I have found that I may substitute ethylene glycol directly for the proportion of glycerol normally used to soften regenerated cellulose film and by providing a suitable topcoat, such, for example, as a moistureproofing coating composition similar to that described above, I can produce a softened, coated pellicle of regenerated cellulose which will retain substantial flexibility at low temperatures, even as low as −30° F., as well as at low atmospheric humidities, and at the same time will remain in the film and exert its softening action at normal temperatures or even at slightly elevated temperatures such as might be encountered in transportation in summer weather.

In the manufacture of regenerated cellulose pellicles as, for example, by the viscose process, a viscose solution is cast by means of a suitable casting device into a coagulating and/or regenerating bath and the completely regenerated film is then washed, purified, and then washed again. Prior to drying, it is passed through an aqueous bath containing the softener which, in the usual practice, is glycerol. The concentration of the glycerol in this bath depends, among other things, on the desired glycerol content of the final film, the speed of the film, the thickness of the film and the completeness of immersion.

In the practice of the present invention, I may use an ethylene glycol bath instead of a glycerol bath. The concentration of the ethylene glycol is, of course, determined by the amount of ethylene glycol which it is desired shall remain in the finished film. Thus, by changing the concentration of the ethylene glycol bath so that its specific gravity varies from about 1.0084 to about 1.015, I may secure in the final dried film an ethylene glycol content varying from approximately 9% to about 20%. Obviously, if it is desired to have more or less ethylene glycol in the final film, appropriate solution concentrations will be chosen.

After the ethylene glycol impregnated film has been dried down to an appropriate moisture content as, for example, 4–7% moisture, it is subjected to a coating operation and the type of coating chosen will obviously depend upon the use to which the coated product is to be put. In its preferred form, my invention contemplates coating with a moistureproofing composition. Since a precise composition of the moistureproofing coating is not critical to the instant invention, it is sufficient to say that coating composi-

tions such as those described in Charch and Prindle U. S. Patent No. 1,737,187 and Charch and Prindle U. S. Patent No. 1,826,696 will serve admirably.

For the purposes of this invention, moistureproof materials are defined as those which, in the form of a thin, continuous and unbroken film, will permit the passage of not more than 690 grams of water vapor per 100 square meters per hour, over a period of 24 hours at approximately 39.5° C. plus or minus 0.5° C., the relative humidity of the atmosphere at one side of the film being maintained at least at 98% and the relative humidity of the atmosphere at the other side being maintained at such a value as to give a humidity differential of at least 95%.

Moistureproofing coating compositions are defined as those which, when laid down in the form of thin, continuous, unbroken films, applied uniformly as a coating with a total coating thickness not exceeding 0.0005" to both sides of a sheet of regenerated cellulose of thickness approximately 0.0009", will produce a coated product which is moistureproof.

For the purposes of experimental tests, especially for those materials adaptable as coating compositions, moistureproof materials include those substances, compounds or compositions which, when laid down in the form of a continuous, unbroken film, applied uniformly as a coating with a total coating thickness not exceeding 0.0005" to both sides of a sheet of regenerated cellulose of thickness approximately 0.0009", will produce a coated sheet which will permit the passage therethrough of not more than 690 grams of water vapor per 100 square meters per hour over a period of approximately 24 hours, at a temperature of 39.5° C. plus or minus 0.5° C. (preferably 39.5° C. plus or minus 0.25° C.) with a water vapor pressure differential of 50–55 m. m. (preferably 53.4 plus or minus .07 m. m.) of mercury. For convenience the number of grams of water vapor passed under these conditions may be referred to as the "permeability value." An uncoated sheet of regenerated cellulose having a thickness of approximately 0.0009" will show a permeability value of the order of 6900.

In the foregoing, it is apparent that under the conditions set forth, a moistureproof regenerated cellulose sheet is capable of resisting the passage of moisture or water vapor therethrough at least ten times as effectively as the uncoated regenerated cellulose sheet.

Moistureproofing compositions which may be used to coat the ethylene glycol-softened cellulosic pellicle comprise, for example, a cellulose derivative, a wax, a plasticizer, preferably also a resin or other blending agent, and a suitable solvent medium. Where it is not desired to produce a moistureproof pellicle, the volatility of the ethylene glycol may be overcome by using any suitable top coating in order to prevent the escape of the ethylene glycol, a suitable coating being any lacquer which does not interfere with the transparency, flexibility and the desired characteristics of the composite film. Such non-moistureproofing coatings may, for example, be the same type of coating as is used for moistureproofing except that the wax is omitted.

