

Jan. 17, 1956

H. A. TOULMIN, JR
METAL BUILDING MATERIAL

2,731,375

Filed Aug. 19, 1953

Fig. 1.

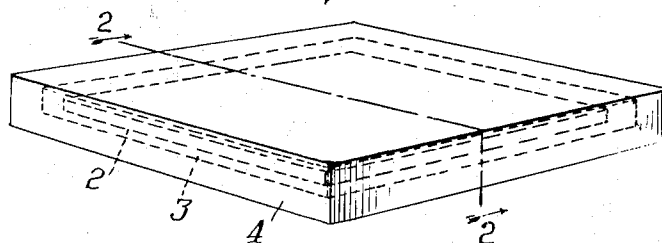


Fig. 2.

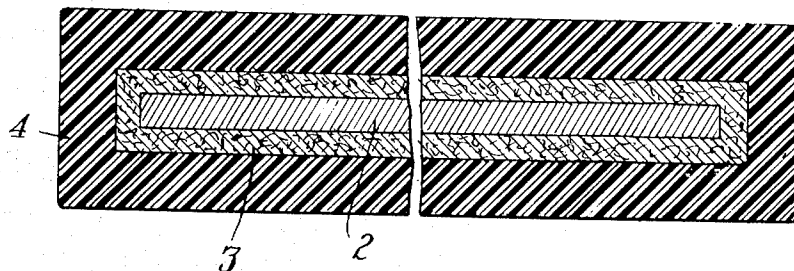
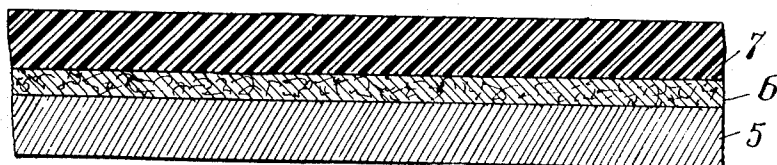


Fig. 3.



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METAL BUILDING MATERIAL

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Application August 19, 1953, Serial No. 375,089

3 Claims. (Cl. 154—45.9)

This invention relates to protected metal articles, and more particularly to protected metal building sheets.

Protected metal building sheets comprising a steel sheet enveloped in an outer weatherproofing coating of a bituminous or asphaltic composition are known. Some of these sheets are made by applying the outer weatherproofing coating over felt layers saturated with a bituminous impregnant and adhered to the metal base. Other types of protected metal building sheets comprise a steel sheet protected by a galvanizing or equivalent coating of fusible metal adhesive on which the fibrous layer is disposed and which serves to anchor the fibrous or felt layer to the metal base. The fibrous layers are impregnated with a bituminous composition and, usually, an outer weatherproofing coating of bituminous character is applied on top of the impregnated felt layers.

Asphalt or similar bituminous compositions are very desirable for use as the impregnant but, as is known, when they are used as the outer or top coating, a limitation is imposed on the color and appearance of the final building sheets, only dark colors being possible. Therefore, it is desirable to provide the sheets with outer weatherproofing coating that is light colored and may be decorative.

Various synthetic resins have been tried but these generally have to be applied in conjunction with a solvent which penetrates into the fibrous layers during application of the resin and then escapes over a long period of time through the resin coating, rendering the resin coating porous and permitting bleeding through or migration of the oily constituents of the bituminous impregnant. The result has been that the resin coating becomes badly discolored in the course of time.

It has been proposed, also, to provide these conventional metal building sheets with an outer coating of certain polyester resins applied in liquid condition without a solvent. However, the resins which have been suggested do not combine dye-receptivity with the required properties of high impact strength and rigidity coupled with sufficient flexibility to permit fitting and bending of the sheets without cracking of the resin coating.

The object of this invention is to provide new building sheets protected by fibrous or felt layers which may be impregnated with a bituminous composition and carry, as the exterior coating, a new dye-receptive resin blend which, in thermoset condition, combines high impact strength and practical rigidity with a capacity to withstand bending stress without cracking whether the outer protective resinous coating is relatively thin or relatively thick.

The new building sheets are obtained by coating an assembly comprising a metal sheet having a bituminous-impregnated fibrous material adhesively bonded to a surface thereof with a polymerizable composition comprising a blend of unsaturated polyester or alkyd resin precondensate and a vinyl-substituted heterocyclic tertiary amine in monomeric or at least still polymerizable condition,

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and curing the blend on the sheet to a hardened insoluble and infusible state.

