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PROCESS FOR PREPARING FIRE-RETARDANT BITUMINOUS SHINGLES BY COATING SAME WITH THERMOSETTING ACRYLIC RESIN

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This invention relates to bituminous surfacing materials. More particularly, this invention relates to flame-retardant bituminous shingles.

Specifically, the invention provides a process for preparing a highly flame-retardant bituminous roofing material which comprises applying a thin coating or overlay of an aqueous solution, suspension or dispersion of a thermosetting cross-linked resin, particularly an acrylic resin, to a bituminous-felt roofing material and then allowing the solvent, which is essentially water, to evaporate.

Prepared bituminous roofing is generally manufactured in large quantities by well-known processes which ordinarily comprise saturating a sheet material, such as felt, with a waterproofing saturant and then applying over the surface or surfaces thereof a coating layer of a bituminous material such as asphalt, pitch or tar, and preferably blown asphalt, after which a mineral surfacing in comminuted or granular form is partially embedded in said coating layer or layers.

In general, the felt is first thoroughly impregnated with a bituminous saturant by one of many procedures such as by passing the preformed web through a bath of the molten saturant. This saturated fabric is then coated with a bituminous coating composition by any of the usual methods. Before the roofing is cooled the conventional surfacing materials such as slate and sand granules are applied to the surface and partially embedded therein. The roofing material is then cooled by any of the means generally employed including water quenching. The roofing material thus fabricated is either cut up into shingle units or strip shingles, and in many instances is also prepared in the form of rolls of substantial length. These prepared shingles generally weigh between about 90 pounds and 300 pounds per 100 sq. ft., although weights outside such limits may be encountered. Of this weight about 25% to 40% is in the form of the mineral granules embedded in the bituminous coating material.

The mineral surfacing overlying the coating layer of the prepared roofing material so fabricated serves to protect to some extent the coating layer from the deteriorating action of heat, cold, rain, sun and fungus attack and functions, to a minor extent, to render the shingle fire-resistant, as well as to provide a decorative finish therefor.

Although the mineral surfacing embedded in the coating layer affords some protection, it frequently happens that the coating layer does not weather evenly and is deleteriously affected after exposure to the elements for a greater or lesser period of time. This granule loss thus not only depreciates the decorative effect of such shingles, but also renders the shingles less resistant to outdoor exposure. Further, and more importantly, whatever slight flame resistance the shingles possessed originally is quickly lost with the loss of granules.

It has now been found quite unexpectedly that these shortcomings have been greatly overcome by the process of the present invention. The bituminous shingles prepared in the instant invention which comprises applying a thin overlay of an aqueous solution of a thermosetting acrylic resin to previously prepared bituminous shingles, not only have excellent granule retention and thereby

greater resistance to weathering and a longer decorative life, but have unexpectedly outstanding flame-retardant properties.

In general, any of the bituminous roofing materials prepared by methods known to those skilled in the art are suitable for use in the present invention. Such roofing materials may consist of one or more plies of a fabric material, which may be paper or felt or both carrying an impregnating body of bituminous material.

The fibrous sheet base material is usually a roofing felt made of rag fiber, paper stock, asbestos fiber or other fibrous material, with or without suitable fillers well-known in the roofing art.

These felted fabrics are generally formed of rag or asbestos fibers, with or without additives, on a machine similar to that used for the manufacture of paper, as for example, the Fourdrinier paper making machine. Especially preferred felts are those designated rag or roofing felt in the roofing art. Roofing felt is oftentimes called "wool felt" although no roofing felt is composed entirely of wool fibers alone. In order to form a satisfactory sheet on a felt machine other fibers must be present to produce a strong, compact sheet that will not break on the calender rolls or driers and that will absorb the proper percentage of bituminous saturation afterwards. Current practice involves the use of rags, waste paper, defibered wood and sawdust as raw materials. Many alternative fibers have been suggested for the manufacture of roofing felts including, among others; organic fibers such as, for example, straw fibers, shredded bark of trees, coconut fibers, sea grass and seaweed, kelp, moss and peat, disintegrated leather, animal hair, kraft pulp, cotton rags, and the like; inorganic fibers such as slag wool or mineral wool, asbestos, glass wool, infusional lath, talc, clay and the like; and combinations of inorganic with organic fibers, such as, asbestos with rag fibers and asbestos with wood pulp.

