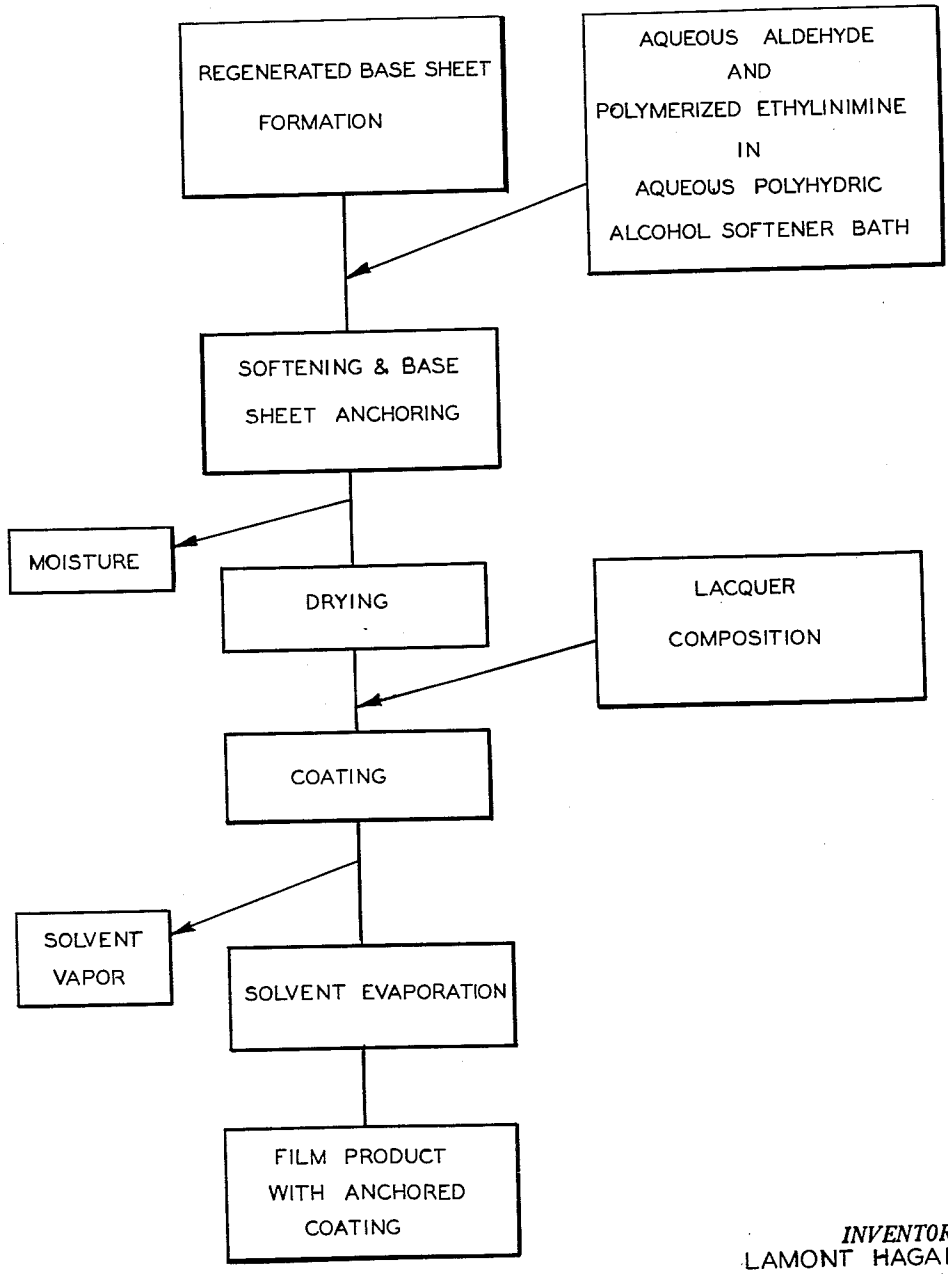
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METHOD OF ANCHORING A NITROCELLULOSE BASE SURFACE COATING TO A CELLULOSE BASE SHEET

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METHOD OF ANCHORING A NITROCELLULOSE BASE SURFACE COATING TO A CELLULOSE BASE SHEET

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The subject invention relates to a composition useful in anchoring surface coatings to base surfaces, to the method of preparing the composition, and to the surface coated article formed thereby.