The unsaturated polyester component of the polymerizable blend is an unmodified or modified polyhydric alcohol polyester of an alpha-unsaturated alpha, beta-polycarboxylic acid or ester-forming derivative thereof such as acid anhydrides, esters and halides. The polyhydric alcohol which may be heated with the polycarboxylic acid or derivative to obtain the unsaturated polyester includes the preferred dihydric alcohols such as ethylene glycol, propylene glycol, the butylene glycols, diethylene glycol, triethylene glycol, trimethylene glycol, tetraethylene glycol, polyethylene glycol generally and unsaturated glycols such as, for example, vinyl ethylene glycol, and may also include alcohols having a functionality greater than two, such as glycerol and pentaerythritol.

Examples of the alpha-unsaturated-alpha-beta-polycarboxylic acids to be reacted with the polyhydric alcohols are maleic, fumaric, chloromaleic, chlorofumaric, citraconic, methylethyl maleic, diethylmaleic, chloromethylmaleic, and mesaconic acids.

In making the unmodified alkyd or unsaturated polyester component of the blend, one or more of the foregoing alcohols is heated with the desired amount, usually a roughly equivalent proportion, of one or more of the acids or their ester-forming derivatives for a time sufficient to effect condensation to the stage at which the condensate occurs as a liquid resinous flowable polyester having the desired molecular weight. When the polyester component is to be of the modified type, a part, or even nearly all, of the unsaturated polycarboxylic acid may be substituted by saturated mono- or polycarboxylic acid such as succinic, adipic, phthalic, sebacic or 12-hydroxystearic acids. Monobasic acids having from 10-20 carbon atoms may be preferred. These acids may be mixed fatty acids derived from vegetable oils or the individual acids present therein. When desired, the vegetable oils themselves may be incorporated by conventional methods, such as by the so-called "alcoholysis" method. As examples of suitable vegetable oils may be mentioned linseed, perilla, soybean, castor, dehydrated castor, palm kernel, coconut and the like. Resins of both these unmodified and modified types are known in the art and available commercially under the different trade names.

The unsaturated polyester is made up of repeating groupings containing alcohol and acid units and may have a molecular weight, as measured by the acid value of the resin, or over 500, molecular weights of 1,000 or over, such as 1,000 to 10,000 being generally preferred. The molecular weight may vary but should be such that the liquid resinous polyester is capable of being blended uniformly with the vinyl-substituted amine in conventional type mixing apparatus.

Examples of the vinyl-substituted heterocyclic tertiary amines which may be used include the vinylpyridines, for instance, 2-vinylpyridine, 5-vinyl-2-methylpyridine, 5-ethyl-2-vinylpyridine, and the vinylpyridines and their alkyl nuclearly substituted derivatives generally in which the alkyl radicals contain from 1 to 4 carbon atoms, the vinylimidazoles, the vinylquinolines, the vinyl-isoquinolines, the vinylthiazoles, the vinyl oxazoles, the vinyl benzooxazoles, etc.

The vinyl-substituted amine functions, initially, as a diluent for the unsaturated polyester and subsequently, on heating of the mix to curing temperature, as a cross linking agent for the polyester chains.

The eventual hardening to thermoset condition and simultaneous cross linking of the polyester chains by the amine are best accomplished in the presence of a catalyst. Introduction of the catalyst may be achieved in various ways calculated to prevent premature polymerization of the composition to the insoluble, infusible state, as during

storage or shipping. One method of accomplishing this is to incorporate in the blend, during preparation thereof, a latent catalyst which does not exert its catalytic action, at least to any appreciable extent, until the building sheet coated or impregnated with the blend is heated to curing temperature. Another method is to mix the catalyst with the blend immediately before the latter is coated onto the building sheet or to apply the catalyst concurrently with the blend, as by spraying. Particularly preferred catalysts for this purpose are organic peroxides such as benzoyl peroxide, succinic peroxide, and especially peroxides derived from fatty acids having from 10-20 carbon atoms, including lauroyl peroxide, stearoyl peroxide, and peroxides made from vegetable oil acids such as cocoanut oil peroxides. Alcohol peroxides such as tertiary butyl hydroperoxide and terpeneoxides such as ascaridole, may also be used. Organic ozonides are also useful catalysts for this reaction, including di-isopropylene ozonide and di-isobutylene ozonide. The catalyst may be used in very small amounts from about 1.1% to about 2% of the blend by weight.

