

- [54] **STABILIZED GLYCOL PLASTICIZED
CELLULOSIC SHEETS**
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- [52] U.S. Cl. **117/144, 117/154**
[51] Int. Cl. **C08j 1/38**
[58] Field of Search..... **117/143 R, 144, 154;
252/404**

- [56] **References Cited**
UNITED STATES PATENTS
2,607,745 8/1952 Magoffin..... 252/404

3,400,717	9/1968	Cubitt et al.....	128/284
3,502,484	3/1970	Kolasinski.....	252/404 X
3,602,225	8/1971	Wielicki.....	128/287
3,656,993	4/1972	Edwards et al.	117/144 X
3,676,055	7/1972	Smith.....	117/154 X
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[57] **ABSTRACT**

Fibrous and non-fibrous cellulosic sheets containing plasticizing amounts of polyalkylene glycols with buffering agents to prevent deterioration of the glycol and subsequent cellulose degradation promoted by the acidic products of glycol deterioration.

10 Claims, No Drawings

STABILIZED GLYCOL PLASTICIZED CELLULOSIC SHEETS

Papers, fabrics and films of various cellulosic materials have been plasticized with polyalkylene glycols of varying molecular weights, as shown, for example, in U.S. Pat. No. 3,400,717 and 3,602,225. On aging of these sheets, an undesirable odor, traced to the deterioration of the glycols, has been observed. Furthermore, the acidic deterioration products cause degradation of the cellulose articles thereby reducing or eliminating their usefulness.

It is an object of this invention to provide water-insoluble, hydrophilic cellulosic sheets plasticized with polyalkylene glycols which are deterioration resistant.

It is a further object of this invention to provide regenerated cellulose films plasticized with polyalkylene glycols resistant to deterioration.

It is another object of this invention to provide a method of preparing water-insoluble, hydrophilic cellulosic sheets plasticized with deterioration resistant polyalkylene glycols.

These and other objects are accomplished in accordance with this invention which comprises fibrous and non-fibrous water-insoluble, hydrophilic cellulosic sheets containing plasticizing amounts of a polyalkylene glycol subject to deterioration under oxidizing conditions, and a buffering agent which buffers the plasticized sheet at a pH of between about 5 and about 8.5, preferably between 6 and 8. A pH above 8.5 will stabilize the glycol but will cause undesirable color formation.

The method of this invention comprises treating a fibrous or non-fibrous water-insoluble hydrophilic cellulosic sheet with an aqueous solution of a polyalkylene glycol buffered with a buffering agent to a pH of from about 5 to about 8.

The water-insoluble, hydrophilic cellulosic sheets of this invention are fibrous, non-fibrous or a combination of these forms. For example, woven and non-woven sheets, paper and the like which contain a substantial proportion of water-insoluble, hydrophilic cellulosic fibers; laminates of fibrous cellulosic sheets and films of fibrous sheets coated with cellulosic films to provide greater wet-strength or other beneficial properties; and cellulosic films usually prepared by extrusion of a cellulosic solution in the form of a pellicle and the coagulation of the pellicle. A preferred sheet material for this invention is regenerated cellulose film based on the greater amount of commercial use of the product. Paper coated with viscose which is subsequently regenerated and hydroxyethyl cellulose ether films are examples of other more commercially important sheets which are used for this invention.

The polyalkylene glycols which are useful for this invention are those which have a softening or plasticizing effect on the cellulosic sheets. Preferably, the polyalkylene glycols are those wherein the alkylene radical has from two to five carbon atoms and the average molecular weight ranges from about 150 to about 1,000. More preferably, the polyalkylene glycol is a polyethylene glycol having an average molecular weight of from about 250 to about 600.

