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3,778,401

RESTORING AND/OR PRESERVING PAPERS OR LIKE MATERIALS

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20 Claims

ABSTRACT OF THE DISCLOSURE

A stable monophasic composition is here taught consisting of a solution of polyvinyl acetals in a solvent mixture consisting of a chlorinated hydrocarbon containing two carbon atoms such as trichloroethylene and basic agents in aqueous solution useful for restoring and preserving papers and similar materials while providing desired basicity.

THE INVENTION

This invention relates generally to new and useful improvements in prolonged preservation of degradable sheet materials and particularly seeks to provide novel means and methods for prolonging the life of original paper documents and the like and for restoring and preserving such materials after damage or degradation has occurred.

It is well known that papyrus and papers, particularly those made from vegetable or wood cellulose fibers, as well as textiles and binding leathers are subject to degradation with age and frequently become stained and brittle. Accordingly, any cultural items such as manuscripts, books, prints, drawings, paintings, maps, photographs, photoreproductions and the like when applied to such papyrus, papers, textiles or binding leathers will suffer comparable damage.

The volume of old and damaged cultural items of the type here contemplated is massive and there is a great need for an effective and safe way for restoring their strength, soundness and clarity and for preserving their lives against further aging. There also is a need for a simple process which can be applied to new and valuable cultural items which can be applied during manufacture of these items to increase their longevity.

Heretofore efforts to solve this problem have consisted of adhesively securing tissue paper or fabrics to damaged areas of such cultural items with animal or vegetable adhesives. This procedure is unsatisfactory because its curative effect is of short duration.

More recently, transparent or translucent films, such as plasticized cellulose acetate or polyvinyl chloride, have been laminated under heat and pressure to the faces of a document, with a light weight fine mesh fabric interposed between the film and the document. Variations of this lamination technique have also been developed. However, these techniques presuppose that the documents being treated retain sufficient strength to withstand manual handling, otherwise laminating cannot be used. Furthermore, such techniques do not restore the appearance of the documents and cannot be used on books because of the cumulative thickness build up and because of technical problems relating to bindings.

In patent application Ser. No. 840,048 filed July 8, 1969, which issued as U.S. Pat. No. 3,698,925 on Oct. 17, 1972, there are described means for restoring degradable sheet materials by treating such materials with polyvinyl acetals. The treatment consists essentially in immersing the materials to be treated in a solution of the copolymers in an organic solvent. These copolymers consist in percentage by weight of about 15–25% of polyvinyl alcohol, 1–3% polyvinyl acetate and 70–82% of one or more polyvinyl acetals selected from acetals of formaldehyde, acetaldehyde and butyraldehyde.

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The compositions and methods of the above-identified patent application provide for safe and permanent restoration of many sheet materials. However, these solutions do not provide adequate protection against deterioration due to acidic materials. It is well known that the most significant cause of deterioration of papers and other sheet materials is the presence of such acidic materials, either in the paper itself (e.g. alum) or in the atmosphere (e.g. carbon dioxide, sulfur dioxide, and nitric oxides).

Present-day methods for deacidification of papers are based primarily on treatment of the papers with aqueous solutions containing basic agents such as calcium or magnesium hydroxide or bicarbonate. The best known deacidification treatment is based on an aqueous process developed by W. J. Barrow utilizing magnesium bicarbonate. This process has the disadvantage that, because it is based on an aqueous solution, it will wrinkle papers, and it will require special drying techniques. If it is desired to treat an entire book, each page has to be deacidified separately.

The treatments of sheet materials with solutions of polyvinyl acetals in organic solvents avoids need for treating each page separately. An entire book, for example, can be immersed directly into such solutions. It would accordingly be desirable to incorporate basic agents in such solutions and thereby avoid need for treating each page separately. While it is possible to use basic agents such as, for example, magnesium acetate, which are soluble in organic solvents (such as ethanol) and to add such agents to ethanolic solutions of polyvinyl acetals, the absence of water from such solutions seriously reduces the neutralizing effect of these basic agents. Furthermore, ethanolic solutions of polyvinyl acetals have been found to be unsuitable for preservation of materials printed after 1900 because of solubility of some printing inks used after 1900, in ethanol. Accordingly, different organic solvents have been used. In particular, a chlorinated hydrocarbon such as, for example, trichloroethylene, has been found useful because post-1900 inks are practically insoluble in this solvent.

