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METHOD OF MAKING AN ASPHALT BONDED PAPER LAMINATE AND PRODUCT

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This invention relates to laminates of paper plies secured together by hot melt resinous adhesives such as asphalt, or similar inexpensive hot melt applied thermoplastic resinous bonding material, and the invention particularly relates to improvements in such laminates and their method of manufacture which especially adapt them for use as covers or blankets in the curing of freshly laid concrete.

It is conventional practice in the construction industry to cover the surface of freshly laid concrete so that evaporation of moisture from the concrete is inhibited and the water needed for the process of hydration involved in the setting is retained in the concrete. A cover which is widely used in the industry because of its effectiveness, serviceability, and low cost, is composed of two sheets of a strong paper, such as kraft, united with a resinous adhesive such as asphalt which is applied hot to take advantage of its high fluidity at elevated temperatures. Such covers are reenforced, as with sisal, glass or other fibers, usually laid lengthwise and transversely in the adhesive before the plies of paper are united.

In the use of such laminates for concrete curing, a problem arises from the effect of the normally alkaline waters which wet the cover, and particularly the paper ply adjacent the concrete, and attack the interfacial bond between the paper and asphalt, resulting in a delamination of the paper plies with consequent weakening and substantial loss of utility of the laminate for this use.

It is an object of the present invention to enhance the strength of the interfacial bond between the paper and the asphalt and specifically to increase the resistance of the bond to deterioration by alkaline waters.

To enhance the wet strength, scuff resistance and other strength factors of the laminate, the paper plies of prior laminates used for this purpose have been pre-treated with a water soluble resinous material, such as dimethylol urea, followed by a heat treatment to set up the material to water insoluble form.

It is a further object of this invention to provide a laminate having a scuff resistance and wet strength substantially greater than in prior laminates treated merely with such resinous materials as dimethylol urea.

It is found, according to the present invention, that an asphalt bonded kraft laminate, in which the kraft paper, prior to application of the asphalt, has been impregnated with an aqueous solution combining a Werner coordination complex trivalent chromium salt containing a high molecular weight organic carboxylic acid in the complex with a resinous material such as dimethylol urea as will be described, has a substantially reduced tendency to separation of the paper plies at the adhesive juncture of the asphalt with the paper when exposed to alkaline liquids in the protective covering of wet concrete, while having enhanced strength characteristics superior to those obtainable by any prior treatments of which I am aware.

This result was not to have been expected from prior known uses of such complex chromium compounds. Without intending to preclude other possible theories explaining the enhanced effects obtained by my invention, I believe that stearato chromic chloride, for example, increases the asphalt to paper bond by forming a chemical bond which supplements the physical bond normally present between the asphalt and paper and that this chemical bond results from the chromium group attaching itself to the surface of the paper, and orienting itself outwardly from the paper for attachment strongly to the hydrocarbon asphalt.

The Werner complex compounds, as well known in the art, are formed by reaction of trivalent basic chromium salts of mineral acids such as the chloride, nitrate, sulphate, etc., including mono- and dibasic forms, with a high molecular weight organic carboxylic acid preferably having at least ten carbon atoms, either cyclic or acyclic, in the presence of a solvent such as carbon tetrachloride and a reducing agent such as a lower alcohol, typically ethyl alcohol. In general the materials are used in proportions ranging from equal numbers of chromium atoms and high molecular weight organic acid atoms up to ten chromium atoms to each high molecular weight organic acid atom. The chromium salt may be the normal trivalent chromium salt which contains basic groups such as mono- basic chromium chloride (which is usually available in hydrated form) having the formula

$$CrOHCl_2.6H_2O$$

but the basicity may range up to 50% to include mixtures of both mono- and dibasic chromium salts containing at least one mineral acid ion.

The reaction is exothermic and it is run by slow addition of the basic chromic or chromyl salt under reflux to a solution of the organic acid and alcohol in carbon tetrachloride as a solvent until the reducing reaction has terminated. The product formed is substantially water and alcohol soluble as well as soluble in organic solvents and dries to a glossy, greenish solid.

The formation of such basic chromium compounds is usually effected by reduction of the chromyl salt, i. e., halide (CrO_2Cl_2), nitrate, sulphate, etc., by the ethyl alcohol which reduces the oxygen groups of the chromyl salt to hydroxy groups ($CrOHCl_2$) while simultaneously oxidizing the alcohol to acetic acid. Thus it is possible to start either with the hydrated salt or the basic chromic salt. Both the high molecular weight organic acid and the acetic acid become bonded into the chromium complex by Werner coordination valences, whereby notwithstanding its high molecular weight, the complex is sufficiently water-soluble for present purposes, so that it can be applied in aqueous solution.

