United States Patent

[11] 3,607,811

[72] Inventor **Sivert Hovd**
Flattenlia, Porsgrunn, Norway

[21] Appl. No. **781,962**
[22] Filed **Dec. 6, 1968**
[45] Patented **Sept. 21, 1971**

[73] Assignee **Norsk Spraengstofindustri A/S**
Oslo, Norway

[32] Priority **Dec. 13, 1967**
[33] **Norway**
[31] **170,967**

---

[54] **STABLE PHENOL FORMALDEHYDE RESIN SOLUTION FOR PREPARATION OF FIRE-RESISTANT LAMINATES**
3 Claims, No Drawings

[52] **U.S. Cl.** **260/29.3,** 117/137

[51] **Int. Cl.** **C08g 51/04**
[50] **Field of Search** 117/137; 260/29.3, 29.4

[56] **References Cited**

UNITED STATES PATENTS

2,415,112	2/1947	Seymour et al.	117/137
2,842,510	7/1958	Robertson	260/29.3
3,017,292	1/1962	Mosher	117/137

Primary Examiner—Donald J. Arnold
Attorney—Wenderoth, Lind & Ponack

ABSTRACT: The invention relates to an aqueous alcoholic phenol formaldehyde resin solution suitable for one-step impregnation of kraft paper for the preparation of fire-resistant laminates, containing alkyl phosphates and/or salts thereof and ammonium bromide.

STABLE PHENOL FORMALDEHYDE RESIN SOLUTION FOR PREPARATION OF FIRE-RESISTANT LAMINATES

The invention relates to phenol formaldehyde resin solutions being particularly suitable for the preparation of fire-resistant laminates and having good storage stability.

It has been known for a long time to impregnate textiles, paper and the like with fire-preventing agents to make these materials less flammable. Among the most commonly used fire-preventing agents are inorganic phosphates and ammonium halides, particularly ammonium bromide. Inorganic phosphates, and partly also organic phosphates, have been used in large amounts also to prevent after-glowing in the impregnated material. Further it is known that by using a combination of phosphates and ammonium bromide a favorable combined effect is obtained with respect to fire-preventing and glow-preventing activity, since the effect of the mixture of the two agents combines the favorable effects which the compounds have separately. By impregnation of materials with all the above mentioned agents the material has first been passed through an aqueous solution of the agent or agents and then dried.

During the recent years the so-called high pressure laminates, i.e. impregnated kraft paper compressed with a surface layer on one or both sides, have attained wide use for several purposes, such as wall covering material and furniture.

These laminates are relatively flammable, and for certain uses, for instance for use in ships, strict requirements have been set up with respect to reduced inflammability and to low smoke development for surface materials, and as a result thereof, fire-preventing agents must be incorporated in such high pressure laminates. If it is tried to dissolve the most commonly used inorganic phosphates and possibly other fire-preventing salts, such as ammonium bromide, in the alcoholic solution of phenol formaldehyde resin used as binder for the laminate manufacture, a separation of resin or salts results long before the necessary concentrations have been obtained. Therefore, the kraft paper is first impregnated with an aqueous solution of one or more fire-preventing agents, usually inorganic salts, whereafter the paper is dried and then impregnated with a solution of phenol formaldehyde resin in aqueous alcohol.

This conventional two-step impregnation is complicated and expensive, and the disadvantages of the ordinary two-step processes for the preparation of laminates have lead to several efforts to find suitable one-step processes, and one such effort has been described in British Pat. No. 989,140, according to which a phosphate which is soluble in the resin solution is used for the first time. The specific phosphate used is a phosphate of an organic amine. Said process definitely means a progress, but the impregnation with phosphate alone necessitates large amounts, such as about 20 percent by weight or more, to satisfy the requirements to fire- and glow-preventing effect, and the use of such large amounts of phosphate is expensive and also results in brittleness and tendency to delamination in the finished laminate.

From U.S. Pat. No. 2,415,113 it is known to use mixtures of ammonium bromide and alkyl substituted diammonium phosphates together with thiourea in aqueous solutions for impregnation of textiles and other cellulose materials to render these fire-resistant. According to the patent thiourea is used as primary fire-preventing component, and there is no mention about the preparation of laminates or the solubility and stability problems involved with laminate manufacture, the solution to which is the purpose of the present invention.

We have carried out experiments to further investigate the effect of ammonium bromide and ammonium methyl phosphates (and partly also other ammonium alkyl phosphates) as fire-preventing components in laminates. The tests were carried out as follows:

In a cubic test chamber three walls and the ceiling were covered with the laminate being tested. On the fourth wall was fixed a propane burner which was burning with a specific amount of propane per minute during the test. On the same wall above the burner there was an outlet passing to a cyclone in which solid particles were separated out, and in the tube beyond the cyclone was mounted apparatus for measuring temperature and light transmission for examination of the smoke temperature and smoke development respectively.