Rag felt is generally marketed on the basis of its weight in pounds per 480 sq. ft., known as the "number," ranging from 17 to as high as 90. A high-grade rag felt will test about 1 mil in thickness per unit "number."

The rag felt may be treated to improve its fire resistance by treating it with various agents prior to its impregnation with the bituminous saturant. A great number of such inorganic fireproofing agents have been proposed and include sodium tungstate; borax; calcium borate; alum; soluble silicates; phosphates, such as ammonium-magnesium phosphate, sodium phosphate, zinc-ammonium phosphate and ammonium phosphate; calcium chloride; zinc chloride, either alone or with one or more of the following: borax, borax and ammonium bromide, ammonia and sodium silicate; titanium or zirconium sulfate; titanium and antimony oxides or chlorides; and Turkey-red oil.

Asbestos felt is made on substantially the same type of machine as rag felt and is generally composed of up to about 15% by weight of animal hair, cotton fibers and the like together with a binder, generally consisting of starch, paste, glue, dextrine, stearic acid or aluminum silicate. Asbestos felts are usually marketed on the basis of weight in pounds per 100 sq. ft., ranging from 6 to 50 pounds.

Occassionally woven fabrics are employed in the manufacture of prepared roofings and include burlap or hessian, drill, duck and osnaburg, among others. These are marketed in various weights, expressed in arbitrary ways. Woven fabrics do not take up as much bituminous saturant as the felted fabrics.

Bituminous materials suitable for impregnating felted or woven fabrics are usually soft in consistency at room temperature, ranging from semi-liquids to semi-solids.

These bituminous materials included both the asphaltic products and the tar products.

Suitable asphaltic products include the soft native asphalts, residual oils, soft residual asphalts, soft blown petroleum asphalts, pressure tars and soft sludge asphalts, fatty-acid pitch, sulfurized fatty-acid pitch wax tailings, and wool grease. Mixtures, such as asphalt fluxed with linseed oil, asphalt fluxed with mineral oil, asphalt containing a liquid silicone, and a mixture of gilsonite, petrolatum and a vegetable drying oil, have also been proposed.

Tar products include coal tar, water-gas tar, oil-gas tar, used either alone or in combination, or tempered to the proper consistency with the corresponding pitch obtained by distilling the tar to expel the highly volatile oils.

Currently, the saturants most commonly employed include soft coal-tar pitch, residual oil, soft residual asphalt and soft blown petroleum asphalt.

A bituminous material is then applied to the saturated fabrics. These bituminous materials not only functions as a surface coating in which mineral granules are later imbedded but also serve as adhesive compositions to cement two or more layers of fabric to manufacture multilayer sheets.

In general, these coating and adhesive compositions include the same groups of substances used for the saturant, but prepared of a harder consistency and usually of a higher fusing-point. Such bituminous materials include, among others, the native asphalts, sludge asphalts, residual asphalts, fatty-acid pitches, fluxed gilsonite and wurtzilite asphalt. Occasionally, vegetable or animal oils with or without sulfur have been added to increase the weatherproof properties.

Currently, the generally preferred bituminous coating and adhesive materials are the blown petroleum asphalts, with or without the addition of suitable fillers, such as slate flour, Fuller's earth, clay, chalk, talc, fly-ash, asbestos floats and the like.

A granular material is then embedded in the bituminous surfacing layer which is intended to be exposed to the weather by any suitable means, such as by impinging said granular material against the hot coated surface or by rolling.

In general, these inorganic surfacing materials are classified as fine mineral particles, moderately coarse mineral granules, and coarse mineral granules.

The fine mineral particles or dust is sifted on the surfacing while hot to prevent the convolutions of the roll from sticking together after it is wound up, or on the backs of shingles to prevent the adjacent layers from sticking together in the package. Suitable such fine materials include the uncolored particles, such as ground talc, mica, silica, insoluble silicates, slate flour, limestone, ground ashes and granular cork and colored particles such as flake graphite, mineral pigments, aluminum powder, metal flakes, iron filings, and the like.

The moderately coarse mineral granules are embedded on one side only of the surface coating for both decorative effect as well as for weatherability and are practically free from fines and generally consist of uniformly sized particles, preferably angular, and may be colored or uncolored. Suitable granules include coarsely ground talc, mica flakes, sand, quartz, marble, dolomite, slate, greenstone, serpentine, colored river sand, crushed brick or tile, glass, slags, clays and silicates.