However, when aqueous solutions of basic agents are added directly to such chlorinated hydrocarbon solutions of polyvinyl acetals, a two-phase system results. Such two-phase systems are not suitable for treatment of sheet materials because uniform application of the treating materials to the sheets is not feasible. Besides, the same problems would arise as occur with use of aqueous solutions.

It is, accordingly, an object of the present invention to provide stable solutions containing both a chlorinated hydrocarbon solution of polyvinyl acetals of the composition described above and an aqueous solution of a basic agent. Preferably, the chlorinated hydrocarbon solvent contains 2 carbon atoms. Examples of such solvents are ethylene chloride, ethylidene dichloride, 1,1,1-trichloroethane, 1,1,2-trichloroethylene, 1,1,2,2-tetrachloroethylene and 1,1,1,2-tetrachloroethylene, 1,1,2-trichloroethylene is preferred.

In accordance with the present invention; stable monophasic solutions of a 1,1,2-trichloroethylene solution of polyvinyl acetals and an aqueous solution of a basic agent obtained by dissolving the polyvinyl acetal in a solution of trichloroethylene and either isopropanol or methyl isobutyl ketone or a mixture of isopropanol and isobutyl ketone, and adding thereto an alcoholic solution of either an aqueous solution of the basic agent or of a hydrated basic agent.

In practice from about 3–6 g. of the polyvinyl acetal is dissolved in 100 cc. of a solution containing from 60–95 cc. of trichloroethylene and from 5–40 cc. of the isopropanol or methyl isobutyl ketone or mixture thereof. If desired, 1 cc. of water may be added in place of either 1 cc. of the isopropanol or the ketone. Other water-miscible

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solvents such as methanol, ethanol, propanol, acetone or methyl ethyl ketone may be used in place of the isopropanol or the methyl isobutyl ketone.

To 100 cc. of the solution of the polyvinylacetal, 2 cc. of an alcoholic solution of the basic agent dissolved in water is added. The basic agent, which may be a hydroxide of sodium, potassium, strontium, barium or lithium; a carbonate of sodium or potassium, a bicarbonate of sodium, potassium or lithium; an acetate of sodium, potassium, lithium, barium or magnesium; or hydrates of said compounds, is first dissolved in water and the aqueous solution then dissolved in about 100 cc. of a water-miscible alcohol. Suitable alcohols include methanol, ethanol, propanol, isopropanol and mixtures thereof. Instead of first dissolving the basic agent in water, a hydrate of the basic agent may be added to the alcohol. From about 0.5 to 20 g. of the basic agent can be present in about 100 cc. of the alcoholic solution.

The invention will be understood more fully from the examples which follow. These examples are given by way of illustration and are not to be considered as limiting.

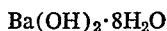
Example 1

1 g. NaOH was dissolved in 5 cc. water, added to 10 cc. methanol and then diluted with 90 cc. isopropanol.

2 cc. of above solution was added to 100 cc. of solution A consisting of: 3.5 g. of polyvinyl acetal dissolved in a mixture of:

	Cc.
1,1,2-trichloroethylene	79
Isopropanol	15
Methyl isobutyl ketone	5
Water	1

Example 2



10 g. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was dissolved in 100 cc. methanol. 2 cc. of this solution was added to 100 cc. of solution A.

Example 3

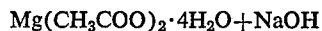


10 g. $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 10 cc. of water and 90 cc. isopropanol added. 2 cc. of this solution added to 100 cc. of solution A.

Newspapers, or any other acid papers such as old books or documents, showing a pH in the range of 3 to 4 when dipped in the above-solutions will show a pH, after drying, of at least 6 to 6.5. The pH of the treated pages can be established either by a universal indicator or by cold water extraction whereby samples of the treated pages are extracted in distilled water for a period of one hour, and the pH of the distilled water is determined.

If it is desired to raise the pH above 6.5 when magnesium acetate is used as the deacidification agent, the addition of small amounts of sodium hydroxide will be found effective as following example will illustrate:

Example 4



10 g. NaOH was dissolved in a mixture of 7.5 cc. of water and 117.5 cc. of methanol. 125 cc. of isopropyl alcohol was then added. This is solution B.

50 g. of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 15 cc. of water and 485 cc. of ethyl alcohol. Then 500 cc. of isopropyl alcohol was added, and finally 500 cc. of methyl alcohol. This is solution C.

To solution C, 150 cc. of solution B was added with stirring, and the mixture slightly warmed to dissolve precipitate which formed on addition. This is solution D.

