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PROTECTED METAL ARTICLE

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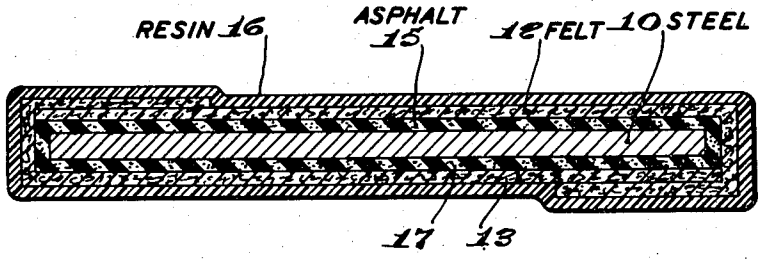

Fig. 1.

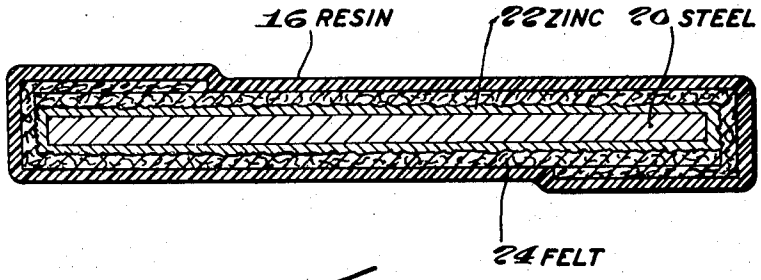

Fig. 2.

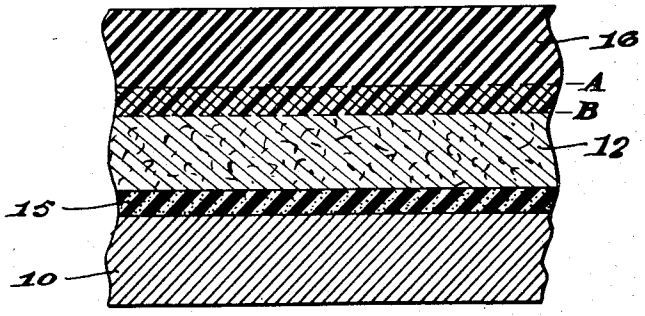

Fig. 3.

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PROTECTED METAL ARTICLE

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Application September 4, 1946, Serial No. 694,814

9 Claims. (Cl. 154—45.9)

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

In general, the object of the invention is to produce novel and superior light-colored protected metal articles, and particularly light-colored protected metal building sheets possessing durable weatherproofing characteristics, which may be manufactured in an economical and practical manner and which are more suitable and attractive in appearance and more commercially valuable than prior protected metal building sheets and articles of which we are aware.

With this general object in view, and such others as may hereinafter appear, the invention consists in the protected metal article and building sheets, and method of making the same hereinafter described and particularly defined in the claims at the end of this specification.

In the drawings illustrating the different features of the invention, Fig. 1 is a vertical section of one form of protected metal building sheet embodying the invention; and Fig. 2 is a similar view of another form of such a sheet embodying the invention.

Fig. 3 is a fragmentary enlarged sectional view of a portion of Fig. 1.

The prior art over which the present invention is an improvement with respect to protected metal building sheets may be illustrated by the United States patents to Robertson No. 1,277,755 and to Coffman No. 2,073,334. In the Robertson patent there is disclosed a protected metal building sheet comprising a steel sheet enveloped in an outer weatherproofing coating of a bituminous or asphaltic composition. In practice this outer weatherproofing coating is applied over felt layers saturated with a bituminous impregnant. Protected metal building sheets as thus constructed have been manufactured continuously in large quantities since the issuance of the Robertson patent and have served well in the construction of industrial buildings as roofing and siding materials, and also for many special purposes where corrosive conditions are particularly severe. In practice the sheets are corrugated in order to provide additional rigidity.