Coarse granules are similarly embedded in the surface coating for decorative effects (commonly termed No. 9 granules), and may be colored or uncolored. Suitable such granules include small pebbles or gravel, crushed granite, granulated coke, crushed sea shells, coarse slate, and granulated slag.

Occasionally organic surfacings are employed and include, wood flour, sawdust, granulated cork, granulated straw and the like and are embedded in the surface coating while hot.

The bitminous shingles may contain other substances and additives such as pigments, waterproofing agents, and fungicides. Fungicides generally employed are the fungotoxic mineral salts such as copper oleate, copper resinate, copper compounds of the naphthenic acids from petroleum refining, copper compounds of carboxylic and cresylic acids, and other copper compounds as well as the respective zinc compounds and the chlorides, bromides, iodides, sulfocyanides of arsenic and antimony.

It is understood that the above discussion relating to the manufacture of bituminous shingles is not deemed to limit the instant invention, but such disclosure is by way of information and background only, since bituminous roofing materials from whatever process manufactured are suitable for use in the present invention. For a more complete discussion of the manufacture of bituminous roofing materials see "Asphalts and Allied Substances," H. Abraham, sixth edition, volume three, chapter 7, D. Van Nostrand Company, Incorporated.

The thermosetting cross-linked remains suitable for use in the present invention include, among others; polyurethane resins, particularly the polyurethane varnishes; polyesters; polyepoxides, including the polyethers, polyesters and other polyepoxy condensates; and acrylic resins.

In general, cross-linked resins are water insoluble, therefore, it is necessary to water solubilize such resins by reacting with ammonium hydroxide to obtain the water-soluble salts thereof. Any other conventional techniques for water solubilizing such resins are suitable.

Very suitable are the thermosetting acrylic resins. Particularly preferred acrylic resins comprise the water soluble acrylic polymers which generally comprise (1) an ammonium salt of a copolymer of an alpha,beta-ethylenically unsaturated carboxylic acid and an alkyl ester of an alpha-beta ethylenically unsaturated monocarboxylic acid and (2) a cross-linking agent. Occasionally, other polymerizable vinylidene monomers containing $CH_2{=}C<$ groups are copolymerized therewith.

Suitable cross-linking agents are water soluble, or at least water dispersable, and include, among others, epoxy compounds such as glycidyl acrylate, glycidyl methacrylate and the like; amides such as acrylamide, methacrylamide and the like; and melamines, particularly the water soluble polymethylol melamines.

Very suitable polymethylol melamines comprise the polymethyl ethers of polymethylol melamines and include the dimethyl ether, the trimethyl ether, the tetramethyl ether, the pentamethyl ether, and the hexamethyl ether of polymethylol melamines. In general, the polymethylol amines are prepared by known methods wherein at least 2 moles of formaldehyde is reacted with 1 mol of melamine.

The water soluble acrylic copolymers may be suitably prepared by first reacting an alpha,beta-ethylenically unsaturated carboxylic acid and an alkyl ester of an alpha, beta-ethylenically unsaturated monocarboxylic acid, and then reacting this copolymer with ammonium hydroxide to render the polymer water soluble.

Suitable monocarboxylic acids include, among others, acrylic, methacrylic, cinnamic and crotonic acid. Suitable polycarboxylic acids include, maleic, fumaric, itaconic, citraconic, aconic, mesaconic as well as the halogenated acids such as chloromaleic acid. The carboxylic acids may be used alone or in combination and in lieu thereof their anhydrides may be employed.

Suitable alkyl esters of the alpha,beta-unsaturated monocarboxylic acid are methylacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, decyl acrylate, lauryl acrylate, ethyl methacrylate, butyl methacrylate, heptyl methacrylate, decyl methacrylate, propyl crotonate, butyl crotonate and the like. These alkyl esters may be employed alone or as mixtures thereof.

Other polymerizable vinylidene monomers containing $CH_2{=}C<$ groups which may be used with the acids and

alkyl esters include, among others, styrene, alkyl-substituted styrenes, chloro-substituted styrenes, vinyl naphthalene, acrylonitrile, methacrylonitrile, acrylamide, mehacrylamide and the like.

