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2,714,568

ASPHALT LAMINATE

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This invention relates to a method for laminating paper, paper to plastics, paper to metal foil, paper to cloth, metal foil to plastics, metal foil to paper to cloth, etc., wherein a cement is used of the kind in which pitch, bitumen, asphalt and the like form the basic element.

It has been proposed to make laminated paper or cardboard of two or more thicknesses cemented together by means of latex, with or without a small quantity of wood tar (pine tar) resin, mineral oils, bitumen, gelatine, resin soaps, gum-arabic, etc., to increase the adhesive power of the latex, such latex being applied so as to provide a coherent impervious and tough membrane of rubber between adjacent layers of the paper or cardboard. Such method of manufacture has also been applied using crepe paper for its flexible and stretchable properties. In both cases, however, it has been emphasized that a sufficient quantity of the latex must be applied to provide a coherent layer of rubber cementing together the adjacent layers of material, and at the same time to give adequate waterproofing or moistureproofing properties.

The use of latex in such manner appreciably increases the cost of manufacture of laminated paper or cardboard compared with the previously known method of manufacture in which pitch or asphalt alone was employed. The latex process, however, avoids the disadvantage of such earlier process in that under hot conditions the pitch was liable to migrate through the paper and cause staining of the goods and under cold conditions, particularly at temperatures of -50°F . or below, the asphalt and pitch would crack or fracture, thus destroying the cement and causing the lamination to come apart.

The object of the present invention is to provide an improved laminated sheet material which is cheap to produce and which, whilst employing pitch, bitumen or the like such as asphalt, wax tailings, etc., as the basic element of the adhesive and water-proofing medium, avoids the disadvantage of migration, as above described.

This invention is based upon a discovery that the addition of a small quantity of a certain type of hydrocarbon copolymer and a small quantity of a naphthenic, aromatic or paraffinic hydrocarbon oil to an oxidized asphalt produces an excellent cement for use in the manufacture of laminated paper, which may be applied or used in small and economical quantities yet sufficient to enable the pitch, bitumen or like constituent to cement the laminations securely together whilst providing a waterproofing property, the polymer apparently operating to retard or substantially prevent migration of the asphalt into the paper or other absorbent material, thereby improving the low temperature flexibility of the laminate.

According to the invention, a laminated paper or cardboard is characterized in that the laminations are united by an adhesive comprising an oxidized asphalt to which has been added a small quantity of a copolymer of a polymerizable hydrocarbon containing a cyclic nucleus and an aliphatic olefin or alkene as, for example, a copolymer of styrene and isobutylene as described in U. S. 2,274,749

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to retard migration of the pitch into the material together with a naphthenic oil as a plasticizer.

As in the old method, the pitch or bitumen performs two functions. Firstly, it acts as an adhesive adequately to combine the sheet materials together and secondly, to give a moisture- or waterproofing film. It is important, therefore, that such pitches or bitumens selected for use possess tenacious or adhesive properties as well as being resistant to water. Such products as oils, waxes and greases could not be used in place of bitumen as they do not give the necessary adhesion, and are, therefore, quite unsuitable.

Broadly, the present invention comprises using as the copolymer to be compounded with a bituminous material, a copolymer of a cyclic alkene and a mono-olefin, which copolymer has intrinsic viscosity greater than 0.7 and having a content of combined styrene or other cyclic constituents of 20 to 80%, preferably 50%, such copolymers being produced at copolymerization temperatures below -50°C ., and preferably below -70°C ., a suitable operating temperature being -103°C ., since this is the boiling point of liquefied ethylene. Copolymers having the desired high intrinsic viscosity cannot be produced at more elevated temperatures, such as between 0°C . and -50°C .

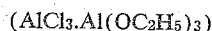
The intrinsic viscosity may be determined in a suitable solvent such as toluene, using the following formula for calculating the intrinsic viscosity:

$$\text{Intrinsic viscosity} = \frac{2.303 \log_{10} \text{relative viscosity}}{\text{Concentration of copolymer/100 ml.}}$$

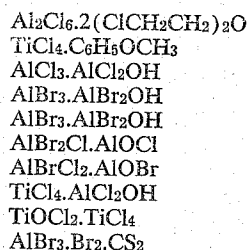
Instead of isobutylene, other aliphatic mono-olefins may be used, preferably having more than 2 carbon atoms and preferably iso-olefins having 4 to 8 carbon atoms, such as isopentene (methyl-2 butene-1) or a pentene obtained by dehydration of secondary amyl alcohol.

Instead of styrene, other polymerizable, mono-olefinic aromatic hydrocarbons may be used, such as indene, the homologues of styrene, e. g. alphas-methyl styrene, paramethyl styrene, alphas-methyl paramethyl styrene or dihydro naphthalene.