The glycol plasticizers or softeners can be present in the sheet or film in an amount ranging from about 20 percent up to about 120 percent based on the weight

of the cellulosic material. For certain end uses, such as disclosed in U.S. Pat. No. 3,602,225, amounts of the glycols in the upper portion of this range, starting at about 75 percent, are preferred while conventional plasticization requires amounts in the middle or lower portion of the given range. Obviously, the more highly plasticized sheets present a more severe deterioration problem on aging. The polyalkylene glycols are preferably incorporated in the sheets and films of this invention by passing the sheet or film through an aqueous bath containing the glycol. The concentration of the bath will depend on the desired pick-up, and to a lesser extent, on the construction of the fibrous or non-fibrous sheet and the residence time of the sheet in the bath. The amount of plasticizer in the aqueous treating bath to obtain the desired amount in the sheet will range, for example, from about 5 to about 40 percent based on the weight of the bath.

Other means of applying the aqueous plasticizer composition to the sheet include spraying and padding. While usually not economically desirable, volatile organic solvents can be used to incorporate the polyalkylene glycol, as well as other constituents of this invention, into the sheet.

Care should be taken to assure the use of a fresh supply of the polyalkylene glycol in which little or no deterioration has taken place.

The buffering agent employed to buffer the cellulosic sheet is any agent which will maintain the pH of the plasticized sheet within the range of about 5 to about 8.5 for at least several months at room temperature. Examples of buffering agents useful for this purpose include dibasic sodium phosphate-monobasic potassium phosphate, sodium hydroxide-potassium acid phthalate, sodium hydroxide-monobasic potassium phosphate, sodium hydroxide-boric acid, Borax-boric acid, dipotassium phthalate-potassium acid phthalate, monobasic sodium phosphate-dibasic sodium phosphate, dibasic sodium phosphate-citric acid, sodium citrate-citric acid, sodium carbonate-sodium bicarbonate and the like. Aqueous solutions of the buffering agent meeting the given pH requirement are readily prepared by those skilled in the art and as shown, for example, in Lange's Handbook of Chemistry, Ninth Edition. The buffering agent is, most preferably, introduced into the cellulosic sheet by incorporating it in the glycol plasticizer bath although it may also be introduced in a subsequent treatment or bath. The sheets of this invention which are prepared by passage through an aqueous bath buffered within a range of about 5 to about 8.5 will, on drying to normal moisture regain, maintain substantially the same pH values as the treatment bath. Some care must be taken in the use of water containing alkaline salts, such as tap water, to prepare the buffered baths since some of the buffering agent may precipitate. If the water is alkaline, some acid, for example, sulfuric acid should be added to bring the pH down to 7 and then the buffering agent may be added.

The pH of the film is defined as the pH of a liquid consisting of 250 ml. of distilled water containing 5 gms. of test film. This test liquid is prepared by cutting sufficient $\frac{1}{2}$ inch squares of the test film to weigh 5 gms. The 5 gms. of film is placed into 250 ml. of distilled water contained in a 500 ml. Erlenmeyer flask and a stopper inserted on the top of the flask. The flask is shaken for 15 minutes at room temperature and the

pH of the resulting liquid is determined on a standard pH meter.

Other incidental additives may be incorporated in the sheets or films of this invention including slip agents, e.g., particulate cellulose, clays or resins; coloring matter; resin precondensates; and the like.

Another aspect of this invention is the introduction of an antioxidant for the polyalkylene glycol into the plasticized buffered cellulosic sheet. The water-soluble butylated hydroxyanisole is the preferred antioxidant agent since it is readily incorporated into the sheet by treating the sheet with an aqueous solution thereof at the desired concentrations. The treatment of the sheets with the aqueous antioxidant advantageously occurs in the plasticizing bath although secondary baths or sprays may be employed for this purpose.

The antioxidant is incorporated in the cellulosic sheet in amounts which effectively inhibit oxidation of the glycol constituent. Preferably, amounts ranging from about 50 to about 1,000 parts of antioxidant, preferably 100 to 400 parts, per million parts polyalkylene glycol are used. If the antioxidant is applied by passing the cellulosic sheet through an aqueous bath, the bath may contain, for example, between 50 and 400 parts per million of antioxidant.

After the cellulosic sheets have been treated as required in accordance with this invention, they are dried and usually rolled up for storage and later shipment to customers.