As noted above, the copolymer is rendered water-soluble by reacting with ammonium hydroxide by known means in generally equivalent amounts, although an excess of ammonium hydroxide may be employed.

In general, one may employ from about 10% to 50% by weight of the cross-linking agent and from about 50% to 90% by weight of the water-soluble copolymer.

A more detailed description of the preparation of suitable water-soluble thermosetting acrylic resins can be found in U.S. Patent 2,906,724, issued September 29, 1959.

Preferred water-soluble thermosetting acrylic resins are those marketed by Rohm & Haas under the trade name of "Acrysol," particularly Acrysol 2003 and Acrysol 2004. Acrysol 2003 is especially preferred due to the generally decreased amount required and the generally greater fire resistance imparted to the shingles. Acrysol 2003 has a solids content of about 36% and the solvent portion (64%) contains 90% water and 10% tertiary-butanol, a viscosity of from about 3000 to 6000 c.p.s. and an approximate pH of 9.1.

The thermosetting resin is applied as an aqueous solution, or substantially aqueous. The solvent medium comprises a greater proportion of water, that is, generally greater than 90%. Other solvents which may or may not be employed in addition to the water present include such solvents as, for example, methyl Cellosolve, ethyl Cellosolve, butyl Cellosolve, and t-butanol.

The thermosetting resin may be applied to the bituminous shingle by any suitable means such as by dipping, spraying, painting and the like. If the thermosetting resin is applied in manufacture, it is generally preferable to spray onto the continuous web or belt of hot roofing material. A distinct advantage is that these thermosetting resins may be conveniently and economically applied to a finished roof by roofing contractors or by the individual via any suitable means such as brush, roller, spray gun, mop or broom.

In general, the thermosetting resin is applied in amounts greater than about 3 grams per square foot of roofing surface. Although this amount will vary somewhat depending upon the particular thermosetting resin utilized, a generally suitable range was found to be between about 5 and 10 grams per square foot of roofing surface. Amounts in excess of this range may be occasionally used; however, economics usually dictate against the use of excess amounts. The resin is applied by any of the above-noted means and the water is allowed to evaporate leaving a cross-linked surface coating. If the thermosetting resin is applied in the manufacture of the roofing materials it may be desirable to apply heat to said coating as by baking at 200–300° F. from 15 to 30 minutes to facilitate evaporation and curing.

It has been observed that when bituminous roofing materials, herein sometimes referred to as asphalt shingles for convenience, are subjected to a flame, the asphalt becomes fluid and runs down into the flame thus perpetuating the fire. In other words, in an untreated shingle the flame progresses as islands of granules break loose and allow the molten asphalt to flow downwards thus "feeding" the flame.

In an experiment to determine the relative temperatures on an asphalt shingle, an untreated asphalt shingle was placed on an inclined plane having a slope of 5 inches per foot and a Bunsen burner flame applied to the lower end of the shingle. At the edge of the flame the surface temperature ranged from about 600° to 700° F. About one-eighth of an inch from the flame, the surface temperature was about 450° F. and about one inch ahead of the flame, the surface temperature was approximately 250° F. Between this point and the flame, the asphalt was very fluid and ran into the fire. This fire sustaining property is of course undesirable.

It was further discovered that if a thermosetting film was applied to the asphalt shingle, said coating had sufficient film strength to prevent this observed flame spread and thus rendered the asphalt shingle flame resistant, or at least, flame retardant. Based upon the burning phenomena observed when the untreated shingle was exposed to a gas flame, a temperature of 600° F. was selected as a temperature at which the film strength should be determined. In other words, if a film had sufficient strength to hold the granules together at 600° F., the flame couldn't spread since the temperature drops off to less than 600° F. at a distance of one granule diameter from the flame.

The invention is illustrated by the following examples. The components, their proportions and other specific embodiments are presented as typical, and various modifications can be made in view of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or of the claims.

EXAMPLE I

This example describes the technique of determining the minimum coverage by the film strength and illustrates the flame retardant properties of a representative thermosetting resin. Film specimens 2¼ inches long, ⅞ inch wide and from 0.003 to 0.012 inch thick were prepared. Aluminum specimen clamps were attached to the ends of the specimen and the specimen suspended in an electric furnace at 600° F. with various weights attached to the lower end. The film strength of the particular film was then determined as pounds per square inch, static load.