If the mixture of polyester resin and vinyl-substituted heterocyclic tertiary amine is to be stored for long periods of time, it is desirable to include a polymerization inhibitor with it. Suitable inhibitors include guaiacol, paraquinone, para tertiary butyl catechol, hydroquinone, ortho trinitro phenols, and the like. From about 0.2% to 1.0% of the inhibitor by weight of the blend is generally sufficient to inhibit or retard polymerization for substantial periods of time.

Under certain circumstances, as when the blend includes a substance which inhibits the polymerization under normal storage and shipping conditions even in the presence of a peroxide or ozonide catalyst, these catalysts may be incorporated in the blends at the time of their preparation. Agents which stabilize the compositions against any marked polymerization on standing under normal conditions include alkoxy-substituted hydroxybenzoic acid in which the alkoxy radical contains up to 18 carbon atoms and not more than one oxygen atom is joined to the hydroxybenzoyl nucleus by an atom other than a carbon atom. Typical of these stabilizers is the substance 4-hydroxy-3,5-dimethoxybenzoic acid.

The relative proportions of the unsaturated polyester and vinyl-substituted amine in the blend may be varied and the blend may even comprise from 5 to 95 parts of the one component to, conversely, from 95 to 5 parts of the other, by weight. However, blends comprising from 5 to 50 parts of the vinyl-substituted heterocyclic tertiary amine such as a 2-vinylpyridine or 5-vinyl-2-methylpyridine for each 100 parts of the unsaturated polyester will generally be found satisfactory for the present purposes.

Preferred compositions for use as the outer or weatherproofing coating for the building sheets are those obtained by coating the sheet with a polymerizable composition comprising the vinyl-substituted amine and a polyester obtained from a glycol, particularly propylene glycol, and a mixture of an unsaturated dicarboxylic acid with a saturated acid, or the acid anhydrides and especially a mixture of maleic and phthalic acids or anhydrides in which the molecular ratio of saturated acid to unsaturated acid is not greater than 60:40. The acid (or anhydride) mixtures may desirably comprise the acids (or anhydrides) in such proportions that the molecular ratio of saturated acid to unsaturated acid is 10:90, 25:75 or 50:50.

The unsaturated polyester component of the blends may be further modified by including with the polyester-forming constituents an alcohol having a terminal $\text{CH}_2=\text{C}<$ group, including allyl alcohol and others of that class having from 3 to 10 carbon atoms. This includes methallyl alcohol, methyl vinyl carbinol, allyl carbinol, beta-allyl ethyl alcohol, monoallyl and monomethallyl ethers of ethylene glycol and the like. Such modified polyesters are known and contain, in addition to the acid and polyhydric alcohol residues, residues of the unsaturated alcohol.

The polyester may also be one produced in the presence of a monohydric aliphatic alcohol such as 1-butanol, and other saturated lower aliphatic alcohols having straight or branched chains, particularly alcohols having 3-6 carbon atoms such as propanol, 1-pentanol, 2-methyl-1-butanol, 2-pentanol, 2-methyl-2-butanol, 2-propanol, 2-butanol, 2-methyl-2-propanol and the like. The final polyester may, therefore, also contain residues of the saturated monohydric alcohol, preferably in an amount up to 1-10% of the total ester linkages.

These blends are clear, essentially colorless resinous liquids. They may be modified by the inclusion of suitable pigments to provide the building sheets with a decorative weatherproofing outer coating, pigments being selected which are capable of withstanding the temperature at which the blend is ultimately cured. One distinguishing feature of the blends is that the vinyl-substituted heterocyclic tertiary amine is strongly receptive of the acid dyestuffs and can be dyed with those dyestuffs to provide the building sheets with a surface coating colored uniformly to any desired depth of shade by an acid dye which is particularly fast because of the attraction for it exhibited by the tertiary nitrogen atom of the vinyl-substituted amine component distributed uniformly throughout the blend. Although the unsaturated polyester component of the blend may be prepared by reacting substantially equal parts of the polyhydric alcohol and polycarboxylic acid, considerable variation may be achieved in the properties of the blend, not only by conducting the esterification reaction in the presence of unsaturated allyl-type alcohols and/or saturated monohydric alcohols, but also by variations in the relative proportions of the primary reactants, and particularly by selecting these reactants so that there is a slight preponderance of either the polyhydric alcohol or of the polycarboxylic acid.

The following examples illustrate the preparation of typical blends for use in coating building sheets in accordance with the invention.

Example I

A modified unsaturated resinous polyester resin was prepared by heating a mixture of 0.5 mol. (49 parts) maleic anhydride, 0.5 mol. (74 parts) phthalic anhydride and 1.2 mol. (92 parts) of propylene glycol to 190° C. until a clear resinous liquid was obtained.