It was found that ammonium bromide had a better inhibiting effect on the smoke temperature (which is an indication of fire-preventing effect) than ammonium methyl phosphates, while the opposite was the case for the smoke development. Thus, the use of ammonium bromide alone makes it necessary to use unreasonably large amounts to obtain a satisfactory low smoke development, while the use of ammonium methyl phosphates (or other inorganic or organic phosphates) alone makes it necessary to use unreasonably large amounts to obtain a satisfactory fire-preventing effect. This also confirms the necessity of using the large amounts of phosphate used according to the above mentioned British Patent, since in the fire-preventing phosphate used it is only the phosphate group itself which exerts any fire-preventing effect.

We have now surprisingly found that it is possible to utilize the favorable combined effect of these two per se known types of fire-preventing agents in a one-step process for the preparation of laminates, said favorable combined effect being that moderate amounts of both of the two types of fire-preventing agents in combination will give a satisfactory fire-preventing effect as well as a satisfactory low smoke development for laminates prepared with resin solutions containing these. This is obtained by using as a solvent for the fire-preventing components and the resin an alcohol-water-mixture having a specifically adjusted ratio between alcohol and water. In this adjusted medium it is not only possible to introduce the fire-preventing components desired but also the required amount of resin. Hereby is not only obtained a utilization of the favorable combined effect of the two fire-preventing compounds, but the phenol formaldehyde resin solution containing the fire-preventing components has a storage stability of several months, exceeding by far the storage stability of known resin solutions containing fire-preventing additives.

Thus, according to the invention is provided a fire-preventing, storage stable phenol formaldehyde resin solution being particularly suitable for one-step impregnation of kraft paper for the preparation of laminates, and the resin solution is characterized in that it contains from 1 to 10 percent by weight of C_{1-4} alkyl phosphates and/or ammonium salts thereof and from 2 to 10 percent by weight of ammonium bromide, and in that it contains a C_{1-4} alkanol and water in a ratio by weight of alkanol/water of at least 0.60, preferably between 0.85 and 2. The percentages by weight stated are calculated as anhydrous substance relative to the total solution of resin and fire-preventing compounds in alcohol and water. The resin content (dry weight) in the resin solution will normally be from 35 to 50 percent by weight. If more than 50 percent by weight is used the stability of the resin solution will not be satisfactory for prolonged storage, and if less than 35 percent by weight is used the solution will contain insufficient resin to give a satisfactory laminate.

EXAMPLE

A solution A was prepared from 450 grams of a phenol formaldehyde resin solution and 150 grams of ethanol. The phenol formaldehyde resin solution consists of about 65 percent by weight of alkali catalyzed phenol formaldehyde resin having a molar ratio of formaldehyde/phenol of 1.44, about 17 percent by weight of water, about 11 percent by weight of ethanol and about 7 percent by weight of free formaldehyde and phenol, so that 450 grams thereof contains about 295 grams of resin, 75 grams of water, 50 grams of ethanol and 30 grams of unreacted formaldehyde and phenol. A solution B was prepared from 44 grams of ammonium bromide, 41 grams of aqueous ammonium methyl phosphates (consisting of about 65 percent by weight of ammonium methyl phosphates and 35 percent by weight of water, i.e. about 27 and 14 grams respectively) and 60 grams of water.

The two solutions A and B were thoroughly mixed and adjusted to a pH of about 5.2 by means of 25 percent ammonia. Thus, the resulting mixture had a content of ammonium methyl phosphates of about 3.5 percent and of ammonium bromide of about 6 percent by weight, and an ethanol/water ratio of about 1.3. The mixture was homogeneous and remained completely clear for more than 4 months at room temperature. Laminates prepared with this mixture fulfilled with good margin the requirements with respect to flame spread and smoke development set up by the Norwegian Veritas for surface materials for use in corridors and stairs.

Instead of ammonium methyl phosphates it is also possible to employ ammonium ethyl-, -propyl- and -butyl phosphates, however, since ammonium methyl phosphates contain most of the active phosphate group per unit weight and also give the most stable solutions they are preferred. The pure $C_{1\text{-}4}$ alkyl phosphates may also be employed, although the stability of the solutions containing these will not be as good as for solutions containing ammonium methyl phosphates.

What is claimed is:

1. A phenol-formaldehyde solution suitable for one-step impregnation of kraft paper for the preparation of fire-resistant laminates and having excellent storage stability, comprising from 35 to 50 percent by weight of phenol formaldehyde resin, from 1 to 10 percent by weight of a phosphate selected from the group of $C_{1\text{-}4}$ alkyl phosphates, and $C_{1\text{-}4}$ alkyl ammonium phosphates, and from 2 to 10 percent by weight of ammonium bromide, and a solvent which is a mixture of $C_{1\text{-}4}$ alkanol and water in a ratio by weight of alkanol to water between about 0.60 and about 2.0.

2. A solution according to claim 1 in which said alkanol to water ratio lies between 0.85 and 2.0.

3. Resin solution according to claim 1, wherein the phosphates are ammonium methyl phosphates.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,607,811 Dated September 21, 1971

Inventor(s) SIVERT HOVD

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, lines 45 and 47; column 3, line 16; and column 4 (claim 1), line 8 (two occurrences) and line 10 (each occurrence), "C_{114}" should appear as --C_{1-4}--.

Signed and sealed this 9th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334