The copolymerization is effected by mixing the two reactants, with or without a mutual solvent, if necessary, such as ethylene, propane, butane, methyl chloride or refined naphtha, and then after the cooling of the reactants to the desired low temperature, adding a Friedel-Crafts halide catalyst such as boron fluoride or boron fluoride catalyst activated by the addition of 0.1% of diethyl ether, aluminum chloride, titanium tetrachloride or aluminum alkoxide-aluminum chloride complex



If desired, such catalyst may be dissolved in a solvent such as carbon disulfide, a low molecular weight sulfur-free saturated hydrocarbon, a lower alkyl halide, e. g. methyl chloride, or ethyl chloride, or a mixture of methyl chloride with butane at or below the boiling point of the catalyst solvent, and then the catalyst solution cooled down, filtered and added to the reaction mixture. Alternative catalysts include:



BF_3 solution in ethylene, activated BF_3 catalyst in methyl chloride solution. Volatile solvents or diluents, e. g. pro-

pane, ethane, ethylene, methyl chloride, alkyl halides, methylene chloride or carbon dioxide (liquid or solid) may also serve as internal or external refrigerants to carry off the liberated heat of polymerization. After completion of the copolymerization, residual catalyst is hydrolysed with alcohol, for example, isopropyl and excess catalyst removed by washing the product with water and preferably also with dilute aqueous caustic soda. The resulting solid copolymer may range from a viscous fluid or a relatively stiff plastic mass to a hard, tough thermoplastic resinous solid, depending upon the temperature of polymerization, the yield of polymer obtained upon the active feed, the type and concentration of catalyst, the proportion of cyclic reactant in the feed, and the temperature at which the physical texture is observed.

When copolymers are prepared according to this invention, using copolymerization temperatures below $-50^{\circ}\text{C}.$, the resultant products will generally have average molecular weights above 6,000, and preferably 10,000 to 150,000, with intrinsic viscosities above 0.7 and preferably 0.8 to 3.0. The higher molecular weight and intrinsic viscosities are obtained with the lowest copolymerization temperatures, and they are also favored by the lower content of cyclic reactant, i. e., a per cent of combined styrene of 20 to 40%. The hardness of the copolymer generally increases with increasing content of combined styrene or other cyclic constituents.

Thus the preferred operating conditions for making the copolymers for use according to this invention, comprises copolymerizing a reaction mixture containing 20–80% of styrene and balance isobutylene, at a temperature below $-70^{\circ}\text{C}.$ in the presence of about 1–4 volumes of methyl chloride or other lower alkyl halides per volume of active polymerization feed, and using as the catalyst the solution of aluminum chloride dissolved in methyl chloride or other lower alkyl halides.

The bituminous material to be compounded with the above described copolymer may be selected from a wide variety of natural and industrial products. For instance, various natural asphalts may be used such as natural Trinidad, Bermudez, gilsonite, grahamite and Cuban. Various petroleum asphalts may be used such as those obtained from a California crude, a Mid-Continental air blown oil. Mexican petroleum asphalt, as well as tarry residues known as cracking coil tar obtained as a by-product during the cracking of gas oil or other heavier petroleum fractions to obtain gasoline or other lighter fractions. Although the above mentioned natural and petroleum asphalts are preferred, still further bituminous materials may be used such as coal tar, wood tar and pitches obtained from various industrial processes, such as a fatty acid pitch.

The term "asphalt" as used in the present specification is intended to mean the asphaltic bitumen per se without any added dust, sand, gravel, etc., as commonly used in talking about paving asphalt. Whatever the bitumen is which is used according to the present invention, but particularly in the case of petroleum asphalt, it may have been subjected to any of the commonly used refining or treating processes, such as distillation, steam reduction, air blowing, etc. The invention is particularly advantageous in the case of oxidized asphalts because they are generally not as cementitious and ductile as the steam reduced asphalt. Furthermore, among the oxidized asphalts, the invention is of greater advantage with asphalt having a high softening point, particularly when used as a metal protecting coating composition. On the other hand, if a steam reduced or other brittle asphalt is to be subjected to cold temperatures, incorporation of some of the copolymer of high intrinsic viscosity according to this invention will greatly reduce the tendency of such an asphalt to crack when subjected to vibration or bending.

The invention may also be applied to the use of asphalt or other bituminous materials in a cut-back condition,

i. e., dissolved in a volatile solvent such as kerosene, toluene, petroleum aromatic solvent fraction, benzene or petrolene or also when emulsified with water, whether in the form of an oil-in-water type emulsion or as a water-in-oil type emulsion.

The oil to be added may be aromatic, naphthenic, or paraffinic, but is preferably a black naphthenic oil having a viscosity from 70 to 1,000 seconds Saybolt Universal (SSU), preferably 80 to 120 at $210^{\circ}\text{F}.$

The proportions in which the primary constituents of this invention, namely, the bituminous material, the oil, and the copolymer, are to be mixed, will, of course, depend upon the intended use of the composition but should broadly range from 1 to 3% by weight each of the copolymer and oil based on the asphalt, but large amounts up to 15% or more may be used when desired. It is important, however, that the oil and copolymer be mixed in equal proportions since this produces the greatest incremental increase in ductility.