Ethylene glycol is by far the most desirable softener for films which are adapted to be subjected to low temperatures due to its desirable softening effect both at ordinary temperatures and at low temperatures, and due to the fact that even when coated with a lacquer having a cellulosic base, since it is not a solvent for the lacquer component, it can be retained in the base film successfully.

While they cannot be said to be as successful as ethylene glycol when used as softeners for film which is subjected to abnormally low temperatures, the broad scope of the invention may include propylene glycol and/or butylene glycol. Still other materials which may similarly be used are triethylene glycol, ethoxy-ethoxyethanol, butoxy-ethoxyethanol and other low viscosity materials.

It is obvious that certain economies may be realized by using mixtures of the softeners disclosed, depending on the purposes to which the product may be applied. Thus, it may be found advantageous to replace a small proportion of the relatively expensive ethylene glycol with glycerol, diethylene glycol, or the like, as set forth above.

Certain of the substances which have been mentioned above as substitutes for the ethylene glycol will be found to have good softening action on the regenerated cellulose, but at the same time will have a solvent action on certain types of topcoatings. Obviously, this may be overcome, by one skilled in the art, by an appropriate choice of coating compositions. Obviously, a combination of softener and coating composition will be chosen such that the softener will not attack appreciably the coating composition, whereby to render it soft or tacky at normal temperatures even though the solvent action may be less pronounced at low temperatures.

The product of my invention offers many advantages over materials of the prior art. Pellicles of cellulosic materials, especially regenerated cellulose pellicles, may be rendered flexible and durable not only for normal atmospheric conditions of storage, transportation and/or use, but also for abnormal conditions. The retention of flexibility and durability reduces losses which would otherwise be objectionably great. The field of use for pellicles of the type described is greatly extended, especially for uses where flexibility and durability at low temperatures and/or humidities is required, such as in the packaging of frozen foodstuffs and the like. In connection with the operation of high speed wrapping machines, the product of my invention provides a wrapping material of admirable flexibility and durability despite the variable atmospheric conditions of storage, transportation and/or use.

The process of my invention contributes greatly to the art of softening cellulosic pellicles of the type described. Softening agents heretofore considered as useless because of their volatility may be employed to great advantage. The process provides a means for the manufacture of very flexible and durable pellicles, especially useful as wrapping tissues, which may be additionally moistureproof and of good surface, which are capable of retaining their desirable properties at very low temperatures, even as low as −30° F., and/or at low humidities. Numerous other advantages will be apparent to those skilled in the art.

Any variation or modification which conforms to the spirit of the invention is intended to be included within the scope of the claims.

I claim:

1. A non-fibrous, cellulosic pellicle, obtained by coagulation of an aqueous cellulosic dispersion, containing ethylene glycol in quantities sufficient to maintain said film flexible at temperatures

ranging as low as —30° F. and having a lacquer coating on both sides of said pellicle which will not be dissolved by said ethylene glycol, said coating functioning to seal the ethylene glycol in the pellicle whereby to obtain a pellicle which will be flexible for long periods of time.

2. A non-fibrous, cellulosic pellicle, obtained by coagulation of an aqueous cellulosic dispersion, containing a softener therefor, said softener consisting of ethylene glycol, said pellicle having a lacquer coating on both sides of said pellicle which will not be dissolved by said ethylene glycol, said coating functioning to seal the ethylene glycol in the pellicle whereby to obtain a pellicle which will be flexible for long periods of time.

3. A non-fibrous, cellulosic pellicle, obtained by coagulation of an aqueous cellulosic dispersion containing ethylene glycol as a softener therefor, said ethylene glycol being present in quantities from 9% to sufficient to maintain said film flexible at temperatures ranging as low as —30° F., a lacquer coating which will not be dissolved by said ethylene glycol on both sides of said pellicle, said coating functioning to seal the ethylene glycol in the pellicle, whereby to obtain a pellicle which will be flexible for long periods of time.

4. A regenerated cellulose pellicle containing ethylene glycol as a softener therefor, said ethylene glycol being present in quantities from 9% to sufficient to maintain said film flexible at temperatures ranging as low as —30° F., a cellulose derivative lacquer coating which will not be dissolved by said ethylene glycol on both sides of said pellicle, said coating functioning to seal the ethylene glycol in the pellicle, whereby to obtain a pellicle which will be flexible for long periods of time.

JAMES E. SNYDER.