The high molecular weight organic acid used has from 10 to 20 carbon atoms and may be an aliphatic acid of saturated character typically lauric, stearic, or palmitic acids; or of unsaturated character such as aleic acid, linoleic acid, oleostearic or linolenic, etc.; or the acid may be cyclic such as aromatic or alicyclic, either saturated or unsaturated, and may contain a hydrocarbon chain, such as lower alkyl substituents; or the acid may comprise aliphatic acids of indefinite size, even low molecular weight compounds substituted by cyclic hydrocarbon radicals. Such cyclic acids may be the carboxylic acids derived by oxidation of petroleum, i. e., naphthenic acids, or from other sources such naphthoic acids, naphthyl acetic acids, or natural resin acids such as abietic or pimaric.

As reported in the literature, the Werner complex compound, stearato chromic chloride, for example, is prepared by first forming a solution of 1400 parts of chromyl chloride dissolved in 4800 parts of dry carbon tetrachloride. This solution is added slowly over a period of two hours to an agitated solution of 1279 parts by weight of stearic acid dissolved in 11,200 parts of dry

carbon tetrachloride and 207.5 parts of dry etheyl alcohol, contained in a flash fitted with a refluxing condenser. Thereafter a slightly yellowish color due to unreduced chromyl chloride is removed by minor addition of about 20 parts of dry ethyl alcohol dissolved in 128 parts of carbon tetrachloride. The carbon tetrachloride is then removed by distillation. The product obtained consists of about 2640 parts of a dark green glassy solid of which 90% is soluble in methanol and analyzed chromium 17.0%, chlorine 18.3%, acetic acid 9.7%, and stearic acid 43.0% indicating about 2.16 chromium atoms per stearato group in the molecule.

For treatment of the paper, according to the present invention, the Werner complex may be first dissolved in water or other solvent such as alcohol, and applied to the dry paper by passing the paper through a dilute aqueous solution, or by spraying the dry paper with a solution containing the Werner complex compound dissolved therein in concentration ranging from .025 to 5% by weight, preferably from 0.05 to 2%, and dimethylol urea dissolved in the same aqueous solution with the Werner complex compound in proportions usually less than 10% preferably from 4% to 8% by weight of the solution. The paper is then heated to set up the water insoluble urea formaldehyde resin and to activate the Werner complex for the purposes aforesaid. Alternatively, but less desirably, the paper may first be treated with either the Werner complex or the dimethylol urea and then treated with the other.

The materials that will be employed for my purposes are not limited to those above described, as a number of equivalents are available, as indicated particularly in the examples which follow. Thus, in place of stearato chromic chloride, I may employ other Werner complex compounds such, preferably, as abieto chromic chloride and laurato chromic chloride.

In place of dimethylol urea, other soluble methylol resin forming compounds may be employed, such, for example, as the polymerizable components of urea formaldehyde, melamine formaldehyde, phenol formaldehyde, and cresol formaldehyde.

Example 1

A 1.0% solution of stearato chromic chloride having the above analysis in water was formed by dissolving the Werner complex in water and to this solution was added dimethylol urea in amount necessary to make a 6% solution. Conventional kraft paper sheets of 30 pound basis weight were dipped into the solution to thoroughly impregnate them. The solution had a pH of about 3.7. These sheets were then heated in an oven at about 280° F. for about 5 minutes. Two sheets of the paper thus treated and dried were formed into a laminate using hot asphalt in a conventional manner to secure the two sheets together. Samples were cut in small 2" by 6" rectangles which were then soaked for one-half hour in 0.1 N. caustic solution in water. Thereafter one end of the laminate was peeled to delaminate for a distance of 2". One of the plies at the delaminated end of the sample was then secured in a fixed clamp from which the sample depended downwardly. A clip having a hook was then secured to the other free delaminated end and small sheets of paper, functioning as weights, were placed on the hook. The weight of the paper on the hook was gradually increased until the sample began to delaminate further. The paper, hook and clip were then weighted and in this way an accurate weight test of resistance to delamination was obtained. It was found that the sample had a resistance of about 100 grams to delamination, in that it supported a weight of that amount before further delamination.

Another sample of the same laminate was tested for a number of further values, namely resistance to shrinkage in the cross machine direction, wet scuff resistance, dry tensile strength, wet tensile strength and percentage of tensile strength retention, wet over dry, and these values were compared with the values in corresponding tests obtained on a blank consisting of an identical laminate made of the same sheets of 30 lb. basis weight kraft paper but which had not been treated with either stearato chromic chloride or dimethylol urea. The results were as follows:

The cross machine direction shrinkage resistance test was performed by measuring the sample in the cross machine direction, subjecting it to a 7 cycle alternate wetting and drying test and then again measuring its dimension in cross machine direction. It was found that the sample had a shrinkage of 0.8% as compared with 3.5% for the blank.

Wet scuff resistance was measured by using the conventional Cloth Crock Recorder accepted by the Association of Textile Colorists and Chemists which is adequate for comparative purposes and was employed by wetting the paper and then rubbing it with the knob on the machine, until the paper is worn through and recording the number of rubs. The sample withstood 55 rubs as compared with 2 rubs for the untreated blank.

