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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,330,954**

(86) 1999/04/23
(87) 1999/11/11

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(51) Int.Cl.[6] C04B 26/04, C04B 14/22, E01F 9/04
(30) 1998/05/01 (60/083,960) US

(54) **MATERIAUX INTEGRES DE MARQUAGE RETROREFLECHISSANTS**

(54) **INTEGRATED RETROREFLECTIVE MARKING MATERIALS**

(57) L'invention concerne une formulation à l'état sec pour matériau de marquage intégré utilisable dans les applications propres au béton et à l'asphalte, qui renferme un mélange à base de ciment, y compris un liant hydraulique ou à base de ciment, un modificateur de ciment polymère redispersible, une charge à agent rétroréfléchissant et, éventuellement, une charge à agent réfléchissant. De préférence, la formulation comprend un pigment, un agrégat, un dispersant, un plastifiant, et/ou un réducteur d'eau. Eventuellement, la formulation comprend au moins un additif choisi entre les produits suivants : substance accélératrice, entraîneur d'air, démousseur, fibres, charge inerte, argile naturel, charge pouzzolanique, retardateur, modificateur de rhéologie, agent expansif, argile synthétique, agent de mise en suspension, et agent épaississant. Une fois appliqué, le matériau de marquage comporte, diffusés à sa surface et intégrés à celle-ci, des agents rétroréfléchissants additionnels.

(57) A dry formulation for an integrated marking material for concrete and asphalt application comprises a cementitious mixture including a hydraulic or cementitious binder, a redispersible polymeric cement modifier, a retroreflective agent filler, and optionally, a reflective agent filler. The formulation preferably includes a pigment, aggregate, a dispersant, a plasticizer, and/or a water reducer. The formulation optionally includes at least one admixture selected from an accelerator, an air entrainer, a defoamer, fibers, an inert filler, a natural clay, a pozzolanic filler, a retarder, a rheology modifier, a shrinkage compensating agent, a synthetic clay, a suspending agent, and a thickening agent. The marking material, when applied, has broadcast onto and embedded into its surface, additional retroreflective agents.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C04B 26/04, E01F 9/04, C04B 14/22	A1	(11) International Publication Number: WO 99/57076
		(43) International Publication Date: 11 November 1999 (11.11.99)

(21) International Application Number: PCT/EP99/02833

(22) International Filing Date: 23 April 1999 (23.04.99)

(30) Priority Data:
60/083,960 1 May 1998 (01.05.98) US

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: INTEGRATED RETROREFLECTIVE MARKING MATERIALS

(57) Abstract

A dry formulation for an integrated marking material for concrete and asphalt application comprises a cementitious mixture including a hydraulic or cementitious binder, a redispersible polymeric cement modifier, a retroreflective agent filler, and optionally, a reflective agent filler. The formulation preferably includes a pigment, aggregate, a dispersant, a plasticizer, and/or a water reducer. The formulation optionally includes at least one admixture selected from an accelerator, an air entrainer, a defoamer, fibers, an inert filler, a natural clay, a pozzolanic filler, a retarder, a rheology modifier, a shrinkage compensating agent, a synthetic clay, a suspending agent, and a thickening agent. The marking material, when applied, has broadcast onto and embedded into its surface, additional retroreflective agents.

INTEGRATED RETROREFLECTIVE MARKING MATERIALS

TECHNICAL FIELD

The present invention relates to integrated retroreflective marking materials for fresh or hardened concrete and asphalt surfaces, such as roads, highways and the like. The present invention relates particularly to cementitious material formulations which contain a redispersible polymer and retroreflective/reflective materials.

BACKGROUND OF THE INVENTION

Currently, the marking of concrete and asphalt for lane striping or cautionary markings is generally accomplished by painting stripes or applying preformed tapes of polymeric material. Disadvantages of these methods include the fact that both are temporary, requiring frequent, periodic reapplication.

To provide a longer lasting product, several marking methods include using a system which consists of a two part epoxy, thermoplastic, polyester, methyl methyacrylate, or polyurethane resin system. Most of these products are solvent- based or reactive resins which require special handling, storage, mixing, application and disposal procedures. With solvent-borne paint products, including the typical one-part traffic paint, the release of solvent into the environment with each application presents certain hazards to the environment as well as for nearby workers and applicators.