In recent years, transparent sheet wrapping material comprising a base sheet of softened, regenerated cellulose having a thin coating of a material containing nitrocellulose as a principal ingredient on its surfaces, has become an important article of commerce. Such coatings may contain a variety of ingredients to impart special properties such as resistance to moisture, low permeability to water vapor and the like, to the finished article. The manufacture of a typical non-fibrous base sheet is described in Patent No. 1,548,864 (Brandenberger). Coating of this base sheet with typical coating compositions is described in Patent Nos. 1,737,187, 1,826,697, 2,147,-180, and others.

When products containing considerable water, as for example cheese, and certain vegetables, are wrapped in a coated transparent wrapping material such as those referred to above, the surface coating separates or loosens in a short time thus impairing the appearance and effectiveness of the wrapping. The loosening or separation usually occurs in a few minutes when the material wrapped has a high content of available water, or when the wrapping material is continuously exposed to a high relative humidity. Such a wrapping material is accordingly said to have low resistance to moisture.

Another problem which has existed in the use of surface coated transparent wrapping materials formed with a regenerated cellulose base is that there is a tendency for a thermal seal, formed by placing two layers of the material together and heating under slight pressure, to become separated due to ambient moisture conditions. This problem has existed for packages which are wrapped in a transparent regenerated cellulose base wrapping material in the conventional manner, as for example, by folding and overlapping the edges and heating the overlapped portions under slight pressure to seal the layers of wrapping together and to secure the wrap about the package. Under high humidity conditions, the seal formed between portions of the wrapping has become loosened due to the effect of moisture on the cellophane and the wrapping has become separated from the article enclosed. Inasmuch as the seal bond is formed largely between the coatings on the contacted surfaces of the sheets, the failure of the coatings to adhere to the base sheets can result in the same loss of wrap as a failure of the bond formed by the seal itself.

A problem which has been encountered in the formation of softened, regenerated cellulose pellicles with strongly anchored or adherent surface coatings is that the anchoring agents, used to enhance the adherence, tend to react with the material used in forming the pellicle and to precipitate or condense to an undesirable degree. Thus, it has been the practice to include an anchoring agent in the softener bath used in imparting the desired concentration of softener to the base sheet. In this way, the anchoring agent is incorporated into the base sheet along with the softener and the surface coating, which is subsequently applied to the base sheet, is strongly retained thereon.

A problem sometimes encountered in following this practice is the problem of reaction between the anchoring agent included in the softener bath and the sulfate ion carried over into this bath from the earlier process steps used in forming the base sheet. For example, where a condensible resin is incorporated in the softener bath, the action of the sulfate ion on this resin may be sufficient to cause its condensation to such a degree that the anchorage enhancing value of the resin in the bath is lost. This leads to a degree of irregularity in the properties of the coated sheet, and in the more severe case, a loss of the contents of the softener bath due to the necessity for discarding them.

Accordingly, one object of the subject invention is to provide an anchoring agent capable of strongly anchoring surface coatings to base surfaces.

Another object of the invention is to provide an anchoring agent which may be employed in a softener bath without danger of reaction with the contents of the bath.

Still another object is to provide a composition which induces strong anchorage between base surfaces and surface coatings formed thereon. A further object is to provide an article having a strongly anchored surface coating thereon. Still further objects will be in part apparent and in part pointed out herein after.

In one of its broader aspects, the objects of the invention are achieved by reacting formaldehyde with polymerized ethylenimine and anchoring the surface coating to the base surface with this product. In one of its narrower aspects, the objects of the invention are achieved by forming an aqueous solution of a softener and the reaction product of formaldehyde and polyethylenimine, impregnating a regenerated cellulose sheet with this composition, drying the base sheet, coating said sheet with a lacquer composition containing nitrocellulose predominantly, and containing an acid selected from the group consisting of itaconic, aconitic, citric, lactic, acrylic, and methacrylic, heating the coated base sheet to evaporate the solvent and anchor the resultant coating to said base sheet.

The process of this invention is illustrated graphically in the attached drawing in which FIGURE 1 is a schematic flow diagram of the steps of the process.