For some purposes comparable building sheets produced in accordance with the disclosure of the Coffman patent find general utility, and as therein disclosed the steel sheet is protected by a galvanizing or equivalent coating of fusible metal adhesive, and the fibrous layers are secured to the steel sheet by the fusible metal adhesive. The fibrous layers are preferably impregnated with a

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bituminous impregnant and in most instances an outer weatherproofing coating of a bituminous nature is applied on top of the impregnated fibrous layers.

The nature of the bituminous materials employed in the felt saturants and in the coatings of the building sheets of Robertson and Coffman has heretofore restricted the possible color combinations and appearance of the building sheets to dark colors such as maroon and black. Experience in the manufacture of the protected metal building sheets of the character described, following the disclosures of the Robertson and Coffman patents referred to, has demonstrated the efficiency, suitability, and the desirability of the use of asphalt or similar bituminous compositions as an ideal material for use in the protection of the steel sheets from corrosion when the building sheets are exposed to weathering for periods of years. This same experience has emphasized the color limitations of the bituminous coatings and the need for more attractive surface colors than are obtainable with this type of coating. Over the past twenty years or more an exhaustive search has been conducted for a suitable coating material which could be utilized as a satisfactory outer weatherproofing coating in place of the heretofore used bituminous compositions in order to enable light-colored protected metal sheets to be produced. The primary object of the present invention is the provision of a satisfactory solution to this problem.

The present invention contemplates the production of protected metal articles and protected metal building sheets of the character specified in which the fibrous layers of the building sheets either of the Robertson patent or the Coffman patent are impregnated with a bituminous composition and coated with a polymerizable resinous coating, the latter then being subjected to treatment to effect the polymerization of the resinous composition to provide the surfaces of the building sheets with a body of infusible, insoluble, weather-resisting material which may be of any desired color. The invention also contemplates the production of building sheets of the character specified in which the polymerizable resinous coating is applied as a decorative and attractive coating over the bituminous outer weatherproofing coatings of the Robertson and Coffman patents.

The desired characteristics of an outer weatherproofing coating for a protected metal building sheet of the character specified include the ability to be brought to a state of fluidity as

required for application by a practical coating method, the ability to be converted rather quickly after application to a tough, flexible, relatively infusible coating, non-tacky over the normal temperature range encountered by such building sheets, the ability to adhere to and to serve as an efficient and durable weatherproofing coating for the underlying bituminous coating and/or fibrous layers impregnated with bituminous materials of the protected metal sheets, the ability to provide an attractive range of surface colors for the sheet, and the ability to resist penetration or solution of the underlying bituminous materials to the extent that there will be no discoloration of the coating.

The search for a satisfactory coating material having characteristics as enumerated has extended over many years and has involved coating of a large number of sample sheets and the weather exposure of the same on the roof, utilizing all materials which from time to time became available and which seemed to offer any prospect of solution of the problem. Prior to the present invention, however, no material has been found which was regarded as suitable or capable of fulfilling the requirements of a satisfactory outer weatherproofing coating as above outlined. Some materials lacked sufficient durability in the weather, others would not lend themselves to any practical method of application, others would not adhere to the impregnated fibrous layers, and others exhibited a tendency to permit bleeding through of the underlying bituminous materials with the accompanying discoloration of the light-colored surface.

A failing common to most of the coating base materials which have been considered in the past has been their lack of resistance to discoloration resulting from bleeding through of the underlying bituminous materials. This bleeding occurred from several general causes. Many of the coating base materials that have been available, and particularly those classes of materials which possess the desired degree of weather durability, require the use of strong solvents in substantial quantity to render them of sufficient fluidity for application in accordance with commercial practice to the surfaces of the saturated fibrous layers of the building sheets. Penetration of these solvents into the fibrous layers, and their subsequent release over long periods of aging, tends to result in a porous coating through which the oily constituents of the bituminous materials can migrate. Very often bleeding has been aggravated by the fact that the solvents for the coating material have also been strong solvents for the underlying bituminous coatings and saturants and have tended to leach out these bituminous materials with resulting discoloration of the coating. Another cause of bleeding experienced with coating materials sufficiently compatible with bituminous saturants to adhere to the impregnated fibrous layers is the mutual solubility of coating base and bituminous materials. This need not be of a very high order to result in pronounced discoloration of the coating under the influence of the sun and the wide changes in temperature experienced by building covering during weather exposure. Whatever the principal cause of the bleeding, the result has been that up to the development of the present coating material no satisfactory light-colored weatherproofing material has been discovered which was unaffected.