In carrying out the invention, the constituents may be compounded in any desired manner, but the preferred procedure will, of course, depend upon the relative proportions of the two primary constituents as well as the type and quantity of any other liquid or solid additives to be used. However, if a small amount of copolymer and oil is to be incorporated into a large amount of bituminous material without the use of any solvents, the asphalt or other bituminous materials may simply be melted, either by direct firing in a kettle by the use of steam coils or a steam jacket, and then the copolymer added to it with stirring either in the form of small solid pieces or chunks or in a molten or at least heat-softened condition. Another alternative in making such compositions is to make a master-batch of asphalt-copolymer of much higher copolymer content than desired in the finished mixture, for instance, by compounding one part of asphalt with 1 to 5 parts by weight of copolymer, by gradually adding the heat-softened asphalt into the copolymer while the latter is being mechanically worked in a hot kneader or on hot steel rolls such as those used in the conventional rubber mill; then, of course, the desired amount of such a master-batch may then readily be blended into a larger batch of molten asphalt.

The object, advantage and details of the invention will be better understood from a consideration of the following experimental data.

Example

Varying amounts of a copolymer of 50% by weight of styrene and 50% by weight of isobutylene were dissolved in a naphthenic oil having a viscosity of 78 SSU at $210^{\circ}\text{F}.$ and the blends incorporated into a 160– $180^{\circ}\text{F}.$ melting point oxidized asphalt in various proportions. The following results were obtained:

	Co-Polymer	Oil, Per-cent	Soft. Pt.	Penetration			Ductility
				$35^{\circ}\text{F}.$	$77^{\circ}\text{F}.$	$115^{\circ}\text{F}.$	
Oxidized Asphalt—heated.....	0	0	189	18	27	45	$3\frac{1}{2}$
Oxidized Asphalt—unheated.....	0	0	170	—	34	—	$3\frac{1}{2}$
Do.....	0.25	2.0	184	19	29	51	4
Oxidized Asphalt+.....	1.02	2.0	174	19	29	49	44
Do.....	2.0	2.0	189	18	28	47	75
Do.....	0.25	0	189	17	25	40	$3\frac{1}{2}$
Do.....	1.0	0	196	16	23	34	5
Do.....	2.0	0	200	16	23	36	16

The above results show clearly that the ratio of oil to copolymer must be 1 to 1 in order to obtain any substantial improvement in the ductility.

In using the above cement for the manufacture of two-ply laminated kraft paper, a small quantity is applied to the face of a sheet by means of back filling rollers and doctor knives. Two sheets, one of which is coated, are

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then brought together and go through rollers providing a tight nip, which rollers may be heated or cold. The cement may be applied in quantity sufficient to yield the type laminate required as, for example, 30-30-30, 30-45-30, 45-30-45, 60-30-60, etc., in which the first and last figures represent the paper weight in pounds per ream of 24 x 36" paper and the middle figure, the pounds of adhesive applied to this quantity of paper.

The nature of the present invention having been thus fully set forth and specific examples of the same given, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. Method of improving the ductility of oxidized asphalt which comprises mixing in equal proportions with oxidized asphalt from 1 to 3% by weight of a hydrocarbon oil having a viscosity at 210° F., between 70 and 1000 SSU, and a copolymer of 20 to 80% styrene and 80 to 20% of isobutylene, said copolymer having an intrinsic viscosity greater than 0.7 and being prepared by copolymerization at temperatures below -50° C.

2. Method according to claim 1 in which the amount of styrene and isobutylene in the copolymer are each 50% by weight.

3. Method according to claim 2, in which the oil has a viscosity of 78 SSU at 210° F.

4. An asphalt composition of improved ductility consisting of an oxidized asphalt and equal proportions of, in amounts of 1 to 3% by weight based on the asphalt, a hydrocarbon oil having a viscosity at 210° F., between 70 and 1000 SSU and a copolymer of 20 to 80% styrene and 80 to 20% isobutylene, said copolymer having an intrinsic viscosity greater than 0.7 and being prepared by copolymerization at temperatures below -50° C.

5. Composition according to claim 4 in which the amount of styrene-isobutylene in the copolymer are each 50% by weight.

6. Composition according to claim 5 in which the oil has a viscosity of 78 SSU at 210° F.

7. A laminated product consisting of at least two sheets of paper, cardboard and the like and a liquid cementitious composition between said sheets, said cementitious composition consisting of an oxidized asphalt having incorporated therein equal proportions of, in amounts of 1 to 3% by weight based on the asphalt, a hydrocarbon oil having a viscosity at 210° F., between 70 and 1000 SSU and a copolymer of 20 to 80% styrene and 80 to 20% of isobutylene, said copolymer having an intrinsic viscosity greater than 0.7 and being prepared by copolymerization at temperatures below -50° C.

8. Product according to claim 7 in which the amount of styrene-isobutylene in the copolymer are each 50% by weight.

9. Product according to claim 8 in which the oil has a viscosity of 78 SSU at 210° F.

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