The following polyvinyl acetal solution was prepared:

35 g. of polyvinylacetal was dissolved in a solution of 120 cc. of isopropyl alcohol and 680 cc. of trichloroethylene. This is solution E.

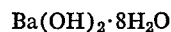
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Addition of various amounts of solution D to the polyvinyl acetal solution results in a clear solution that will neutralize and strengthen old, brittle and acidic papers. The effect on the pH of acid papers such as, for example, newspapers of various concentrations of solution D in solution E is shown in Table 1. pH was measured by indicator after newspapers were dipped into solution for five minutes and dried.

TABLE 1

Cc. of—		
Solu- tion E	Solu- tion D	pH
100	0	4.0-4.5
100	16	6.5-7.0
100	20	7.0-7.5
100	32	8.0-8.5

Example 5



10 g. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was dissolved in a mixture of 3 cc. water and 97 cc. methanol. 6 cc. of this solution was added to 100 cc. of solution E. Newspapers dipped for five minutes in this solution showed a pH of about 7.5.

Example 6



10 g. $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 3 cc. water and 97 cc. of ethyl alcohol. 10 cc. of this solution, together with 20 cc. of isopropyl alcohol, were added to 100 cc. of solution E. After thorough mixing, a clear solution resulted which neutralized newspaper after five minutes dipping and drying to a pH of about 6.5. This solution showed a trace of crystals on the bottom of the flask after standing about fifty hours, indicating a saturated solution of magnesium salt.

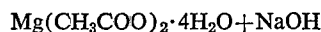
Example 7



This example is identical to Example 6 with the exception that 20 g. of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in the water-ethanol mixture. Again, a newspaper dipped in 100 cc. copolymer solution to which was added 10 cc. of this magnesium solution, plus 20 cc. of isopropyl alcohol, showed a deposition of crystals and a heavy layer of crystals were present on the bottom of the flask after fifty hours standing, confirming that Example 6 resulted in a saturated solution.

Since crystals may deposit on the papers, it is obvious that a clear solution, without crystals, is preferable for coating applications.

Example 8



50 g. of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 7.5 cc. of water and 242.5 cc. of ethyl alcohol. Then 250 cc. of isopropyl alcohol was added and finally 200 cc. of methyl alcohol. This is solution F. To this solution F, 50 cc. of solution B as prepared in Example 4 was added with stirring, and the mixture slightly warmed to dissolve precipitate which formed on addition. This is solution G.

The following copolymer solution was prepared:

35 g. of polyvinylacetal was dissolved in a solution of 50 cc. of isopropyl alcohol and 950 cc. of 1,1,1-trichloroethane. To 100 cc. of this copolymer solution was added 16 cc. of solution G. Newspapers dipped for five minutes in this solution showed a pH of about 7.5.

I claim:

1. A composition for restoring and preserving papers consisting of a solution of a polyvinyl acetal in a solvent mixture consisting of a chlorinated hydrocarbon containing 2 carbon atoms and a solvent selected from the group consisting of isopropanol, methyl isobutyl ketone and mixtures of isopropanol and methyl isobutyl ketone, to

which solution has been added a solution in a water-miscible alcohol of a basic agent dissolved in water or of a hydrated basic agent, said polyvinyl acetal consisting in percent by weight of 15-25% of vinyl alcohol units, 1-3% of vinyl acetate units, and 70-82% of vinyl alcohol units acetalized with one or more of aldehydes selected from the group consisting of formaldehyde, acetaldehyde and butyraldehyde, and said basic agent is selected from the group consisting of a hydroxide of sodium, potassium, strontium, barium, or lithium, a carbonate of sodium or potassium, a bicarbonate of sodium, potassium or lithium, an acetate of sodium, potassium, lithium, barium or magnesium, and hydrates thereof.

2. A composition according to claim 1 wherein the chlorinated hydrocarbon is 1,1,2-trichloroethylene.

3. A composition according to claim 2 wherein 3-6 g. of the polyvinyl acetal is dissolved in 100 cc. of a solution containing from 60-95 cc. of 1,1,2-trichloroethylene and from 5-40 cc. of a solvent selected from the group consisting of isopropanol, methyl isobutyl ketone and mixtures of isopropanol and methyl isobutyl ketone.

4. A composition according to claim 3 wherein the water-miscible alcohol is selected from the group consisting of methanol, ethanol, propanol and isopropanol.

5. A composition according to claim 4 wherein about 0.5 to 20 g. of the basic agent is present in solution in about 100 cc. of the alcohol.