In accordance with the present invention a satisfactory material for producing a durable light-colored weatherproofing coating for protected metal building sheets comprises one or more unsaturated polyester resins conjointly polymerized with one or more polymerizable monomeric solvents. Such a coating may and preferably will be pigmented and filled with suitable materials for producing the color and physical properties desirable for the particular application involved.

Suitable unsaturated polyesters for use in the present invention comprise reaction products produced by heating at least one dihydric alcohol with at least one dicarboxylic acid, or ester-forming derivative thereof, at least one of said dicarboxylic acids being of the type usually referred to as alpha, beta-unsaturated dicarboxylic acids. Dihydric alcohols which may be used comprise ethylene glycol, propylene glycol, the butylene glycols, diethylene glycol, triethylene glycol, the polyethylene glycols, and unsaturated glycols such as, for example, vinylethylene glycol. Alpha, beta-unsaturated dicarboxylic acid materials which may be used include maleic anhydride, maleic acid, fumaric acid, citraconic anhydride, citraconic acid and itaconic acid. Although the unsaturated acid may constitute the sole acidic reactant, a wide variation in the properties of the polymerized resins is obtainable by using varying proportions of other dicarboxylic acid materials such as phthalic acid, phthalic anhydride, and tetrachlorophthalic anhydride, as well as the straight chain aliphatic dicarboxylic acids such as succinic, adipic, azelaic and sebacic acids. The term "ester forming dicarboxylic acid materials" as used throughout the claims is intended to include dicarboxylic acids and the anhydrides, esters and acid halides thereof, all of which are ester forming.

While a bi-bifunctional resin is preferred for most purposes, reactants of higher functionality such as glycerol and citric acid may be used, with the reservation that such polyfunctional reactants must not constitute a sufficiently large proportion of the total reactants to cause the resin to become insoluble before the molecular weight reaches the desired value.

It is within the scope of the present invention to use monohydric alcohols and/or monocarboxylic acids as modifiers in the preparation of the unsaturated polyesters. Unsaturated monofunctional reactants such as allyl and crotyl alcohols and acrylic and crotonic acids may be used. The unsaturated polyesters may be of the oil-modified type.

Polyesters of very low molecular weight are not suitable for use in the present invention. This is probably due to the fact that it is necessary to have a minimum average number of points of unsaturation per polyester chain in order for the copolymerizing solvent to act effectively as a cross-linking agent. Polyesters containing large amounts of unsaturation give useful compositions at lower intrinsic viscosities than those having smaller amounts. For example, polyethylene maleate(40%)-adipate(30%)-phthalate(30%) gave a useful product with half its weight of styrene at an intrinsic viscosity of about 0.040, while poly-(diethylene)-maleate(10%)-phthalate(90%) became useful for the purposes of the present invention only at an intrinsic viscosity of about 0.070, and polypropylene (80%) - ethylene(20%)-maleate(3%)-sebacate(97%) did not give useful materials even at the very high molecular weight indicated by an intrinsic viscosity of 0.75.

For the purposes of the above discussion and that which will follow, intrinsic viscosity is defined as follows:

$$\text{Intrinsic viscosity} = \frac{\frac{T_s}{T_a} - 1}{C}$$

where T_s and T_a represent the time of flow of a dilute acetone solution of the resin and pure acetone, respectively, in an Ostwald viscosimeter, and C is the concentration expressed as grams per 100 cc. of solution. In order to avoid errors due to differences in concentration, all solutions tested were made up to contain one gram per 100 cc. of solution.

The nomenclature "polypropylene(80%)-ethylene(20%)-maleate(3%)-sebacate(97%)" indicates that the polyester was prepared by reacting eighty mole per cent of propylene glycol and twenty mole per cent of ethylene glycol with three mole per cent of maleic anhydride and ninety-seven mole per cent of sebacic acid.