A sufficient amount of monomeric 2-vinylpyridine was mixed, at room temperature, with the resinous polyester to obtain a mass comprising, on a weight basis, the equivalent of 40 parts of the vinylpyridine per each 100 parts of polyester.

Example II

An unmodified resinous polyester was prepared by heating together equimolecular proportions of triethylene glycol and maleic acid until a partial condensate having the form of a resinous liquid was obtained.

The polyester was mixed, at room temperature, with a sufficient amount of 5-vinyl-2-methylpyridine to produce a blend containing the equivalent, on the weight basis, of about 15 parts of the 5-vinyl-2-methylpyridine per 100 parts of the polyester.

Example III

A modified resinous polyester was prepared by heating a mixture of ingredients as in Example I. The resin was blended with 2-vinylpyridine containing 1% by weight of hydroquinone to obtain a homogeneous mix containing 30 parts of the vinylpyridine per 100 parts of polyester.

It will be understood that the vinylpyridines used in the examples may be replaced by other vinyl-substituted heterocyclic tertiary amines or their nuclearly substituted alkyl substitution products in the amounts in which the amine is compatible with the polyester. Compositions as in Examples I and III were prepared by blending

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2-vinylpyridine with the polyester in amounts of 5, 10, 20, 30 and 50 parts per 100 parts of the polyester. Similar compositions in which 2-methyl-5-vinylpyridine was substituted for the 2-vinylpyridine were also prepared. All these blends were clear, liquid but viscous, products which could be polymerized to hardened condition.

When these clear resinous liquids are applied to the bituminous-saturated felt layers of building sheets as described herein, and cured to the hardened condition on the sheets, the latter are provided with a dyeable, durable film that is insoluble, infusible, resistant to deterioration on exposure to changing weather conditions, and which, though hard and sufficiently rigid for this purpose, has enough flexibility to permit bending and flexing of the building sheet without cracking of the protective outer coating. The polymerized vinylpyridine cross-links impart rigidity to the resin coating without depriving it of flexibility, and the balance between flexibility and rigidity can be controlled and varied by varying the amount of polymerizable vinyl amine blended with the liquid resinous polyester. The blends may be converted to the hardened condition at temperatures varying over a wide range and even including room temperature if time is not an important factor of production. However, it is generally preferred to use higher temperatures permitting shorter curing cycles, such as temperatures between 50° C. and 200° C. A cure of ten minutes at 100° C. in a conventional baking oven is generally satisfactory.

Since the liquid blend is applied directly to the metal sheet or other article carrying the fibrous or felt layers as such and without the use of a solvent, there is no seepage of solvent from the finished product and, therefore, no tendency for the oily constituents of the bituminous material to migrate through the top coating and discolor the outer or exposed surface of the building sheet.

The liquid polymerizable blend adheres to the fibrous material bonded to the metal base and is cured in contact with it so that the cured blend is permanently anchored to the metal base through the intermediate fibrous layer, to provide a strong coherent laminated structure, the laminae of which, including the top surface or film of cured resin, do not tend to separate even when the building sheet is subjected to bending stress. The resin blend also adheres to bituminous impregnant occurring at the surface of the fibrous layers.

If desired, during the curing the assembly may be subjected to pressure, such as pressures of from 0.5 pound per square inch above atmosphere to 20 pounds per square inch (gauge) or even higher, and up to 300-500 pounds per square inch.

The building sheet provided with the coating or top film of the polymerizable blend may comprise a sheet of steel or other metal having bonded thereto a layer of fibrous material impregnated with bituminous material. Bituminous material may also be coated on the fibrous layer, the blend being applied over such coating. Bonding of the fibrous layer to the metal sheet may be by means of the usual adhesives commonly employed for this purpose or by a galvanized or equivalent coating of fusible metal adhesive disposed on the metal sheet. The fibrous layer and cured blend may occur at only one major surface of the metal sheet, or the sheet may be sheathed in the fibrous material and the surface thereof completely covered with the cured resin blend.

The attached drawing is illustrative of the invention. In the drawing:

Figure 1 is a perspective view of a protected metal building sheet according to the invention,

Figure 2 is a sectional view of the sheet taken on line 2-2 of Figure 1, and

Figure 3 is an enlarged fragmentary view of another embodiment.