The method, composition, and articles of the subject invention will be understood with greater clarity by reference to the following examples, although it will be understood that these examples are given for illustrative purposes only, and are not to be interpreted as limiting or defining the scope of the subject invention.

Example I

A solution of polymerized ethylenimine in 1 kilogram of an aqueous glycerol solution containing 10% by weight of glycerol was prepared by dissolving therein 4.3 grams of an aqueous solution containing 50% solids of the ethylenimine therein. To this solution 8.1 grams of 37% formaldehyde in water were added. The bath was observed to be slightly cloudy. A specimen of regenerated cellulose gel film was dipped into the bath until it was completely wet with the solution. The excess liquid was removed from the surfaces. The specimen was again dried and then surface coated with a thin layer of lacquer composition.

The coated base sheet was then heated to evaporate the solvent and anchor the surface coatings formed.

The coated cellophane was then tested by immersion in water at 75° C. The coating remained intact on the base sheet for 120 minutes.

Example II

Substantially the same procedure of solution prepara-

tion, coating, and testing was carried out but the formaldehyde addition and reaction were omitted. The coating formed in this manner remained intact for less than two minutes.

Example III

A solution was formed by heating 17.2 grams of ethylene glycol with 4.3 grams of a 50% aqueous solution of polyethylenimine. To this solution 8.1 grams of 37% formaldehyde was added at room temperature and a solution resulted. A softener bath containing less than 1.0% by weight of the reaction product of formaldehyde and polyethylenimine and 10% by weight of glycerol was formed.

A cellulose sheet was impregnated with this solution, dried, and coated as described above. A sample of the coated film was immersed in water at 75° C., and it was observed that the coating did not disengage from the base sheet for a period of two hours.

Where this same procedure of solution preparation was followed by using only 8.6 grams of ethylene glycol in place of 17.2 grams, an insoluble gel was formed. Accordingly, the preferred procedure is to use the larger amount of ethylene glycol.

Example IV

A solution was formed by heating 17.2 grams ethylene glycol, 17.2 grams of water, and 4.3 grams of polyethylenimine together at room temperature. This was followed by the addition of 8.1 grams of 37% formaldehyde in water to the solution.

A softener bath containing 10% by weight of glycerol and less than 1.0% by weight of the reaction product of formaldehyde and polyethylenimine, was formed. A cellulose base sheet was softened with this composition. The sheet was dried and coated with a lacquer composition as described above, and the resultant coated sheet was tested by immersion in water at 75° C. The coating did not disengage from the base sheet for a period of two hours.

Example V

A solution was formed by dissolving 4.3 grams of a 50% aqueous solution of polyethylenimine in 17.2 grams of water at room temperature. To this solution 8.1 grams of 37% formaldehyde in water was added, and the solution formed thereby was employed to form a softener bath containing less than 1.0% by weight of solids and 10% by weight of glycerol. It was found that this solution could be used successfully to soften a regenerated cellulose base sheet so that when a nitrocellulose coating was subsequently formed thereon, as described above, it was not detached from the base sheet after immersion in water for a period of two hours.

From the foregoing, it is apparent that a versatile and effective method of anchoring nitrocellulose coatings to cellulose base sheets is disclosed. It is further apparent that novel compositions of matter are also taught. It will be understood that alternative materials may be used in place of a number of the ingredients disclosed and that changes in the concentrations of the ingredients may be made without departing from the scope of the subject invention.

An organic resinous surface coating formed from an organic lacquer may have the following approximate composition:

	Percent
Nitrocellulose	40 to 60
Plasticizer	30 to 40
Blending resin	3 to 15
Wax	1 to 5
Polymeric plasticizer	5 to 15

With regard to the aldehyde which is reacted with the ethylenimine polymer, it will be understood that although formaldehyde is preferred for this purpose, other aldehydes such as polyaldehyde, acetaldehyde and the like

may also be used or on mixtures of such other aldehydes may be employed with formaldehyde.

Where the reaction product of the aldehyde and ethylenimine polymer is to be employed in a solution, as for example in a softener bath, it is preferred that it be formed in such manner as to limit the formation of the product in gel or dispersion form in the bath.

Where the reaction product is to be employed in a coating composition, such as in a lacquer coating composition or in an aqueous dispersion coating composition, the formation of the gel-like product may be satisfactory.