One-half of an asphalt shingle specimen 8" by 12" was coated with various thermosetting materials. The other one-half (4" x 12") was untreated and used for control. This prepared shingle specimen was then supported on a wire mesh screen (1" mesh, approximately 3/32" diameter wire) at a slope of 5 inches per foot. A Fischer or Bunsen burner flame was then applied to the lower end of the asphalt specimen. The amount of thermosetting resin which provided flame-retardant properties was noted. By flame retardant it is meant that the flame is extinquished shorly after the initial burning. In other words, the fire is non-sustaining due to the non-flow downwards of the melted asphalt. In every instance the flame progressed up the shingle and continued to burn the untreated asphalt portion.

From the static loading tests, coverages, and performances of the materials in the above-noted burning test, it was found that the film must have a strength at 600° F. of approximately 0.02 pound/lineal inch or greater. The film thickness required in order to achieve this 0.02 pound/lineal inch film strength can be readily calculated from the strength at 600° F. under static loading. This will then give the minimum coverage of the particular thermosetting resin.

Using the above-described technique and methods, one-half of a Pabco, 230 lb., three-tab asphalt shingle was treated with Acrysol 2003 (a thermosetting acrylic resin in water solution, containing 36% solids, 10% t-butanol in the aqueous solvent, an average viscosity of approximately 5000 cp., and sold by Rohm & Haas Company) so that a coverage of 6.0 grams of said polymer per square foot of shingle was obtained. The treated portion of the shingle exhibited excellent flame retardation whereas the untreated portion continued to burn when the initiating flame was removed. The tensile strength of the polymer at 6.0 grams per square foot and at 600° F. was in excess of 8.6 p.s.i. Thus, a thin overlay of the acrylic polymer applied to the surface of the asphalt shingle renders the shingle fire retardant by preventing the asphalt flow thereby extinguishing the flame. In the untreated shingle, the asphalt flows down into the flame and continues to supply fuel to the flame. In addition to the fire resistance properties the weathering life of the

treated portion of the shingle was considerably improved due to greater granule retention.

EXAMPLE II

The procedure in Example I was substantially repeated wherein the thermosetting cross-linked resin employed was Acrysol 2004 (an acrylic resin in water solution having a solids content of 36% containing about 5% butyl Cellosolve in the aqueous solvent, a viscosity of about 8000 cp., and manufactured by Rohm & Haas). Excellent flame retardant properties were obtained when the coverage was approximately 10.0 grams per square foot.

EXAMPLE III

The procedure of Example I was essentially repeated wherein the polymer was an epoxy ester paint. Similar improved fire resistance was exhibited by the treated shingle.

EXAMPLE IV

The procedure of Example I is essentially repeated wherein the polymer was an acrylic baking enamel (Armorcote, manufactured by Cook Paint and Varnish Co.). Similar improved fire resistance was exhibited by the treated shingle.

EXAMPLE V

The procedure of Example I is essentially repeated using a polyepoxide/trimer acid emulsion. Related improved fire resistance is observed.

EXAMPLE VI

Into a suitable reaction vessel 65 parts of dioxane is introduced and heated to reflux temperature. Thereupon a mixture of 65 parts of butyl acrylate, 10 parts acrylic acid and 1 part styrene is added incrementally over a two-hour period. Concurrently under the same incremental conditions, 6.0 parts of cumene hydroperoxide is

added. The reaction is refluxed for an additional 6 hours. The dioxane is then stripped off leaving a clear viscous terpolymer. The resulting terpolymer is then treated with dilute ammonium hydroxide to render the polymer water soluble.

Approximately 50 parts of a 20% ammonium hydroxide solution of the above polymer is mixed with 5 parts of methacrylamide.

The resulting polymer solution is then applied to an asphalt shingle as in Example I at a coverage of about 10 grams per square foot. Improved fire retardant properties are observed.

I claim as my invention:

1. A process for preparing flame-retardant bituminous roofing material which comprises applying a coating of a substantially aqueous solution of a thermosetting acrylic resin to a bituminous-felt roofing material and then evaporating said solvent.

2. A process as in claim 1 wherein the solvent evaporation is effected by baking the coated material at 200° to 300° F.

3. A process as in claim 1 wherein the coating is applied in amounts from about 5 to 10 grams per square foot of bituminous material.

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