Referring to Figures 1 and 2, there is shown a protected metal building sheet comprising the steel sheet 2 sheathed in a felt formed of asbestos or equivalent fibers

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3 secured thereto by bituminous material. The assembly comprises the top or outer coating 4 of polymerized polyester resin cross-linked by the polymerized vinyl-substituted heterocyclic tertiary amine.

Figure 3 illustrates a somewhat different form of structure in which the steel sheet 5 has a felt layer 6 of asbestos or equivalent fibers impregnated with bituminous material adhered to one surface thereof by a galvanized coating of fusible metal adhesive. The outer or surface weatherproof coating or film 7 of polymerized polyester cross-linked by the vinyl-substituted heterocyclic tertiary amine is cured and bonded to the asbestos layer.

Various embodiments and specific details have been given in the above discussion of the invention. Instead of flowing the polymerizable blend onto the fibrous layer or sheath adhered to the metal base, or applied directly to the fibrous layer or sheath in any other suitable way, the polymerizable composition may be deposited on a suitable base to which it does not adhere and which may be heated to a temperature such that the condensation or polymerization is advanced to a stage at which the composition sets to a condition in which it can be handled, but short of complete curing or hardening, the sheet thus obtained may be dyed to any desired color and shade using an acid dyestuff, and thereafter the dried, dyed sheet may be deposited on the asbestos or other fibrous layer adhered to the metal building sheet and brought to the completely cured and hardened condition. In this embodiment the fibrous layer may be provided with a coating of the liquid polymerizable blend before the preformed dyed sheet is deposited on it, the final heating serving to cure both the liquid blend and the preformed sheet to thermoset condition and bond the preformed sheet to the fibrous layer through the interposed initially liquid coating on the fibrous layer.

Other methods of obtaining the preformed partially cured sheet to be deposited on the fibrous layer may be used, such as a method in which the liquid polymerizable blend is coated onto a metal conveyor or belt which travels through a heating zone in which the blend is heated at a controlled temperature such that the conversion of the blend to a coherent sheet is effected. The polymerizable liquid blend coated on the surface of the fiber layer before the preformed sheet is deposited thereon may be a blend which has been heated to a stage of advanced condensation such that further heating to convert the preformed sheet to final cured condition also induces condensation of the interposed coating to the hardened fusible insoluble state.

It will be understood that it is not intended to limit or circumscribe the invention by the details given since modifications may be made in practicing the invention without departing from the spirit and scope of the disclosure and appended claims.

I claim:

1. As a new article of manufacture, metal building material comprising a metal sheet, a layer of bituminous-carrying fibrous material covering and bonded to a surface of the metal sheet, and an outer, weatherproofing layer self-adhered to the surface of the fibrous layer removed from the metal sheet and formed by depositing on said fibrous layer surface a blend consisting of (a) a liquid, resinous condensate of components consisting essentially of a polyhydric alcohol and a substance selected from the group consisting of straight-chain alpha-unsaturated-alpha, beta-dicarboxylic acids and anhydrides thereof with (b) from 5 to 50 parts by weight of a monovinylpyridine per 100 parts of the condensate, and curing the blend on the fibrous layer to set it in hard, infusible, insoluble condition.

2. As a new article of manufacture, metal building material comprising a metal sheet, a layer of bituminous-carrying fibrous material covering and bonded to a surface of the metal sheet, and an outer, weatherproofing layer self-adhered to the surface of the fibrous layer re-

moved from the metal sheet and formed by depositing on said fibrous layer surface a blend consisting of (a) a liquid, resinous partial condensate of propylene glycol, maleic anhydride and phthalic anhydride with (b) from 5 to 50 parts by weight of 2-vinylpyridine per 100 parts of the condensate, and curing the blend on the fibrous layer to set it in hard, infusible, insoluble condition.

3. As a new article of manufacture, metal building material comprising a metal sheet, a layer of bituminous-carrying fibrous material covering and bonded to a surface of the metal sheet, and an outer, weatherproofing layer self-adhered to the surface of the fibrous layer removed from the metal sheet and formed by depositing on said fibrous layer surface a blend consisting of (a) a

liquid, resinous partial condensate of triethylene glycol and maleic acid, with (b) from 5 to 50 parts by weight of 5-vinyl-2-methylpyridine per 100 parts of the condensate, and curing the blend on the fibrous layer to set it in hard, infusible, insoluble condition.

References Cited in the file of this patent

UNITED STATES PATENTS

2,073,334	Coffman	Mar. 9, 1937
2,472,963	Singleton et al.	June 14, 1949
2,491,409	Kropa et al.	Dec. 13, 1949
2,600,457	Wynstra	June 17, 1952