To demonstrate the sheet of this invention, the following example is set forth.

EXAMPLE

a. A 12 inch by 8 inch sample of water washed, wet gel (never dried) film of regenerated cellulose, freshly prepared by the viscose process, was treated by immersing it in a one liter aqueous solution of 30 percent polyethylene glycol having an average molecular weight of about 400 at a bath temperature of 50°C.

a mixture of buffering agent (dibasic sodium phosphate-monobasic potassium phosphate) adjusted to maintain the pH of the baths at 5.29, 6.47 and 7.73, respectively.

c. Three more 12 inch by 8 inch samples of the same film were treated as in (b) above except that each separate glycol bath also contained 200 parts of butylated hydroxy anisole (BHA) per million parts by weight of glycol. The bath was prepared by first dissolving 0.06 gm. of BHA in 300 gms. of polyethylene glycol 400. Water was then added slowly to make up 1,000 gms. of bath.

Aging of the film samples was carried out by placing the test samples in jars. The jars were closed tightly to minimize loss of volatile acids. The jars were kept in an air circulated oven at 65°C. for 1 to 4 weeks. Every week, the glass jars were taken out, cooled to room temperature, cap removed and the odor recorded. A piece of film sample was removed for titration, and aging of the remainder of the samples was continued at 65°C.

The film sample to be tested for acidity was conditioned at 45 percent R.H. for 4 hours and then weighed in a conical flask correct to the fourth place of decimal. One hundred ml. of distilled water was added to the film, shaken well and left for ten minutes before titration with N/10 NaOH. Methyl red was used as an indicator for the titration. The end point was erratic with phenolphthalein as the indicator because at pH changes between 6-8, there was evidence of some buffering action of the solution which resulted in consumption of a considerable amount of N/10 NaOH solution before a permanent end point could be reached. With methyl red as the indicator, a sharp and permanent end point was reached between pH 5.5-6.

The acidity of the film was measured as the number of milliequivalents of acid per gm. of the film conditioned at 45 percent relative humidity for 4 hours.

The following table is set forth to demonstrate and compare the aging properties of the film samples prepared as reported above.

TABLE I

Bath Composition	Days of Aging of Film Sample					
	7		14		28	
	Acidity*	Odor**	Acidity	Odor	Acidity	Odor
1. PEG***	0.013	+	0.39	+++	0.48	+++
2. PEG + buffer (5.29 pH)	0.004	-	0.004	-	0.004	-
3. PEG + buffer (6.47 pH)		-		-		-
4. PEG + buffer (7.73 pH)		-		-		-
5. PEG + buffer (5.29 pH) + BHA		-	0.004	-	0.004	-
6. PEG + buffer (6.47 pH) + BHA		-		-		-
7. PEG + buffer (7.73 pH) + BHA		-		-		-

*-Acid formation measured as number of milliequivalents of acid per gram of film conditioned at 45% relative humidity for four hours.

**-Odor rating - No odor
+ slight pungent odor
++ moderate pungent odor
+++ strong pungent odor

***-polyethylene glycol 400

After five minutes immersion the film sample was removed from the bath, excess plasticizer squeezed off and the film dried in a frame at room temperature.

b. Three other 12 inch by 8 inch samples of the same film were treated as in (a) above except that each was placed in a separate glycol bath containing amounts of

In addition to the above, the glycol baths used to prepare the same films were also tested for aging characteristics. The test results are set forth in the following table. The acidity of the plasticizer baths was measured by taking 25 ml. of the bath and diluting to 100 ml. and titrating as usual.