With regard to the softener bath composition, the glycerol softener may be replaced by other suitable polyhydric alcohol softeners, as the needs of the softener bath and content of the regenerated cellulose sheet may dictate.

With particular regard now to the base sheet impregnated with this composition, a base sheet of regenerated cellulose is preferred although numerous other base sheets, such as a sheet of cellulose nitrate or other hydrophilic base sheets, may be employed.

Whereas the foregoing examples are given with particular reference to the coating of a base sheet with nitrocellulose, it will be understood that other coatings may be employed. For example, a coating of polymerized vinylidene chloride, dispersed in an aqueous medium, may be employed. Such coatings should preferably either contain an acid medium such as acrylic or methacrylic acid or the like, or should have a sufficiently low pH value so that the coating becomes strongly anchored to the base sheet.

A number of lacquer solvents such as cyclohexanone, tetrahydrofuran, mixtures of ethyl acetate and toluene lower ketones and the like may be used. It is preferred to include an acid condensation catalyst in the lacquer as indicated above.

A polyethylenimine product found suitable for carrying out the subject method is a polymer product available from Hansborg and Company of New York. Polyethylenimines available from other sources may also be used.

One particular advantage of the subject method is the ease of incorporating the novel reaction product of formaldehyde and polyethylenimine into the film. As noted above, it can with great facility be incorporated either into the base sheet or into the coating composition.

This advantage is further illustrated by the fact that the reaction can be brought about at the time the base sheet and coating composition are brought into contact and formed into a film. Thus, the formaldehyde reactant may be incorporated in the base sheet and the polyethylenimine may be incorporated in the coating. The two are brought onto contact and the reaction of these two reactants takes place. Heating of the film to evaporate the carrying medium from the composition and to consolidate the coating layer enhances the conditions for reaction. Excess formaldehyde is volatile and is removed during the drying treatment.

Conversely, the formaldehyde may be incorporated into the coating composition, particularly a latex coating composition and the polyethylenimine may be incorporated in the base sheet. Reaction of these two reactants occurs when the base sheet and composition are brought together and treated to form them into a film.

These alternative procedures further illustrate the ease and facility of imparting improved properties to films in accordance with the subject method.

Since many examples of the foregoing procedures, compositions, and articles may be carried out and made, and since many modifications can be made in the procedures and articles described without departing from the scope of the subject invention, the foregoing is to be interpreted as illustrative only, and not as defining or limiting the scope of the invention.

We claim:

1. The method of anchoring a nitrocellulose-base sur-

face coating to a cellulose base sheet which comprises impregnating said base sheet with the reaction product of formaldehyde and polymerized ethylenimine, drying said sheet and applying to the surfaces thereof a lacquer coating having an organic acid condensation catalyst and over 30 percent of nitrocellulose.

2. The method of anchoring an organic resinous surface coating to a regenerated cellulose base sheet, which comprises incorporating the reaction product of an aldehyde and polymerized ethylenimine into said base sheet, forming an acidic organic lacquer composition containing an organic acid condensation catalyst and said organic resinous substance, applying said lacquer to said sheet and heating to evaporate the solvent from said lacquer and to bond the resultant surface coating to said base sheet.

3. The method of claim 2 wherein the aldehyde is formaldehyde.

4. The method of claim 2 wherein the organic resinous substance has the following approximate composition:

	Percent
Nitrocellulose	40 to 60
Plasticizer	30 to 40
Blending resin	3 to 15
Wax	1 to 15
Polymeric plasticizer	5 to 15

5. The method of anchoring an organic resinous surface coating to a regenerated cellulose base sheet which comprises forming a softener bath by adding about 0.2% by weight of polyethylenimine and about 0.3% by weight of formaldehyde to an aqueous solution of a polyhydric alcohol softener to form the reaction product of polyethylenimine and formaldehyde in said bath, softening said sheet in said softener bath, coating said sheet with a lacquer composition containing an organic film forming resin in an organic solvent and an organic acid condensation catalyst, and heating said sheet to evaporate said solvent and to bond said resin to said sheet.

6. The method of claim 5 wherein the lacquer composition contains an organic acid of low pH value.

7. The method of claim 5 wherein the acid lacquer composition contains an acid selected from the group consisting of itaconic, aconitic, citric, lactic, acrylic, and methacrylic and the resin is nitrocellulose.

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