Copolymerizable solvents suitable for use in the present invention comprise polymerizable unsaturated organic liquids which are compatible with the unsaturated polyesters defined above. Such materials include polymerizable hydrocarbons such as styrene, dichlorostyrene, indene, and the coumarone-indene fraction of coal-tar distillates; vinyl ketones; vinyl ethers; allyl esters such as ally maleate and allyl phthalate esters of unsaturated acids such as ethyl acrylate, methyl methacrylate, and ethyl crotonate; and miscellaneous other unsaturated compounds such as acrylonitrile and acrolein. Styrene is the preferred copolymerizing solvent for use in the present invention because it ranks high in availability and low cost, and imparts desirable properties of water resistance, chemical resistance, color, and physical characteristics to compositions containing it.

Coating compositions of the present invention comprising an unsaturated polyester and a solvent copolymerizable therewith, together with suitable pigments and fillers, may and preferably will have incorporated therein, prior to the coating operation, an amount equal to from about one-tenth of one per cent to about five per cent of any of the well-known chain-initiating catalysts. Examples of such catalysts which have been found to be particularly adapted to use according to the present invention are aliphatic acyl peroxides such as acetyl peroxide, lauryl peroxide and stearyl peroxide; peroxides of the aromatic acid series such as benzoyl peroxide; peroxygen esters such as tertiary butyl perbenzoate; and organic derivatives of hydrogen peroxide such as tertiary butyl hydroperoxide.

In addition to the chain-initiating catalysts described above we prefer to use a small amount of a cobalt salt such as, for example, one-tenth of one per cent of cobalt nitrate or naphthenate in order to promote complete polymerization at the surface of the coating where it is in contact with atmospheric oxygen.

It has been found that when such a resinous composition is applied in liquid form to the bituminous saturated felt layers of the building sheets of either the Robertson or Coffman patents referred to, and the coated sheets subjected to an elevated temperature for a period of time which varies depending upon the temperature chosen, but which may be about ten minutes at about 100° C., there is produced an insoluble and infusible film upon the sheets which fulfills all

of the requirements with respect to weathering durability, lack of porosity, and the ability to prevent bleeding of the underlying bituminous materials.

The ability of the present coatings to resist discoloration by the underlying bituminous materials is believed to be due largely to two factors. In the first place, the unsaturated polyester resins, even in their uncured state, are non-solvents for asphalt, and, in the second place, the solvent is polymerizable and does not remain in the liquid condition. The rate of cure is such that the polymerizable solvent, e. g., styrene, is polymerized before it has had an opportunity to act to any substantial degree on the bituminous material. The small amount of solvent which penetrates the resin asphalt-saturated felt interface is tied up by subsequent polymerization or reaction of the solvent with the asphalt to produce a bonding layer having bituminous material commingled with the resin. The said layer may be defined as a bonding zone having a resin-bituminous component. The lines A and B of Fig. 3 indicate the zone referred to. It has been discovered that styrene, for example, will polymerize in bituminous compositions and that it will react with polynuclear hydrocarbons of the types present in bituminous materials. In any case the practical and very valuable results obtained are independent of any theory.

Illustrating the production of light colored protected metal building sheets of either the Robertson or Coffman type above referred to, the following examples are given although it will be understood that resins may be selected according to the above definition and that various fillers and pigments may be selected from any of the known fillers and pigments according to the particular color and other characteristics which it is desired to impart to the outer weatherproofing film.