6. A composition according to claim 5 wherein about 2 cc. of the alcoholic solution of the basic agent is added to 100 cc. of the solution of the polyvinyl acetal.

7. A composition according to claim 6 wherein 1 cc. of the solvent selected from the group consisting of isopropanol, methyl isobutyl ketone and mixtures of isopropanol and methyl isobutyl ketone is replaced by 1 cc. of water.

8. A composition according to claim 7 wherein 2 cc. of a solution of 1 g. of sodium hydroxide in 5 cc. water, 10 cc. methanol, and 90 cc. isopropanol, is added to 100 cc. of a solution of 3.5 g. of polyvinyl acetal in 79 cc. 1,1,2-trichloroethylene, 15 cc. isopropanol, 5 cc. methyl isobutyl ketone, and 1 cc. water.

9. A composition according to claim 7 wherein 2 cc. of a solution of 10 g. barium hydroxide octahydrate in 100 cc. methanol, is added to 100 cc. of a solution of 3.5 g. of polyvinyl acetal in 79 cc. 1,1,2-trichloroethylene, 15 cc. isopropanol, 5 cc. methyl isobutyl ketone, and 1 cc. water.

10. A composition according to claim 7 wherein 2 cc. of a solution of 10 g. magnesium acetate tetrahydrate in 10 cc. of water and 90 cc. isopropanol, is added to 100 cc. of a solution of 3.5 g. polyvinyl acetal in 79 cc. 1,1,2-trichloroethylene, 15 cc. isopropanol, 5 cc. methyl isobutyl ketone, and 1 cc. water.

11. A composition according to claim 1 wherein the chlorinate hydrocarbon is 1,1,1-trichloroethane.

12. A composition according to claim 11 wherein 3-6 g. of the polyvinyl acetal is dissolved in 100 cc. of a

solution containing from 60-95 cc. of 1,1,1-trichloroethane and from 5-40 cc. of a solvent selected from the group consisting of isopropanol, methyl isobutyl ketone and mixtures of isopropanol and methyl isobutyl ketone.

13. A composition according to claim 12 wherein the basic agent is selected from the group consisting of a hydroxide of sodium, potassium, strontium, barium or lithium, a carbonate of sodium or potassium, a bicarbonate of sodium, potassium or lithium, an acetate of sodium, potassium, lithium, barium or magnesium, and hydrates thereof.

14. A composition according to claim 13 wherein the water-miscible alcohol is selected from the group consisting of methanol, ethanol, propanol and isopropanol.

15. A composition according to claim 14 wherein about 0.5 to 20 g. of the basic agent is present in solution in about 100 cc. of the alcohol.

16. A composition according to claim 15 wherein about 2 cc. of the alcoholic solution of the basic agent is added to 100 cc. of the solution of the polyvinyl acetal.

17. A composition according to claim 16 wherein 1 cc. of the solvent selected from the group consisting of isopropanol, methyl isobutyl ketone and mixtures of isopropanol and methyl isobutyl ketone is replaced by 1 cc. of water.

18. A composition according to claim 17 wherein 2 cc. of solution of 1 g. of sodium hydroxide in 5 cc. water, 10 cc. methanol, and 90 cc. isopropanol, is added to 100 cc. of a solution of 3.5 g. of polyvinyl acetal in 79 cc. 1,1,1-trichloroethane, 15 cc. of isopropanol, 5 cc. methyl isobutyl ketone, and 1 cc. water.

19. A composition according to claim 17 wherein 2 cc. of a solution of 10 g. barium hydroxide octahydrate in 100 cc. methanol, is added to 100 cc. of a solution of 3.5 g. of polyvinyl acetal in 79 cc. 1,1,1-trichloroethane, 15 cc. isopropanol, 5 cc. methyl isobutyl ketone, and 1 cc. water.

20. A composition according to claim 17 wherein 2 cc. or a solution of 10 g. magnesium acetate tetrahydrate in 10 cc. of water and 90 cc. isopropanol, is added to 100 cc. of a solution of 3.5 g. polyvinyl acetal in 79 cc. 1,1,1-trichloroethane, 15 cc. isopropanol, 5 cc. methyl isobutyl ketone, and 1 cc. water.

References Cited

UNITED STATES PATENTS

2,120,935	6/1938	Groff	106-22
2,494,547	1/1950	Waldie	117-41
3,393,172	7/1968	Breskman	260-33.4
3,586,689	6/1971	Nickerson et al.	260-29.6

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