In some situations, retroreflectivity of the markings is desired for enhanced night-time visibility. This has been proposed to be accomplished by several techniques. In one technique, preformed reflector devices are partially embedded in the roadway at regular intervals. The exposed portion of the reflector soon gathers a deposit of dirt or silt, which reduces visibility. The exposed portion of such a reflector may be damaged and worn away with repeated contact with vehicle tires, and cleaning or snow removal

equipment.

Another technique is to precast a panel of concrete having reflective or retroreflective materials embedded into its surface, and then to position or affix the panel to the roadway surface or highway barrier. This requires custom prefabrication of the structures, and storage, transportation and placement of the heavy articles.

One on-site highway marking technique involves broadcasting a quantity of reflective or retroreflective materials onto the surface of a coating of paint applied to the surface of the roadway, optionally including a second coating of paint to lock in the particles. Similarly, it has been proposed to broadcast reflective glass beads onto a bonding polymer coating (such as epoxy) on the roadway, followed by application of a weathering top coat (such as a urethane). Again, these road markings are temporary, and require frequent reapplication.

A variant of the marking tape technique has been proposed, in which several layers of polymeric materials are adhesively bonded in the tape, at least one of which carries transparent microspheres or other reflective elements. In a related proposal, a single layer of polymeric tape carries embedded ceramic spheroids, to be used for marking lines on roadways.

These tapes are also temporary in nature, wearing rapidly because of the friction of vehicle tires, or peeling away from the roadway because of such friction or poor adhesion to the road surface. Because these tapes are polymeric, they have different thermal properties than has the substrate to which they are applied. In hot weather for example, preformed tapes tend to soften, collect debris, crack and delaminate. They can also require an epoxy-bonding agent to improve adhesion to the substrate. This complicates the application to the pavement, and introduces yet another thermally dissimilar material to the system.

Australian Patent 667210 proposes a surface coating composition for road

marking, delivered to the site in two parts, one being a dry blend and the other being a liquid mixture. The dry blend includes white portland cement, titanium dioxide, refractory cement, and aggregate in the form of 150 to 600 μM sized garnet, or 250 to 600 μM sized garnet and 150 to 600 μM sized glass spheres. The liquid mixture includes acrylic cement polymer modifier, acrylate/styrene copolymer cement modifier, foam control agent, non retarding mortar, plasticiser and water. The two components are mixed on-site, and applied to the road as a paste. A stream of glass beads, 0.85 mm to 1.18 mm (850 to 1180 μM) in size are sprayed on to the paste to partially embed them for reflectivity.

There are several shortcomings with the marking material described in the Australian Patent. First, the fact that the marking material is a two-phase system introduces variability and the possibility of improper dosage during the on-site preparation of the paste to be applied to the roadway. The liquid portion, being susceptible to uncertain loading level, and being susceptible to spillage, is of concern to the environmental and structural integrity of the worksite. One must rely on the road crew to correctly measure and thoroughly mix the liquid and dry portions of the system, even if one could be sure that the correct loading levels of ingredients were present in the liquid portion.

Even if the liquid portion is pre-proportioned, it has to be mixed with additional water to achieve the desired workability. If the correct amount of water is not added, both the plastic and hardened properties of the finished product will be compromised. If the consistency of the marking material is too wet or too dry, the use of a liquid polymer as a primary component does not allow for any adjustments in dosage without affecting the performance of the finished product. The proportion of polymer in the marking material disclosed in the Australian Patent is quite high, raising concerns about the strength and abrasion resistance of the resulting product. The high polymer level also causes set retardation, as evidenced by the use of a stream of hot air to accelerate the setting time and embed the glass beads. The hot air can cause rapid drying of the surface and differential hydration of the cement.

The glass spheres incorporated in the mixture of the marking material is more suitable for utility as an aggregate for the cementitious component, rather than promoting dry and wet night-time visibility and retroreflection, once the surface-borne glass beads are worn. Also, due to the ratio of garnet to glass beads used in the material, the small proportion of integral beads would be overshadowed by the larger and darker mineral aggregate after the surface is worn.

It would be preferred that a cementitious marking material be formulated as a one-phase system, preferably a dry system, to ensure that the component levels are precise and uniform throughout, and to avoid storage restrictions (such as to prevent freezing) and transport of large quantities of liquid product with its attendant disadvantages of added cost and the need for disposal of plastic packaging containers.

However, the use of a significant portion of dry polymeric materials in cementitious mixtures presents other disadvantages. The polymer needs to be wetted out before use. The polymer often acts as a retarder for the system, and additionally, entrains more air in the cementitious mixture. Also, the polymer often presents a foaming problem.

It is therefore an object of the present invention to provide a marking material for fresh or hardened concrete or asphalt applications that is integrated, versatile in its mode of application, and long lasting with respect to the marked concrete or asphalt surface.

It is a further object of the present invention to provide an integrated marking material for fresh or hardened concrete or asphalt applications that can be stored and transported as a dry formulation.

It is a further object of the present invention to provide a dry formulation for an integrated marking material for concrete or asphalt applications that can be mixed with water on site for simple application to a road or highway.

It is a further object of the present invention to provide a dry formulation for an integrated marking material for concrete or asphalt applications that avoids the problems attendant with the incorporation of a large proportion of polymer in cementitious materials.

It is a further object of the present invention to provide a dry formulation for an integrated marking material for fresh or hardened concrete and asphalt, which can be formulated to meet various product application and performance demands.

It is a further object of the present invention to provide a dry formulation for an integrated marking material for concrete or asphalt applications that has high initial retroreflectivity when tested in accordance with ASTM standards (such as ASTM D-4061).

It is a further object of the present invention to provide a dry formulation for an integrated marking material for concrete or asphalt applications that retains high retroreflectivity even after wear of the exposed surface occurs.

It is a further object of the present invention to provide a dry formulation for an integrated marking material for concrete or asphalt applications that has high ultimate compressive strength, and is abrasion resistant.

SUMMARY OF THE INVENTION

The present invention therefore provides a dry formulation for an integrated retroreflective marking material for concrete or asphalt applications comprising a cementitious mixture including a hydraulic or cementitious binder, a redispersible polymer cement modifier, a retroreflective agent filler, and preferably, a reflective agent filler.

The present invention further provides a dry formulation for an integrated

retroreflective marking material for concrete or asphalt applications wherein the polymeric cement modifier is a dry, redispersible polymer selected from the group consisting of acrylates, methacrylates, ethylene vinyl acetate, styrene-acrylate, styrene-butadiene, polyvinyl acetate, acrylonitrite-butadiene, polychloroprene, vinyl chloride, vinyl laurate, vinyl versatate, vinyl acetate, and blends, copolymers, or terpolymers thereof.

The present invention further provides a dry formulation for a marking material for concrete or asphalt applications wherein the retroreflective agent filler is selected from the group consisting of glass beads, glass bubbles, glass flakes, glass spheres, ceramic spheres, plastic beads, fluorescent glass beads, fluorescent plastic beads and mixtures thereof, wherein the retroreflective filler has an average particle topsize of at least about 600 μM.

In a preferred embodiment, the cementitious marking material is formulated to include both integral and surface retroreflective/reflective agents to ensure visibility as the surface wears with time.

In a preferred embodiment, the dry cementitious formulation includes at least one of an inorganic pigment, organic pigment, or inorganic/organic hybrid pigment. The pigment can be natural or synthetic.

The dry formulation of the present invention is capable of being applied to a pavement, highway or the like, by mixing with water on site and applying as a thin coating on the surface or as a thicker topping that becomes integral with the highway surface. The marking material, when applied to the highway or pavement, preferably has broadcast on to and embedded into its surface additional retroreflective agents.

The present invention therefore provides a dry formulation for a cementitious marking material for concrete or asphalt, compatibilized for accepting retroreflective agents, comprising a cementitious mixture including a hydraulic or cementitious binder,

and a redispersible polymeric cement modifier.

The present invention further provides a cementitious marking material for concrete or asphalt prepared substantially on-site from a mixture of water with a dry formulation comprising a cementitious mixture including a hydraulic or cementitious binder and a redispersible polymeric cement modifier, said marking material having retroreflective agents at least partially embedded in its surface.

The present invention further provides an integrated marking material for pavement applications prepared on-site from a mixture of water with a dry formulation comprising a cementitious mixture including a hydraulic or cementitious binder, a redispersible polymeric cement modifier, a retroreflective agent filler, and preferably, a reflective agent filler.

The present invention further provides a process of marking a surface of concrete or asphalt, by applying thereto a cementitious marking material or an integrated marking material as hereinabove described.

In one embodiment, the integrated marking material of the present invention comprises a topping of at least about one-eighth inch (3.2 mm) average thickness, preferably further comprising an at least partially embedded broadcast of retroreflective agent particles having a topsize of at least about 600 μM, preferably at least about 850 μM, at the surface of the topping.

In another embodiment, the integrated marking material of the present invention comprises a coating of less than about one-quarter inch (6.4 mm) average thickness, preferably further comprising an at least partially embedded broadcast of retroreflective agent particles having a topsize of at least about 600 μM, preferably at least about 850 μM, at the surface of the coating.

In a preferred embodiment, the cementitious marking material is applied in a

recessed groove or depression to make it an integral part of the substrate and to prolong its service life.

In a preferred embodiment, the integrated marking material includes at least one of a natural or synthetic inorganic pigment, organic pigment, or inorganic/organic hybrid pigment.

In an alternative embodiment, the present invention provides a dry formulation for an integrated retroreflective marking material for concrete or asphalt applications comprising a mixture including a hydraulic binder of at least one of magnesium phosphate cement and magnesium potassium phosphate cement, a retroreflective agent filler, and optionally, a reflective agent filler, as well as an integrated, retroreflective marking material for pavement applications prepared substantially on-site from a mixture of water with said dry formulation.

The present invention further provides an integrated retroreflective marking material for concrete or asphalt applications comprising a surface including a hydraulic binder of at least one of magnesium phosphate cement and magnesium potassium phosphate cement, having an at least partially embedded broadcast of retroreflective agent particles having a topsize of at least about 600 μM at the surface.

DETAILED DESCRIPTION OF THE INVENTION

In order to provide a marking material for pavement applications such as for roads and highways, floors such as warehouse floors, sidewalks, toll booths, handicap spaces, parking lots, parking garages and parking decks, airfield runways and the like, that would be simple to apply, yet which would last substantially for the lifetime of the pavement surface, it was necessary to develop a material that could be easily prepared on-site, and would have uniform properties throughout the application. The material would also need to exhibit structural integrity and strength substantially comparable to the pavement to which it was applied, and provide visibility both during the day and at

night. The material would preferably exhibit retroreflectivity of vehicle headlamps that was substantially comparable to existing temporary marking materials such as paints and reflective tape.

Such a marking material has been developed, particularly in the form of an easy-to-prepare, -store and -transport, dry formulation, comprising a cementitious mixture including a hydraulic or cementitious binder, and a dry or powdered redispersible polymeric cement modifier. In a preferred embodiment, the cementitious mixture includes a retroreflective agent filler, and preferably, a reflective agent filler.

In the dry formulation, the hydraulic or cementitious binder is a hydraulic cement, preferably a portland cement such as that used for highway, bridge, or airfield runway construction, and the like, or a quick setting cementitious binder such as magnesium phosphate or magnesium potassium phosphate cement, or any other suitable hydraulic binder. Suitable portland cements for use as the cementitious binder include Type I, Type II, Type III, Type IV and Type V portland cements. For specific marking applications, a white portland cement or a grey cement binder may be used. Other hydraulic or cementitious binders useful in the present invention include calcium sulfoaluminate (CSA) cements, such as type K cement, DENKA (trade mark) cement, ROCKFAST (trade mark) cement or ULTIMAX (trade mark) crystal modified portland cement and calcium aluminate cements such as SECAR (trade mark) calcium aluminate cement, high alumina cements, activated fly ash, activated clay, and slag cements.

An important ingredient in the dry formulation for the cementitious integrated marking material is a redispersible polymeric cement modifier, namely a dry polymer. By "redispersible polymer" is meant a solid grade latex, such as is produced by spray drying a latex emulsion. When water is added to the dry polymer, it redisperses back to a latex emulsion. Examples of polymers which can be utilized as dry redispersible polymers include, but are not limited to, acrylates, methacrylates, ethylene vinyl acetate, styrene-acrylate, styrene-butadiene, polyvinyl acetate, acrylonitrite-butadiene, polychlorprene, vinyl chloride, vinyl laurate, vinyl versatate, vinyl acetate, and blends,

copolymers, or terpolymers of these polymers. Preferably, the redispersible polymeric cement modifier is a dry acrylic polymer.

Examples of preferred redispersible polymeric modifier for use in the permanent marking material dry formulation include, but are not limited to DRYCRYL (trade mark) DP2903 or DP2904 acrylic polymer available from Rohm & Haas, ACRONAL (trade mark) S 420P flexible styrene acrylate polymer resin available from BASF, VINNAPAS SP-102 acrylic polymer or VINNAPAS SP-490 vinyl chloride polymer available from WACKER Polymer Systems and SB powder styrene butadiene polymer available from Rhodia.

The polymer cement modifier is useful to compatibilize the cementitious material with the retroreflective and reflective fillers that are used in the marking material, but should not be present in amounts that would unfavorably diminish the strength of the resulting concrete material. The resin is therefore preferably present in the amount of about 0.2 to about 10% by weight of the dry formulation, preferably about 0.5 to about 8% by weight of the dry formulation when the binder is portland cement, and most preferably about 2 to about 6% by weight. The relatively low percentage of the polymeric cement modifier needed for the dry formulation according to the present invention, avoids the problems attendant with the incorporation of a large proportion of polymer in cementitious materials.

When the hydraulic binder is a quick setting cement such as magnesium phosphate or magnesium potassium phosphate, the polymeric cement modifier is preferably used in the amount of about 0.2 to about 2% by weight of the dry formulation. It has been found that, in contrast to the portland cement binder-based formulations, the magnesium phosphate or magnesium potassium phosphate binder-based formulations having acceptable performance, may have incorporated or embedded in them retroreflective agent filler and optionally reflective agent filler, without the polymeric cement modifier, or at least, with lower levels of the polymeric component.

As stated above, the polymeric cement modifier should be dry, such as in powder form, so as to provide ease of handling, measuring, and mixing in the dry cementitious formulation, and to avoid separation and resulting pockets of low strength materials in the final topping or coating product.

The dry formulation can contain other customary components of cementitious mixtures, such as aggregate, including fine aggregate or sand, and preferably also coarse aggregate, such as silica, quartz, crushed rounded marble, glass spheres, granite, limestone, calcite, feldspar, alluvial sands, other durable aggregate, mixtures of aggregate and the like.

The dry formulation can include various admixtures useful in cementitious mixtures, such as a dispersant, a plasticizer, or a water reducer, and/or one or more other common admixtures as needed for the particular application and environment, such as an accelerator, an air entrainer, a defoamer, fibers, an inert filler, a natural clay, a pozzolanic filler, a retarder, a rheology modifier, such as a water-soluble gum or polymer, a shrinkage compensating agent, a synthetic clay, a suspending agent, a thickening agent, and the like, and mixtures of the foregoing. Suitable examples of these admixtures are known to those skilled in the art, and representative examples are listed in US Patent No. 5,728,209, incorporated herein by reference.

For durability considerations, the marking material dry formulation may include a pozzolanic filler such as fly ash, kaolin, silica fume, blast furnace slag, calcined clay and the like, and mixtures of such fillers. Other inert fillers can be included, such as calcium carbonate, ceramic microspheres, mica, talc, silica flour, diatomaceous earth, rice husk ash, and the like, and mixtures of these fillers.

In order that the marking material provide visibility at night or in other low light conditions, the dry formulation preferably contains a retroreflective agent filler, such as glass beads, glass bubbles, glass spheres, ceramic spheres, plastic beads, fluorescent glass beads, fluorescent plastic beads and the like, and mixtures of these retroreflective

agents, for incorporation into the matrix of the cementitious topping or coating materials. To provide retroreflective properties throughout the life of the pavement to which the integrated marking material is applied, the incorporated, or integral, retroreflective agent has an average topsize of at least about 600 μM, preferably about 850 μM and up. The topsize of the retroreflective agent is limited only by availability and ease of incorporation into and mixing with the other components of the cementitious formulation.

Although it is preferred that the retroreflective agent fillers be introduced into the dry formulation at an early stage, such as during blending of the cementitious topping, it is within the scope of the invention that the retroreflective agents be introduced, with mixing, into the dry mixture of the cementitious binder, polymeric cement modifier, etc., at any time prior to the addition of liquid to the formulation. This can be accomplished, for example, by combining the preproportioned contents of a bag of the retroreflective agent and the contents of a container of the cementitious binder mixture at a job site, prior to adding the aqueous hydration liquid.

To provide improved dispersibility in the dry formulation, the retroreflective agent filler preferably has a surface treatment or a coating of a moisture-proof, antistatic agent, examples of which include but are not limited to silicones, modified silicones such as alkylhydroxy silicones, carbinols, silanols, and the like.

To provide improved adhesion in the cementitious mixture upon hydration and drying, the retroreflective agent preferably has a surface treatment or coating of an adhesion promoter. Examples of such adhesion promoters include but are not limited to silanes and modified silanes, such as those containing functionalities selected from amino, vinyl, acrylic, alkoxy, alkyl, (meth)acryloxy, glycidoxy, methacryl, epoxy, acetoxy, methoxy, ethoxy, arylalkoxy, chloro, mercapto, carboxyamide, and the like.

Retroreflectivity refers to the process of reflection in which the incident rays and reflected rays are antiparallel. For example, a beam of an auto or aircraft headlamp

that shines on the retroreflective agent is reflected back toward the source, being then visible to a driver or pilot. Not all reflective materials, and not all glass spheres are retroreflective. For glass spheres and the like, the minimum size to promote the optimum dry and wet night-time visibility is about 600 μM. Therefore, glass spheres that have formerly been incorporated into concretes as inert fillers, have not inherently imparted retroreflectivity to the concrete. To provide optimum retroreflectivity, the retroreflective agent filler, such as glass beads, preferably has a refractive index of greater than about 1.5, preferably about 1.5 to about 2.1.

In order to enhance visibility of the marking material, the dry formulation optionally contains reflective agents as filler to reflect light from other sources, such as smaller glass beads (less than 600 μM diameter), glass bubbles, glass flakes, glass spheres, ceramic spheres, plastic beads, fluorescent glass beads, fluorescent plastic beads and mixtures of these.

In order to function as lane or runway stripes or markers for hazards or other special marked areas, such as where delineation, accenting or site/area marking is desired, the formulation for the integrated marking material according to the present invention may include at least one pigment. For example, titanium dioxide can be used for white striping, and Hansa yellow for the yellow striping commonly used on highways. A black pigment such as black iron oxide can be used to provide contrast for an adjacent or overlaid white or colored material stripe. For other purposes, the formulation may contain a pigment from the classes of fluorescent metal oxide pigments and phosphorescent metal oxide pigments, to create a "glow in the dark" effect.

The dry formulation may therefore contain a natural or synthetic pigment such as inorganic pigment, an organic pigment or an inorganic/organic hybrid pigment, including any suitable mixed metal oxide, dye or colorant. Such pigments include but not limited to, carbon black, Hansa yellow (2-[(4-methoxy-2-nitrophenyl)azo]-N-(2 methoxy phenyl)-3-oxo butanamide), chrome oxide, iron oxide, titanium dioxide, zinc sulfate, zinc sulfides, LumiNova (trade mark) modified zinc sulfide (United Minerals Corp.), Lithopone zinc sulfide/barium sulfate, zinc oxide, titanates, nickel antimony

titanates, phthalocyanines, mixed phase spinels and oxides, and mixtures of these, or any pigment meeting the requirements listed in ASTM specification C-979. The marking material of the present invention can therefore be tailored, in color and consistency, to meet special aesthetic or design needs.

The dry formulation generally contains the above-described components in the following ranges, set forth in weight percents based on the total weight of those components listed: binder, about 15 to about 50%; redispersible polymer, about 0.2 to about 10%; retroreflective agent, about 10 to about 75%; reflective agent, about 5 to about 35%; aggregate, about 10 to about 70%; pigment, up to about 10%.

The relative proportions of the components are varied according to the requirements of the particular application, for example, as a thick topping or a thin coating, to fresh or hardened concrete, or to asphalt, and the end-use performance characteristics desired in terms of strength and durability.

The integrated marking material for pavement applications, according to the present invention, is prepared on-site from a mixture of water with the dry formulation described above. The measurement of the dry formulation mix, and a quantity of water, is easier and more accurate than the calculation of a solids-containing solution or dispersion of uncertain concentration, together with the need to compatibly and uniformly mix the same. Of course, it is within the scope of the invention to include components in solution in the water that are not readily phase-separable or critical in terms of absolute percentage to the dry formulation mixture, such as dispersants, plasticizers, water reducers, accelerators, air entrainers, defoamers, retarders, rheology modifiers, shrinkage compensating agents, suspending agents, thickening agents and the like.

The water-cement ratio for the marking material is selected according to considerations known in the art for the particular binder utilized, generally ranging between about 0.22 and about 0.65.

The marking material of the present invention is therefore advantageous in that it can be stored and transported as a dry formulation and can be mixed with water on-site for easy application to the fresh or hardened concrete or asphalt pavement such as a road or highway.

The area to be marked can be prepared in a variety of ways. By one technique, the marking material can be applied as a topping comprising a mixture of water and the dry formulation to a freshly-laid concrete surface, preferably in a slight depression as compared to the contiguous pavement surface, so that the marking material fills the depression to form an area having a surface approximately even with, or slightly elevated with respect to the contiguous pavement.

By another technique, the marking material topping is applied to a cured or hardened pavement surface that has been prepared with a depression to receive the topping, or in which the depression has been subsequently formed, or cut.

By still another technique, a coating comprising a mixture of water and the dry formulation is applied to a pavement, such as an asphalt or a hardened or precast concrete surface, without the need for first preparing a ridge or depression to receive the marking material.

The marking material of the present invention, when applied as a thick topping according to the techniques described generally above, is of at least about one-eighth inch (3.2 mm) average thickness, and is preferably one-quarter inch (6.4 mm) or greater.

The marking material of the present invention, when applied as a thin coating according to the techniques described generally above, is generally less than about one-quarter inch average thickness, preferably less than about one-eighth inch (3.2 mm) in thickness. It is preferred, when the marking material is to be applied as a thin coating, that the percentage of redispersible polymeric cement modifier in the dry

formulation be greater than that of a corresponding topping formulation, most preferably on the order of about 4 to about 8 percent by weight based on the total dry formulation.

Whether applied as a thin coating or a thick topping, in order to enhance the retroreflectivity of the marking material, the material is preferably seeded with retroreflective agents, and optionally, reflective agents, such as being broadcast on the surface prior to setting of the cementitious marking material. Suitable retroreflective agents and reflective agents are listed above, being selected from those which are capable of being incorporated integrally in the matrix of the cementitious material by formulation in the dry mix.

The marking materials of the present invention, therefore include an at least partially embedded broadcast of retroreflective filler particles having a topsize of at least about 600 μM at the surface of the topping or coating. Preferably, the retroreflective filler particles have a topsize of at least about 850 μM. Optionally, a clear coat may be applied over the broadcast particles, such as an acrylic resin or a polyurethane coating.

It has been found that the consistency of the cementitious material applied to the pavement, at the time of the seeding of the retroreflective or reflective particles, affects the depth to which the particles sink into the material, and thus the percentage of the individual particles which are embedded into the matrix. Generally, the higher the percentage of the exposed particles, the higher the initial retroreflectivity or reflectivity of the marking material. However, even a small percentage of exposed retroreflective agents provides an acceptable reflective performance.

With wear of the pavement (and marking material) surface, both the surface-embedded retroreflective agents and the retroreflective fillers incorporated in the matrix of the marking material become exposed, and perform the desired function of low light or night reflectivity or visibility. Visibility in light environments is also enhanced by

the presence of the retroreflective agents. The permanence of the integrated cementitious topping or coating marking materials as compared with conventional paint or tapes is thus demonstrated.

The marking material is a cementitious material having high strength, such as compressive, tensile and flexural strength similar to the concrete pavement, with retroreflective fillers at the surface and preferably throughout the matrix for "replenishment" of the surface as the surface of the marking material abrades together with the contiguous pavement. The marking material has a setting time approximately equal to concrete, and a volume stability and thermal expansion compatible with concrete. Similarly to concrete, the marking material is resistant to UV light and to de-icing salts. The incorporated polymer provides enhanced bonding to the integral particles, and also to the substrate pavement.

SPECIFIC EMBODIMENTS OF THE INVENTION

Example 1

A sample mixture of a fast setting magnesium phosphate, white cementitious topping is prepared according to the present invention. Sample panels of the mixed topping are cast and allowed to harden, then retroreflectivity measurements are taken using a portable 30 meter geometry retroreflectometer. Two sample panels are cast to compare the retroreflectivity of a sample sealed with a clear acrylic sealer versus an unsealed sample of the topping.

Topping Formulation	Weight Percent
Silica Sand	26.30
Silica Flour (140 mesh silica sand)	20.00
Magnesium Oxide	8.50
Mono Ammonium Phosphate	8.50
Sodium Tripolyphosphate	0.80
Boric Acid	0.50
Titanium Dioxide	3.50
Acrylic Polymer	0.80
Defoamer	0.10
16-18 Mesh Glass Beads (Visa-Bead L-511)	31.00
Percent Mix Water	10.75
Mix time, minutes	3.0
Flow, inches (2"x4" (5.1 cm x 10.2 cm) cylinder)	5.75
Final Set, hrs.	1.0
Retroreflectivity, mcd/lux/m^2	
Sealed	691
Unsealed	698

Example 2

Samples of dry formulation cementitious marking material mixtures are prepared with incorporation of varying amounts of retroreflective glass beads into the formulation. The glass beads used are soda-lime, with refractive index 1.5-1.52 or greater. FLEXOLITE (trade mark) BT-3 glass beads is an example of suitable glass beads.