Example 1

	Grams
(2.6 moles) diethylene glycol	275.6
(0.4 mole) maleic anhydride	39.2
(1.6 moles) phthalic anhydride	236.8
(0.3%) p-toluenesulfonic acid	1.6

The reactants were placed in a Claisen flask and were heated to 200° C. in five hours and at this temperature for three additional hours. The pressure was then reduced to 0.1 mm. and heating was continued at 200° C. for two hours, an atmosphere of nitrogen being maintained throughout the reaction. The product, when cool, was a very viscous, almost colorless liquid. The following coating composition was made up:

Above polyester	parts	200
Styrene	do	100
Titanox B–30	do	30
Chrome oxide green	do	30
Benzoyl peroxide	do	3
Cobalt nitrate per cent (on resin)		0.1

The polyester was dissolved, with stirring, in the styrene and the pigments and cobalt nitrate were milled into this solution in a ball mill. Just before use the benzoyl peroxide, in the form of a fifty per cent paste in tricresyl phosphate, was stirred in. The resulting coating composition was used to coat a number of 6" x 12" exposure panels including both the Robertson and Coffman products. In certain of these the resinous thermosetting composition was applied to the asphalt-saturated felt layers while other sheets had been given the bituminous weatherproofing

coating and the resinous coating was applied directly over this. These coated sheets were then baked in an oven at different temperatures and for different periods of time. It was found that a cure of ten minutes at about 100° C. gave good results. Temperatures above 130° C. resulted in volatilization of the light constituents of the bituminous materials and consequent disruption of the resinous color coat. Temperatures below 70° C. gave good cures but required considerably more time. No discoloration due to bleeding of the bituminous compositions was noted in any case either during application or during cure. Panels exposed to the weather for four months have shown no tendency to bleed and accelerated laboratory tests designed to test coatings for bleeding have been completely negative.

Example 2

A polyester prepared in a manner similar to that of Example 1 was produced in which adipic acid was substituted for the phthalic anhydride of the former example. The resulting unsaturated polyester was similar to that described above but was more fluid. It produced a more flexible polymerized coating when formulated as described in the previous example.

Referring now to the drawings, in Fig. 1 I have illustrated in vertical section a protected metal building sheet of the general type illustrated in the Robertson patent above referred to wherein 10 represents a steel sheet; 12, 13, the layers of asbestos or other equivalent felt which are secured to the metal sheet by the interposed layers of bituminous material 15, 17. The felt layers may themselves be impregnated with an asphaltic or other bituminous material and the methods of manufacturing the protected metal product as thus far described may and preferably will comprise those now common in practice in the production of the type of protected metal building sheet shown in the Robertson patent above referred to.

In accordance with the present invention the felt layers impregnated with bituminous material are coated with a polymerizable resinous coating composition of the type above referred to, and after application thereof the resinous layer is subjected to treatment to effect polymerization thereof into a hard infusible resinous layer 16.

In Fig. 2 I have illustrated another form of protected metal sheet of the general type shown in the Coffman patent in which a steel sheet 20 is protected by a galvanized or equivalent coating 22 of fusible metal adhesive, and felt layers of asbestos or other felt are secured to the steel sheet by the interposed metal adhesive all as described in the Coffman patent above referred to. The felt layers 24 are impregnated with a bituminous impregnant and the resinous composition applied over the impregnated felt layers. After application of the resinous coating the sheet is subjected to treatment to effect rapid cure.

From the description thus far it will be observed that the present protected metal articles, and particularly protected metal building sheets either impregnated or coated with the present resinous coating composition lend themselves to the production of light-colored and light-surfaced protected metal articles and sheets. The hard infusible resinous layer or impregnant after curing provides a durable weather-resisting abrasion-resisting weather-proofing coating which will prevent bleeding of the underlying bituminous materials and serves to protect the underlying protective coatings and layers of the complete protected metal article or sheet when the same are exposed to weathering over long periods of time.

The addition of small amounts of cuprous oxide or of cuprous salts, preferably in a finely divided state, such as from 0.01% to 5% or more, so activates the peroxide catalyzed polymerization of the present resinous coatings that they polymerize readily at ordinary temperatures in a time which is easily adjusted to individual requirements by varying the amount of cuprous compound. This so-called "copper effect" extends the usefulness of the present invention to those applications where heating subsequent to application of the coating is difficult or impossible. The "copper effect" also enables the coating operation to be carried on either in the plant or in the field.

