High vinylidene chloride copolymer seal coat

Color coat and wear layer

Oleoresinous layer

Asphalt impregnated felt

Filled paint backing

INVENTORS
George William Stanton
Thomas C. Spence

BY
Sterns, & Burdick
ATTORNEYS
APPLIANCE, IMPREGNATED LINOI'EUM-TYPE ARTICLES AND METHOD OF MAKING SAME

George William Stanton, Walnut Creek, and Thomas C. Spence, Concord, Calif., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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This invention relates to an improvement in floor or wall coverings of the linoleum type, having an asphalt-impregnated fibrous base. It relates in particular to such articles in which a felt or other fibrous base is impregnated with asphalt, one side of the coated sheet is leveled with an oleoresinous coat, and the latter, after being dried, is coated with a pigmented wear layer or color coat for the pigmented surface coating commonly carries a distinctive color pattern. When the asphalt employed is of western (e.g., California) origin, it has been undesirable to use an oleoresinous coating because of the strong tendency for fractions of the asphalt to bleed through the oleoresinous layer, causing objectionable and unsightly discoloration in the color coat. Such discoloration becomes apparent before the manufacturing process is complete, as the bleeding is accelerated by the heat employed to speed the drying or curing of the composite article. At temperatures above 150° F. the oleoresinous leveling coat has been made impractical because they are all sensitive to water and, even if some of them show initial adhesion to the oleoresinous layer or the underlying pigmented coats, they fail in storage or service when exposed to moisture. It has also been proposed to use a styrene-butadiene synthetic rubberlike copolymer as a seal between the color or wear layer and the oleoresinous layer, and, while this has given some degree of success with rubber and imported asphalts, it has been unsuccessful with asphalts from the western states.

It is the principal object of the present invention to provide linoleum-type linoleum articles which will adhere to an oleoresinous coating over western asphalt impregnated fibrous base and to an underlying pigment-coated wear layer, even in damp service, with a color coat of asphalt impregnated felt, thereby avoiding discoloration by the asphalt. A related object is to provide a linoleum-type article, based on western asphalt impregnated felt, or the like, in which the color coating may be of white or pastel shades without danger that the asphalt will strike through and discolor the outer coatings.

It has now been found that the prior difficulties can be avoided, and the foregoing objects may be realized, by applying over the oleoresinous coat and under the color or wear coat, a continuous coating of a film forming composition, the solids portion of which consists chiefly of a copolymer in which vinylidene chloride is a characterizing copolymerized constituent. Such copolymers include the binary and ternary copolymers of 70 or more per cent by weight of vinylidene chloride, the balance being one or two monomerically unsaturated compounds such as vinyl chloride, vinyl acetate, acrylonitrile, and the alkyl (1 to 8 carbon atoms) acrylates and methacrylates. All such copolymers are inert to the action of drying oils and other linoleum raw materials at the temperatures employed in making linoleum. The copolymers may be applied as a solvent-coat coating over the oleoresinous leveling layer, but it is preferable to apply them as a aqueous latex-like emulsion of those vinylidene chloride copolymers whose latices deposit a continuous, oil impervious film. After the first copolymer coat is dried, a second such coat may be applied, if desired, to cover and seal any "pinholes" in the first coat. Over the dried sealing coat or color coat of copolymer there is applied the wear layer, which may also be a color coat. The wear layers most commonly used are long oil paints or enamels or they may be asphalt impregnated vinyl resin organosols or plastisols. Whatever the nature of the wear layer, the seal coat of vinylidene chloride copolymer protects it from discoloration due to asphalt bleeding, and white or pastel shades can be used safely in such surface coatings.

When the seal coat of the present invention is a latex-like emulsion of a vinylidene chloride copolymer, it is preferred to modify the normal latex-like emulsion by dispersing therein a water dispersible protein such as casein or soya protein, or a hydrophilic cellulose ether such as methyl or hydroxethyl cellulose, in amounts from 0.1 to 15 per cent of the weight of the dispersed polymer. These agents aid the cohesion between the deposited copolymer film and the underlying oleoresinous layer. They are not necessary, and are omitted when the oleoresinous layer contains an emulsifiable asphalt. Thus, coatings as light as 0.5 to 5 pounds of copolymer over an area of 100 square yards are capable of effecting the desired result. It is preferable to apply two successive thin coats of the copolymer rather than a thicker coat, as the possibility of pinholes in a double coat is materially less than in any single coat.

The following examples illustrate the practice of the invention. In all the tests reported in the examples there was used a commercial asphalt-impregnated felt, made from western asphalt, having a highly filled paint backing coat and a commercial and highly filled 0.001 inch thick and the 0.0016 inch thick, with intervening and subsequent curing treatment to dry the oil in the film. In such case, the seal coat was applied to samples 3.5 inches wide and 12 inches long, at the reported rate and the resulting assembly was dried. There was then applied a white pigmented enamel color coat at a wet thickness of 0.012 inch. The color coat, when dried, was about 0.008 inch thick. The effectiveness of the seal coat as an asphalt barrier was determined by subjecting the article to temperatures of 60° C. in a circular oven for 48 hours. This is a normal treatment in the manufacture of linoleum products, or is the equivalent of a shorter curing treatment at slightly lower temperatures at the end of this curing period any defects in the product are readily observable, including any surface discoloration due to migration of asphalt fractions or any separation of the color coat. The water-resistance of the color coat is made after the heat treatment and after flexing a sample of the product at room temperature from 5 to 10 times through an angle of about 90 degrees with a bending radius of about 1 inch. It is then attempted to peel the color coat from the article, first on the dry article, then on a water-soaked sample, then on a redried sample. The results are rated according to an arbitrary numerical scale, perfect adhesion being rated as 1, and complete failure at 5. Ratings from 1 to 3 are considered satisfactory for commercial use.

The effectiveness of the seal coat as a barrier aginst asphalt staining is rated by a visual or mirror-indexical method in which an unstained product is rated at 1, a product with 1 to 2 small stains is rated 2, and a product with 8 small stains, or with any massive stains, in the 42 square inch area of the sample, is rated not more than 2. Ratings of 1 or 2 are acceptable in a commercial product. The examples merely identify the sealing composition and the method in which it was applied, and comparative tests of the products are tabulated after the examples.

EXAMPLE 1

The seal coat was applied as two successive layers at a total weight of about 3 pounds of polymer solids per 100 square yards, the first layer being air dried before the second was applied. The coating composition was an aqueous emulsion initially containing 50 per cent by weight of the ternary copolymer of 90 per cent vinylidene
chloride, 3 per cent acrylonitrile and 7 per cent ethyl acrylate, the latex having been diluted with water to 26 per cent solids before use.

**EXAMPLE 2**

The coating procedure was that of Example 1, and the coating composition was the same except that 0.1 per cent, based on the weight of polymer solids, of hydroxyethyl cellulose was dissolved in the aqueous phase of the emulsion.

**EXAMPLE 3**

The coating method was that of the prior examples. The composition employed was an aqueous emulsion containing 50 per cent by weight of a copolymer made from 85 per cent vinylidene chloride and 15 per cent acrylonitrile, containing 20 per cent as much dibutyl phthalate plasticizer as the amount of copolymer and 0.2 per cent of a water-soluble alkyd resin, based on the weight of polymer solids.

**EXAMPLE 4**

The procedure of Example 1 was used, and the copolymer emulsion was modified by dispersion therein of one of the following: (a) 5 per cent casein; (b) 10 per cent casein; (c) 9 per cent alphaprotein; (d) 5 per cent corn protein; (e) 5 per cent soya protein; (f) 5 per cent water-soluble urea-formaldehyde resin.

**EXAMPLE 5**

A dried and powdered copolymer made from 85 per cent vinylidene chloride and 15 per cent acrylonitrile was dissolved to form a 20 per cent solution in methyl ethyl ketone. This was applied at a coating weight (solids basis) of 1.3 pounds per 100 square yards, and the solvent was evaporated before applying the color coat.

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Asphalt Sealing Rating</th>
<th>Adhesion Rating</th>
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It is observed that best results are obtained when a water-dispersible protein or a water-dispersible resin or hydrophilic colloid is present in the aqueous phase of the copolymer emulsions employed. Such agents are not helpful when copolymer lacquers are used to deposit the seal coat.

Numerous other tests have shown the general utility for the present purpose of copolymers of vinylidene chloride, which, by virtue of their high vinylidene chloride content (at least 70 per cent), are impervious to the usual staining fractions of asphalt, especially to western asphalt. If applied from aqueous emulsion, the emulsion should be capable of depositing a continuous film. This is possible with many vinylidene chloride copolymers in their unmodified condition, and with the others when 10 to 20 per cent plasticizer is dispersed in the emulsion, as is well known. Thus, plasticized emulsions of a copolymer of 85 per cent vinylidene chloride and 15 per cent vinyl chloride, or an unplasticized emulsion of a copolymer of 85 per cent vinylidene chloride and 15 per cent ethyl acrylate may be used with about equivalent sealing effect. Unplasticized copolymers of 70 to 77 per cent vinylidene chloride and 30 to 23 per cent vinyl chloride, when made in emulsion, form continuous films which may be used in the present invention.

The invention finds its greatest utility in those linoleum articles which have white or light colors in their wear layer, but is useful also in avoiding changes in color of darker pigmented coatings. While a seal coat which will prevent bleeding of other asphalt may not be suitable with western asphalt, the seal coats of this invention will prevent staining by any asphalt used in linoleum manufacture. Since the color coat or wear layer in most linoleum is either an enamel or paint with a vegetable oil vehicle or is a synthetic resin or polymer plastisol, and since all such coats are capable of absorbing and dispersing the discoloring fractions of asphalt, the precise nature of the wear layer is not critical to the invention. Similarly, since the various drying oil compositions used in leveling and bodying a linoleum structure are all penetrable by the discoloring constituents of asphalts, the identity of such oleoresinous layer is not critical to the invention.

The new article of the present invention is illustrated in cross-section in the single figure of the accompanying drawing.

We claim:
1. A linoleum type article comprising an asphalt impregnated fibrous sheet and having thereon a wear layer which is compatible with discoloring fractions of asphalt and comprises a material from the class consisting of oil base paints and enamels and synthetic resin and polymer plastisols, the improvement which consists in interposing between the asphalt impregnated sheet and the wear layer a sealing coat consisting essentially of a continuous deposit of a water-dispersible resin or plastisols from 1 to 8 carbon atoms in the alkyl group.
2. The article claimed in claim 1, wherein the said sealing coat is interposed between the wear layer and an oleoresinous leveling coat which is immediately over the asphalt impregnated fibrous sheet.
3. The article claimed in claim 1, wherein the asphalt is a Western asphalt.
4. The article claimed in claim 1, wherein the wear layer contains light colors, easily discolored by asphalt constituents.
5. The article claimed in claim 1, wherein the sealing coat consists essentially of a copolymer of about 90 per cent vinylidene chloride, about 3 per cent acrylonitrile and the balance ethyl acrylate.
6. The article claimed in claim 1, wherein the sealing coat consists essentially of a copolymer of about 85 per cent vinylidene chloride and complementarily about 15 per cent acrylonitrile.
7. The article claimed in claim 1, wherein the sealing coat contains, in addition to the copolymer, from 0.1 to 15 per cent of a water-dispersible protein adhesive.
8. The article claimed in claim 1, wherein the sealing coat contains, in addition to the copolymer, about 10 per cent of casein.
9. The article claimed in claim 1, wherein the sealing coat contains, in addition to the copolymer, about 5 per cent of a water-soluble urea-formaldehyde resin.
10. The article claimed in claim 1, wherein the copolymeric sealing coat represents from 5 to 50 pounds of copolymer per 100 square yards of the article.
11. In a method of making a linoleum type article, the improvement which consists in depositing over an oleoresinous level coated asphalt impregnated fibrous base a continuous coating of a copolymer containing at least 70 per cent vinylidene chloride, the balance of the copolymer being composed of 1 to 2 compounds from the group consisting of vinyl chloride, vinyl acetate, acrylonitrile, and the alkyl esters of acrylic and methacrylic acid containing 1 to 8 carbon atoms in the alkyl group, drying said coating, and applying the wear layer over the copolymer coat, said wear layer being one which is compatible with discoloring fractions of asphalt and comprises a material from the group consisting of oil base paints and enamels and synthetic resin and polymer plastisols.
12. The method claimed in claim 11, wherein the copolymer coat is deposited from a film-forming emulsion of the copolymer.
13. The method claimed in claim 11, wherein the copolymer coat is applied at a rate to leave from 1.5 to 3 pounds of copolymer per 100 square yards of the article.

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