Dry tensile strength was tested in a conventional Scott tester and measured 26.5 lbs. per inch for the sample and 26.0 lbs. per inch for the untreated blank showing no diminution in dry tensile strength. The values are in pounds per inch.

Wet tensile strength was also tested in a Scott tester, after the laminate had been soaked for one hour at about 73° F.; it showed 10.5 lbs. per inch for the sample as compared with virtually 0 lb. per inch for the untreated blank.

The percentage strength retention was calculated at 39.5% for the sample and 0% for the untreated blank.

Example 2

The same paper as in Example 1 was treated first with a 6% solution of dimethylol urea in water acidified with hydrochloric acid to a pH of 3.9. Sheets of paper were dipped into the solution to thoroughly impregnate the same and were then heated in an oven at 280° F. for about 5 minutes. The sheets thus treated were then dipped into a 1% solution of stearato chromic chloride having the above analysis in water to thoroughly impregnate the same and the sheets were again heated in an oven at 280° F. for about 5 minutes. Two sheets of paper thus treated were formed into a laminate using hot asphalt as in Example 1 and samples were similarly cut in small 2 inch by 6 inch rectangles and subjected to the same tests as described under Example 1. The following values were obtained:

Resistance to delamination	grams	105
Cross machine direction shrinkage	percent	0.8
Wet scuff resistance	rubs	55
Dry tensile strength	lbs. per inch	26.0
Wet tensile strength	do	10.5
Percentage retention	percent	40.4

Example 3

The test procedures of Examples 1 and 2 were repeated using laurato chromic chloride and abieto chromic chloride in each instance instead of the stearato chromic chloride with no perceptible variation in the results obtained in Examples 1 and 2.

In using a bath combining the Werner compound, such as stearato chromic chloride, with a methylol resin forming compound such as dimethylol urea, which is my preferred treatment, I have found that the acid catalyst, such as hydrochloric acid or preferably ammonium thiocyanate which is conventionally employed in treatments to obtain wet strength and shrinkage resistance from such resin forming materials, need not be employed because the stearato chromic chloride serves as an excellent catalyst for reacting the resin forming compound with paper under the subsequent heat treatment.

Although my invention has a special utility for use in

concrete curing blankets, it also has exceptional utility for many other uses such as in packaging of young plants containing moist alkaline earth, or the packaging of chemicals having a substantial degree of alkalinity and some moisture, such as fertilizers.

As the term is used herein, the "Werner complex" will be understood to refer to a coordination type chromium compound formed from a trivalent basic chromic or chromyl and a high molecular weight carboxylic acid having at least 10 carbon atoms bonded to one or more chromium atoms as a complex.

It is intended that the above description be regarded as exemplary and not limiting except as defined in the claims appended hereto.

I claim:

1. A laminated paper product resistant to delamination by aqueous alkaline liquid comprising sheets of paper bonded with resinous hydrocarbon adhesive into a laminate, at least one of said sheets being homogeneously impregnated with a small quantity of a Werner complex of a trivalent chromium salt containing a high molecular weight unsubstituted long hydrocarbon chain organic carboxylic acid having at least 10 carbon atoms and a water soluble methylol resin forming compound polymerized in situ in the paper.

2. Asphalt bonded kraft paper laminate resistant to aqueous alkaline delamination between the paper and asphaltic bonding agent, adapted as a protective cover for wet concrete in the curing thereof, said laminate comprising at least two sheets of kraft paper secured together by said asphalt bonding agent and having at least the paper ply to be placed adjacent the alkaline wet concrete homogeneously impregnated with a small quantity of a Werner complex of a trivalent chromium salt containing a high molecular weight unsubstituted long hydrocarbon chain organic carboxylic acid having at least 10 carbon atoms and a water soluble methylol resin forming compound polymerized in situ in the paper.

3. Asphalt bonded kraft paper laminate resistant to aqueous alkaline delamination between the paper and asphaltic bonding agent adapted as a protective cover for wet concrete in the curing thereof, said laminate comprising at least two sheets of kraft paper secured together by said asphalt bonding agent and having at least the paper ply to be placed adjacent the alkaline wet concrete homogeneously impregnated with a small quantity of a Werner complex of a trivalent chromium salt containing a high molecular weight unsubstituted long hydrocarbon chain organic carboxylic acid having at least 10 carbon atoms and a small quantity of water soluble dimethylol urea polymerized in situ in the paper.

4. The method of forming a paper laminate which is substantially resistant to delamination in the presence of alkaline waters with which it is wet in use, comprising impregnating the plies of the paper to be assembled into a laminate with a dilute aqueous solution of a Werner complex of a trivalent chromium salt containing a high molecular weight unsubstituted long hydrocarbon chain organic carboxylic acid having at least 10 carbon atoms and a methylol resin forming compound, setting the impregnant in the plies by heating and drying, and then securing said plies into a laminate by hot bonding with a hot melt resinous hydrocarbon adhesive.

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