Having thus described the invention, what is claimed is:

1. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting a polymerizable liquid monomeric ethylenic - group - containing solvent for said bituminous material selected from the group consisting of allyl monomers, vinyl monomers and acrylic monomers, with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material, and any remainder being selected from the group consisting of aliphatic saturated dicarboxylic ester-forming materials, aromatic dicarboxylic ester-forming materials, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

2. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting styrene with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material, and any remainder being selected from the group consisting of aliphatic saturated dicarboxylic ester-forming materials, aromatic dicarboxylic ester-forming materials, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

3. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an inter-

posed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting a polymerizable liquid monomeric ethylenic-group-containing solvent for said bituminous material selected from the group consisting of styrene, dichlorostyrene, allyl esters including allyl maleate and allyl phthalate, ethyl acrylate and methyl methacrylate, with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material, and any remainder being selected from the group consisting of aliphatic saturated dicarboxylic ester-forming materials, aromatic dicarboxylic ester-forming materials, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

4. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting a polymerizable liquid monomeric ethylenic-group-containing solvent for said bituminous material selected from the group consisting of allyl monomers, vinyl monomers and acrylic monomers, with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material selected from the group consisting of maleic anhydride, maleic acid, fumaric acid, citraconic anhydride, citraconic acid and itaconic acid, and any remainder being selected from the group consisting of aliphatic saturated dicarboxylic ester-forming materials, aromatic dicarboxylic ester-forming materials, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

5. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting styrene with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material selected from the group consisting of maleic anhydride, maleic acid, fumaric acid, citraconic anhydride, citraconic acid and itaconic acid and any remainder being selected from the group consisting of aliphatic saturated dicarboxylic ester-forming materials, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

6. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting a polymerizable liquid monomeric ethylenic-group-containing solvent for said bituminous material selected from the group consisting of styrene, dichlorostyrene, allyl esters including allyl maleate and allyl phthalate, ethyl acrylate and methyl methacrylate, with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material selected from the group consisting of maleic anhydride, maleic acid, fumaric acid, citraconic anhydride, citraconic acid and itaconic acid, and any remainder being selected from the group consisting of aliphatic saturated dicarboxylic ester-forming materials, aromatic dicarboxylic ester-forming materials, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

7. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting a polymerizable liquid monomeric ethylenic-group-containing solvent for said bituminous material selected from the group consisting of allyl monomers, vinyl monomers and acrylic monomers, with a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material, and any remainder being selected from the group consisting of phthalic acid, phthalic anhydride, tetrachlorophthalic anhydride, succinic acid, adipic acid, azelaic acid and sebacic acid, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

8. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting styrene with

a polyester resin formed by reacting a glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material, and any remainder being selected from the group consisting of phthalic acid, phthalic anhydride, tetrachlorophthalic anhydride, succinic acid, adipic acid, azelaic acid and sebacic acid, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

9. As a new article of manufacture, a protected metal building sheet comprising a metal sheet, a layer of bituminous-bearing fibrous material covering a surface of the metal sheet, an interposed layer of adhesive bonding the fibrous layer to the metal sheet, and an outer weather-proofing coating applied over said fibrous material and comprising an insoluble and infusible layer bonded to the bituminous material carried by said fibrous layer, said coating comprising the resinous reaction product formed by reacting a polymerizable liquid monomeric ethylenic-group-containing solvent for said bituminous material selected from the group consisting of styrene, dichlorostyrene, ally esters, including allyl maleate and allyl phthalate, ethyl acrylate and methyl methacrylate, with a polyester resin formed by reacting a

glycol and an ester-forming dicarboxylic acid material, said material having at least 10 mol percent of an unsaturated alpha-beta-dicarboxylic acid material, and any remainder being selected from the group consisting of phthalic acid, phthalic anhydride, tetrachlorophthalic anhydride, succinic acid, adipic acid, azelaic acid and sebacic acid, and mixtures thereof, said coating being bonded to said bituminous material along a zone at their interface wherein said coating material and said bituminous material are co-mingled.

FRED G. SINGLETON.
PAUL W. JENKINS.

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The following references are of record in the file of this patent:

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1,887,681	Loetscher	Nov. 15, 1932
2,073,334	Coffman	Mar. 9, 1937
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