TABLE II

Bath Composition	Days of Aging of Glycol Bath at 65°C.							
	0		7		14		28	
	pH	Acid- ity*	pH	Acidity	pH	Acidity	pH	Acidity
1. PEG	5.25	—	4.00	0.09	3.70	0.27	3.40	0.74
2. PEG + buffer (5.29 pH)	5.55	0.03	4.10	0.13	4.00	0.29	3.80	0.64
3. PEG + buffer (6.47 pH)	7.0	—	4.95	0.05	4.35	0.18	4.18	0.32
4. PEG + buffer (7.73 pH)	8.0	—	7.00	—	6.50	—	5.00	0.10
5. PEG + buffer (5.29 pH) + BHA	5.8	0.02	4.65	*0.05	4.50	0.06	4.35	0.09
6. PEG + buffer (6.47 pH) + BHA	7.35	—	6.30	—	5.20	0.05	4.92	0.08
7. PEG + buffer (7.73 pH) + BHA	8.05	—	8.10	—	8.20	—	8.25	—

*-Acidity of the bath is given as milliequivalents per 25 ml. of bath.

As can be seen from the test results set forth in Table I, glycol plasticized, buffered cellulose films did not develop any odor or acidity on aging at 65°C. for at least 4 weeks. It is estimated that the glycol in the film would not deteriorate appreciably for at least a year at 25°C. The films containing both buffer and antioxidant also showed the same excellent stability. It is believed that the antioxidant significantly increases the induction period for the start of oxidation of the glycol and will offer additional long range protection against deterioration in combination with the buffering agent.

The results shown in Table II demonstrate the benefits of the method of this invention for the continuous preparation of polyalkylene glycol plasticized cellulosic sheets. Polyalkylene glycol plasticizing baths can be used for much longer periods without producing sheets which are subject to early deterioration. Table II also shows the added benefit of the antioxidant-buffer combination in the plasticizer bath.

Various changes and modifications may be made in practicing the invention without departing from the spirit and scope thereof and, therefore, the invention is not to be limited except as defined in the appended claims.

I claim:

1. Fibrous and non-fibrous water-insoluble, hydrophilic cellulosic sheets containing a plasticizing amount of a polyalkylene glycol having an average molecular weight of at least 250 and a buffering agent which buffers the plasticized sheet to a pH of between about 5 and about 8.5.

2. The cellulosic sheet of claim 1 wherein the polyalkylene glycol is a polyethylene glycol having an average molecular weight ranging between about 250 and about 600.

3. The cellulosic sheet of claim 1 wherein the buffer-

ing agent buffers the sheet to a pH of from about 6 to about 8.

4. The cellulosic sheet of claim 1 wherein the sheet also contains butylated hydroxyanisole in an amount sufficient to suppress oxidation of the polyalkylene glycol.

5. The cellulosic sheet of claim 1 wherein the sheet is a non-fibrous regenerated cellulose film.

6. The cellulosic sheet of claim 5 wherein the polyalkylene glycol is polyethylene glycol having an average molecular weight ranging between about 250 and about 600 and said glycol is present in the film in an amount ranging between about 75 and about 120 percent based on the weight of the cellulose.

7. The cellulosic sheet of claim 6 wherein the buffering agent is a mixture of dibasic alkali metal phosphate and monobasic alkali metal phosphate.

8. The cellulosic sheet of claim 6 wherein the film also contains from about 50 to about 1,000 parts of butylated hydroxyanisole per million parts of said glycol.

9. A method of preparing a deterioration resistant polyalkylene glycol plasticized, water-insoluble, hydrophilic cellulosic sheet which comprises passing a water-insoluble, hydrophilic cellulosic sheet in contact with an aqueous medium containing a polyalkylene glycol having an average molecular weight of at least 250 in an amount sufficient to plasticize said sheet and a buffering agent which maintains the aqueous medium at a pH of between about 5 and about 8.5.

10. The method of claim 9 wherein the cellulosic sheet is a regenerated cellulose film, the polyalkylene glycol is polyethylene glycol having an average molecular weight ranging between about 250 and about 600, and the aqueous medium also contains from about 50 to about 1,000 parts of butylated hydroxyanisole per million parts of said glycol.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,840,395 Dated October 8, 1974

Inventor(s) Walter T. Koch

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:
Col. 1, line 45, "films of fibrous sheets" should read
--films or fibrous sheets--.

Signed and sealed this 7th day of January 1975.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents