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(54) **PAVEMENT MARKINGS COMPRISING SYNTHETIC POLYMERIC FIBERS**

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(57) **ABSTRACT**

The invention relates to thermoplastic pavement marking compositions comprising synthetic polymeric fibers.

PAVEMENT MARKINGS COMPRISING SYNTHETIC POLYMERIC FIBERS

RELATED APPLICATIONS

[0001] This application claims priority from U.S. provisional patent application serial No. 60/325279 filed Sep. 27, 2001 and U.S. patent application Ser. No. 10/078771 filed Feb. 18, 2002.

FIELD OF THE INVENTION

[0002] The invention relates to thermoplastic pavement marking compositions comprising synthetic polymeric fibers.

BACKGROUND OF THE INVENTION

[0003] Pavement markings are typically used to delineate the boundaries for lanes of traffic on a roadway. The marking may extend continuously, such as along the outermost boundaries of the driving lanes, or intermittently, such as between lanes.

[0004] U.S. Pat. No. 4,490,432 relates to a pavement-marking sheet material which comprises a non-crosslinked elastomeric precursor such as acrylonitrile-butadiene polymer; a thermoplastic polymer such as polyethylene which reinforces the sheet material, e.g., by orientation of the thermoplastic polymer so that the calendered product exhibits greater strength downweb than crossweb; and a particulate inorganic filler, which preferably includes platelet-type fillers such as talc, mica, or magnesium silicate.

[0005] U.S. Pat. No. 5,194,113 (Lasch et al.) relates to thermoplastic-based pavement marking sheets. The marking sheets employ a conformant composite material including: polyolefin a nonreinforcing mineral particulate; and/or a thermoplastic upper surface. Preferably, the sheet's thermoplastic upper surface is embedded with reflective elements and/or skid-resistant particles. A solventless process of embedding particles in thermoplastic pavement marking sheets is disclosed. Processes for preparing marking sheets are also disclosed. Conformant pavement marking sheets which may be applied in cooler conditions are also disclosed.

[0006] Thermoplastic pavement marking materials are 100% solids compounds typically containing a thermoplastic polymeric material, pigments, filler and glass spheres. Hot-applied thermoplastic is prepared for road deposition in a melting apparatus where granular or block material is introduced and heated until the material liquefies at temperatures in excess of 400° F. (204° C.). Alkyd thermoplastics tend to be preferred over hydrocarbon thermoplastic compositions in view of such compositions being oil impervious. Thermoplastic pavement markings have had limited commercial success in cold climates due to the tendency of such markings to shatter from the roadway upon impact with a snowplow.

SUMMARY OF THE INVENTION

[0007] It has since been discovered that pavement marking sheets having a greater strength in one direction (e.g. downweb) versus the other direction (e.g. crossweb) tend to result in reduced conformability and reduced shear strength. Accordingly, industry would find advantage in pavement marking compositions that exhibit a similar downweb and crossweb tear. Further, industry would also find advantage is thermoplastic pavement markings having improved cold temperature performance.

[0008] The Applicants have discovered that thermoplastic pavement markings can be improved by the addition of synthetic polymeric fibers.

[0009] In one embodiment the invention relates to a pavement marking composition comprising synthetic polymeric fibers dispersed within a thermoplastic-based polymeric material. The synthetic polymeric fibers have a melt point greater than the polymeric material such that the fibers retain their fiber form.

[0010] In another embodiment the invention relates to a method of making a pavement marking comprising providing a composition comprising a thermoplastic-based polymeric material and synthetic polymeric fibers, heating the composition to a temperature wherein the composition is extrudeable and the synthetic polymeric fibers are unmelted; and extruding the composition on a pavement surface.

[0011] In another embodiment the invention relates to a method of making a pavement marking comprising dry blending a thermoplastic polymer and synthetic polymeric fibers, melting and mixing the blend; and extruding the blend onto a pavement surface at a temperature less than the melt point of the synthetic polymeric fibers. In each of these embodiments, the fibers are preferably randomly dispersed within the polymeric material throughout the sheet. Preferred polymeric fiber materials typically have a melt point greater than about 400° F. (204° C.) such as in the case of polyester, polyamide, polypropylene and tetrafluoroethylene. In a preferred embodiment the marking composition is sufficiently conformable such that the downweb direction and crossweb direction has a tear ratio ranging from about 0.7 to 1.3 when measured according to ASTM 1938. In another preferred embodiment that composition exhibits good cold temperature properties such that the composition does not shatter into pieces upon impact at cold temperatures. The amount of synthetic polymeric fibers preferably ranges from about 0.2 weight-% to about 2 weight-%. The composition optionally comprises other ingredients selected from the group comprising reflective elements, extender resins, fillers (e.g. magnetic fillers), and pigments. The synthetic polymeric fibers preferably have a fiber length of at least 6 mm.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] The pavement marking composition of the invention comprises synthetic polymeric fibers incorporated into a thermoplastic polymeric material. The synthetic polymeric fibers may be thermoplastic or thermosetting. If the synthetic polymeric fibers are comprised of a thermoplastic material, such material has a melt point greater than the thermoplastic polymeric material the fibers are incorporated within. This insures, that the synthetic polymeric fibers do not substantially melt and thus retain their fiber form. Thus, the synthetic polymeric fibers are dispersed randomly three-dimensionally throughout the polymeric material in the finished marking.

[0013] The composition of the synthetic polymeric fibers is chosen based on the melt point of the intended thermoplastic-based polymeric material and/or the intended processing temperature. Typically, thermoplastic-based polymeric materials have a softening point or melt point ranging from about 240° F. (116° C.) to about 450° F. (232° C.). For improved cold temperature properties, it is surmised to employ synthetic polymeric fibers that don't fracture at cold temperatures such as fibers comprised of a material having a low glass transition temperature (Tg) as measured according to Diffferential Scanning Calorimetry (DSC). For moderate climates, the Tg of the synthetic polymer fiber material is preferably less than 30° F. (−1° C.), for colder climates, the Tg is preferably less than 0° (−18° C.), for even colder climate the Tg is preferably less than −20° F. (−29° C.), and more preferably less than −40° F. (−40° C.).

[**0014**] Suitable synthetic polymeric fiber materials include such polymers as polyolefins, vinyl copolymers, polyethers (e.g. polyamides), polyacrylates (i.e. acrylic polymers), styrene-acrylonitrile copolymers, polyesters, polyurethanes, tetrafluoroethylene, and copolymers thereof. The synthetic polymeric fiber is preferably comprised of polyester, polypropylene, tetrafluoroethylene, and copolymers thereof. Although the fiber length may range from about 3 mm to 40 mm, the synthetic polymeric fibers preferably have a fiber length of at least 6 mm (6000 microns, 0.24") and more preferably a length of at least 10 mm.

[**0015**] The pavement marking composition comprising the synthetic polymeric fibers within a polymeric material in combination with other optional ingredients such as retroreflective elements (e.g. glass beads), filler, pigment, etc. preferably exhibits certain properties. In one aspect the pavement marking composition is conformable. The ability of the marker to conform to gross defects, such as deep cracks or other depressions commonly present on a pavement surface, can provide a substantial durability advantage over preformed adhesive tapes. In general, the composition of the invention has a downweb and crossweb tear strength of at least 2.5 kilograms per square centimeter at 25° C. when measured according to ASTM 1938. Further, the ratio of the downweb average tear strength of the pavement marking sheet to crossweb tear strength preferably ranges from 0.5 to 2 and more preferably ranges from 0.7 to about 1.3.

[**0016**] Alternatively or in addition thereto, the pavement marking exhibits improved cold temperature properties. The cold temperature properties can be evaluated by extruding the composition into a 4 inch wide (101 mm) strip having a thickness of 1 to 2 mm. The sheet can then be conditioned at the temperature of interest for 4 hours. Immediately after removing the sheet from the conditioning chamber the sheet is struck with a hammer. Poor cold temperature properties is indicated by the sheet breaking into pieces. Good cold temperature properties is indicated by the sheet remaining intact in a single piece, although cracking may be evident. Upon inspection one can typically see the fibers in the cracks.

[**0017**] The pavement marking composition generally comprises at least 0.1 weight-% synthetic polymeric fiber, but no more than about 20 weight-%. Typically, the amount of synthetic polymeric fiber is less than 10 weight-%, preferably less than 5 weight-% and more preferably less than 2 weight-%, and even more preferably about 1 weight-% or less. The amount of synthetic polymeric fiber is preferably at least 0.2 weight-% and more preferably at least about 0.3 weight-%. The amount of polymeric material preferably ranges from about 10 weight-% to about 85 weight-%. The pavement marking composition may optionally comprise up to about 75 weight-% of other ingredients selected from reflective elements (e,g, glass beads), extender resins, fillers and pigment. Further, in addition to the synthetic polymeric fibers, the pavement marking composition may further comprise other fibers such as inorganic fiber or other synthetic polymeric fibers, provided the presence of such does not detract from the intended properties. Preferably, the pavement marking composition is free of glass fibers.

[**0018**] The thermoplastic polymeric material provides a viscoelastic character, which permits absorption of the forces and pressures of wheeled road traffic without creating internal forces that tend to remove the marking from the roadway. Typically, a hydrocarbon or alkyd thermoplastic material is employed. Preferred hydrocarbon thermoplastic materials include acid containing ethylene copolymers. Representative acid containing ethylene copolymers include ethylene acrylic acid (EAA) copolymers and ethylene methacrylic acid (EMAA) copolymers, and mixtures of EAA and EMAA; as well as ionically cross-linked EMAA. Alternative thermoplastic materials, although less preferred for the topmost layer, include ethylene n-butyl acrylate (EnBA), ethylene vinyl acetate (EVA) and blends thereof, as well as polyolefins. Particularly preferred thermoplastic materials include EMAA polymer commercially available from the E. I. Dupont de Nemours and Company (Dupont) of Wilmington, Del. under the trade designation "NUCREL" and ionically cross-linked ethylene methacrylic acid (EMAA) ionomers available from Dupont under the trade designation "Surlyn". Other suitable thermoplastic materials suitable for thermoplastic pavement markings as described in U.S. Pat. No. 6,217,252 (Tolliver); incorporated herein by reference. Although this reference relates to flame-sprayed pavement markings, the polymeric materials (i.e. binders) described therein would also be suitable for conventional thermoplastic-based pavement marking applications methods. Polymeric materials described therein include acrylic polymers and copolymers, olefin polymers and copolymers preferably having a number average molecular weight greater than about 10,000, urethane polymers and copolymers, curable epoxy resins, ester polymers and copolymers, and blends thereof. For improved cold temperature performance, it is surmised that the pavement marking is based on a thermoplastic material having a low glass transition temperature as previously described with regard to the fiber material.

[**0019**] Fillers are generally included in the composition at least for the purpose of enhancing the visibility of the exposed top layer. However, fillers also advantageously enhance properties such as reinforcement, extending, surface hardness, and abrasion resistance. Platelet fillers, i.e., fillers having a plate-like shape, such as magnesium silicate, talc, or mica, have been found to contribute the best abrasion resistance and downweb strength properties. Also the platelet fillers make the sheet material harder, which contributes to maintaining a white appearance on the roadway. In addition, the platelet fillers have a high ratio of surface area to volume, which enhances their reinforcing ability. Magnetite particles such as strontium platelet fillers may also be employed. Such platelets become aligned in a north south orientation such that high magnetic strength can be achieved for magnetic lane awareness markings. Such markings are described in greater detail in copending U.S. patent application Ser. No. 10/039654 filed Dec. 31, 2001; incorporated herein by reference. Other fillers, such as needle-type or bead-type fillers, may be employed instead of or in addition to low concentrations of platelet fillers. The amount of filler included in the sheet material of the invention varies with the kind of filler used. Preferably, at least 3 weight-% of platelet fillers are used. With lower amounts of synthetic polymeric fibers, higher amounts of filler are typically desired though fillers in an amount of more than 50 weight-% tend to stiffen the product excessively. Preferably, the amounts of filler ranges from about 5 and about 20 weight-%.

[0020] Retroreflective elements (e.g. transparent microspheres, cube-corner particles derived from ground sheeting) or and skid-resisting particles (e.g. sand particles) are also preferably included in the pavement marking composition at concentration up to about 45 weight-% to provide reflectivity at night and to give the sheet material skid-resisting qualities. Preferably, about 25 weight-% to about 40 weight-% reflective glass beads are dispersed throughout the thickness of the pavement marking sheet. An exterior layer of such particles may be provided on the top of the sheet material, partially embedded in the sheet material and partially protruding from the sheet material, to provide immediate reflectivity and skid-resistance; and other particles may be embedded in the sheet material to become exposed as the sheet material is worn away. The particles may be held in the partially protruding position by use of a support film adhered to the sheet material of the invention, for example, as taught in column 4 of U.S. Pat. No. 4,988,541; incorporated herein by reference.

[0021] Typically the synthetic polymeric fibers are dry blended with the polymeric material and other optional ingredients forming a relatively homogeneous mixture. The mixture can be supplied in either a granular form or is the form of a block. Various apparatus are commercially available for receiving such forms. Such apparatus heat and agitate the thermoplastic composition until melted and then transfer the melted composition into a screed, ribbon or spray device wherein it is then shaped into the specified width and thickness as a line, legend or symbol. When applied on asphaltic pavement, the thermoplastic marking material typically forms a sufficient thermal bond via heat fusion. When applied to Portland concrete cements or on oxidized or aged asphaltic paved surfaces, application of a primer is recommended in order that a sufficient mechanical bond is achieved.

[0022] Following application, the marker should be allowed to cool so that the solidified binder material becomes tack-free. Adequate adhesion of the marker to the transportation surface can be evaluated in a variety of ways. Exposure to normal environmental or traffic conditions for a period of time, e.g., one day or more, will give the most reliable test results. However, relatively simple tests such as a boot scuff test or attempting to remove the marker with a putty knife will often be sufficient to determine whether marker has adhered adequately to the transportation surface. In cases where the marker has been applied to asphalt, it may be necessary to allow the asphalt to cool for several hours or more before evaluating adhesion. Asphalt can retain significant heat from the preheating step and may undergo cohesive failure within the asphalt if marker adhesion is tested too soon after the marker has been applied.

[0023] Similarly, the composition can be extruded onto a release paper forming a sheet for the purpose of evaluating properties such as conformability and cold temperature properties of the pavement marking composition. Further, the composition may be employed in a pavement marking tape as a conformance layer, such as described in U.S. Pat. No. 5,194,113 (Lasch et al.).

[0024] Conformability of a marking can be evaluated in other ways as well. One simple way is to press a layer or sheet of the material by hand against a complex, rough, or textured surface such as a concrete block or asphalt composite pavement, remove the sheet, and observe the degree to which the surface has been replicated in the sheet. Another assessment of the conformance of a marking tape may be obtained as follows. First, the force required to deform the sheet material a suitable amount is measured. Second, a portion of the induced strain is relieved. Finally, the retractive force remaining in the material at the reduced strain level is measured. A specific example of this process would be to deform a sample to 115% of its original length by stretching the sample at a strain rate of 0.05 sec^{-1} and measuring the stress at 115% deformation, release the strain at the same rate, allow the material to return to 110% of its original length, and measure the retractive force. This measurement may be made using a standard tensile testing apparatus such as, for example, the servohydraulic tensile testers available from MTS Systems Corporation of Minneapolis, Minn. Preferred comformable materials exhibit a force to deform the sample to 115% of its original length of less than 35 NT per cm width (20 lbs per inch width), and a retractive force at a subsequent 110% deformation of less than 14 NT per cm width (8 lbs per inch width), although lesser forces are even more preferred. Other measures of conformability are described in U.S. Pat. No. 5,194,113, and may also be used in conjunction with the pavement marking tapes of the present invention to evaluate conformance of a sheet material to an irregular surface.

[0025] The pavement marking preferably has good abrasion resistance as may be indicated by a modified Taber abrasion test. The test uses an H-22 Taber abrader wheel, with a one kilogram weight on the wheel. The test specimen is held under water, and the abrader wheel passed over the specimen for 500 cycles. Sheet material of the invention generally exhibits a loss of no more than about 5 grams in this test.

[0026] Objects and advantages of the invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in the examples, as well as other conditions and details, should not be construed to unduly limit the invention. All percentages and ratios herein are by weight unless otherwise specified.

EXAMPLES

[0027] Table I, as follows, identifies the chemical description, trade designation, supplier and location for each of the ingredients employed in the examples.

TABLE I

Chemical Description	Trade Designation	Supplier	Location
Ethylene Acrylic Acid Copolymer	"AC 5120"	Allied Signal	Morristown, NJ
TiO_2-Pigment	"TI PURE 960"	DuPont	Wilmington, DE
Magnetic Filler	"UHE-9"	Fermag Industries	Edison. NJ
Polyester Fiber			
(¼")	"6-3025-¼"	Mini Fibers	Johnson City,
(½")	"6-3025-½"	Inc.	TN
Glass Fiber	"731A-16-W-¼")	Owens Corning	Toledo, OH

[0028] Table II as follows sets forth the weight percentage of each ingredient employed in Comparative Example A, and Examples 1-2.

TABLE II

Example 1	Example 2	Comparative Example A	Trade Designation
81.9	81.9	81.9	"AC 5120"
17.7	17.7	17.7	"TI PURE 960"
0.4	—	—	"6-3025-¼"
—	0.4	—	"6-3025-½"
—	—	0.4	"731A-16-W-¼"

[0029] The materials were dry blended in gallon jars. The mixture was heated on a hot plate until the temperature reached 305° F. (152° C.) and poured into a heated (300° F./152° C.) extrusion head that delivers the mixture unto silicone release paper forming a 1-2 mm thick 4"(101 mm) wide tape.

[0030] For each of the examples the tear strength was evaluated according to ASTM D1938. Table III, as follows sets forth the test results:

TABLE III

	Example 1	Example 2	Comparative Example A
Down Web Average	2.49	2.26	3.13
Tear Lb (kg)	(5.48)	(4.97)	(6.89)
Cross Web Average	2.39	2.98	1.89
Tear Lb (kg)	(5.26)	(6.56)	(4.16)
Ratio-Down Web Tear/Crossweb Tear	1.04	0.76	1.65

[0031] The results show that the ratio of down web tear to crossweb tear of the synthetic polymeric fiber containing extruded sheet is considerably closer to 1 than the composition comprising glass fibers. Further the ½" synthetic polymeric fiber contributes a higher crossweb tear strength, particularly in comparison with the glass fibers.

[0032] Examples 1 and 2 and Comparative Example A were conditioned for 4 hours at −40° F. The sample were removed from the freezer and struck with a hammer. Comparative Example A shattered into several pieces. Examples 1 and 2 cracked, yet the pieces did not separate along the crack.

[0033] Prepared in the same manner, Table III as follows sets forth the weight percentage of each ingredient employed in Comparative Example B, and Examples 3-5.

TABLE III

Example 3	Example 4	Example 5	Comparative Example B	Trade Designation
39.42	39.26	39.18	39.4	"AC 5120"
17.7	17.7		17.7	"UHE-9"
0.394	0.785	.98	—	"6-3025-¼"

[0034] The cold temperature properties of these samples were evaluated in the same manner at −10° F. Comparative Example B shattered; whereas Examples 3-5 cracked yet remained intact.

What is claimed is:

1. A pavement marking composition comprising synthetic polymeric fibers dispersed within a thermoplastic-based polymeric material, wherein the synthetic polymeric fibers have a melt point greater than the polymeric material.

2. The pavement marking sheet of claim 1 wherein the fibers are randomly dispersed within the polymeric material.

3. The pavement marking composition of claim 1 wherein the synthetic polymeric fibers have a melt point greater than 400° F.

4. The pavement marking composition of claim 1 wherein the synthetic polymeric fibers are selected from the group comprising polyester, polyamide, polypropylene, tetrafluoroethylene and copolymers thereof.

5. The pavement marking composition of claim 1 wherein said composition is provided as a sheet having a thickness ranging from about 0.25 mm to about 5 mm, said sheet having a downweb direction and crossweb direction.

6. The pavement marking sheet of claim 5 wherein the sheet is conformable.

8. The pavement marking sheet of claim 5 wherein the downweb direction and crossweb direction has a tear ratio that ranges from 0.5 to 2 when measured according to ASTM 1938.

9. The pavement marking sheet of claim 5 wherein the downweb direction and crossweb direction has a tear ratio that ranges from 0.7 to 1.3 when measured according to ASTM 1938.

10. The pavement marking composition of claim 1 wherein the synthetic polymeric fiber ranges from about 0.2 weight-% to about 2 weight-%.

11. The pavement marking of claim 1 wherein the polymeric material is selected from the group comprising alkyd thermoplastic and hydrocarbon thermoplastic.

12. The pavement marking of claim 11 wherein the polymeric material is a hydrocarbon thermoplastic.

13. The pavement marking of claim 12 wherein the polymeric material comprises an acid containing copolymer of ethylene.

14. The pavement marking composition of claim 1 wherein the composition comprises other ingredients selected from the group comprising reflective elements, extender resins, fillers, and pigments.

15. The pavement marking of claim 1 wherein the composition comprises magnetic particles.

16. The pavement marking composition of claim 1 wherein the synthetic polymeric fibers have a fiber length of at least 6 mm.

17. The pavement marking composition of claim 1 wherein the synthetic polymeric fibers have a fiber length of at least 10 mm.

18. A method of making a pavement marking comprising:

providing a composition comprising a thermoplastic-based polymeric material and synthetic polymeric fibers;

heating the composition to a temperature wherein the composition is extrudeable and the synthetic polymeric fibers are unmelted; and

extruding the composition on a pavement surface.

19. A method of making a pavement marking comprising:

dry blending a thermoplastic polymer and synthetic polymeric fibers;

melting and mixing the blend; and

extruding the blend onto a pavement surface at a temperature less than the melt point of the synthetic polymeric fibers.

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