Marking Material Formulation	Mix 1	Mix 2	Mix 3
50 mesh white silica sand	23.8	12.5	20.1
Glass Beads (20/30 mesh)	24.0	37.8	30.2
1/8“ (3.2 mm) Glass flakes	2.5	--.-	--.-
Titanium dioxide	3.5	3.5	3.5
Acrylic-Polymer	0.7	0.7	0.7
Melamine water reducer	0.3	0.3	0.3
Defoamer	0.2	0.2	0.2
Calcium Carbonate	10.0	10.0	10.0
White Type 1 Portland cement	35.0	35.0	35.0
	100.0	100.0	100.0
Percentage Water Added	20.0	15.0	16.0
Consistency	screedable	screedable	screedable

All percentages are by weight. Concrete beams are cast from the following

concrete mixture using freeze-thaw molds. The cementitious marking material formulations were placed over the concrete 15 to 30 minutes after screeding.

Concrete Mixture	Weight Percent
Medusa Type I	14.85
Stone (3/8" (9.5 mm) and ½" (12.7 mm))	47.77
Sand	37.38
Water/cement ratio	0.40

All three mixes exhibit stiffening approximately 5-10 minutes after mixing. Mixes screed off fine, and are not sticky.

A light test is conducted on the composite beam from Mix 1. The surface of one half of the beam is screened to expose the interior matrix, approximating a worn roadway. The reflectance of the as cast and exposed concrete beam is compared with a standard pavement marking tape.

Comparison of composite beam from Mix 1 to striping tape

Luminance	Test 1	Test 2
Reference Standard	3.76	
Striping Tape (3M – STAMARK (trade mark) L420)	3.44	3.47
Composite Beam (surface ground to expose integral beads)	3.36	3.32
Composite Beam (as cast with integral beads)	3.47	3.41

Reflectance %	
Striping Tape (3M – STAMARK L420)	92.0%
Composite Beam (surface ground to expose integral beads)	89.0%
Composite Beam (as cast with integral beads)	91.5%

The as cast, integrated marking material provides luminance values and reflectance percentages substantially equal to the standard pavement marking tape. The simulated worn pavement, with the glass beads incorporated throughout the matrix, shows little decrease in reflectance.

Example 3

Samples of dry formulation integrated marking material cementitious mixtures are prepared with both reflective glass flakes and retroreflective glass beads incorporated into the formulation. Percentages are reported by weight.

Marking Material Formulation	Mix 1	Mix 2	Mix 3	Mix 4
White Silica Sand (50 mesh)	30.00	35.20	35.40	30.40
1/64“ (0.4 mm) glass flakes	5.00	5.00	5.00	5.00
Glass beads 20/30 mesh (FLEXOLITE BT-3)	15.00	15.00	15.00	15.00
Titanium dioxide	3.50	3.50	3.50	3.50
Melamine water reducer	0.60	0.40	0.20	0.20
Defoamer	0.20	0.20	0.20	0.20
Acrylic Polymer	0.70	0.70	0.70	0.70
Calcium hydroxide	-.--	5.00	-.--	-.—
Silica flour	-.--	-.--	-.--	15.00
White silica sand (100 mesh)	10.00	-.--	-.--	-.—
White Type I cement	35.00	35.00	40.00	30.00
	100.00	100.00	100.00	100.00
Percentage Water Added	17.0	18.0	18.0	22.0
Consistency	bleed	stiffened		sl. stiffened

Mix time was four (4) minutes each.

A composite beam is cast using Mix 4 marking material overlayed on the following fresh concrete at 30 minutes after placement.

Concrete Mix	Weight Percent
Medusa Type I	14.67
Concrete sand	37.46
Concrete stone	47.87
Water/cement ratio	0.40

A light test is conducted on the composite beam from Mix 4. The surface of one half of the beam is screened to expose the interior matrix, approximating a worn roadway. The reflectance of the as cast and exposed concrete beam is compared with a standard pavement marking tape.

Comparison of composite beam from Mix 4 to striping tape

Luminance

Reference Standard	3.36
Highway Striping Tape (3M - STAMARK L420)	3.11
Highway Striping Tape - Notched (3M - STAMARK L380I)	2.78
Composite Beam	2.82

Reflectance %

Highway Striping Tape (3M - STAMARK L420)	92.6%
Highway Striping Tape - Notched (3M - STAMARK L380I)	82.7%
Composite Beam	84.0%

The integrated, cementitious marking material of the present invention exhibits a reflectance of within 10% of the standard highway striping tape, and a reflectance greater than that of a notched highway striping tape.

Example 4

Testing is conducted of the compressive strength of an integrated cementitious marking material according to an embodiment of the invention.

Marking Material Formulation	Weight Percent
Silica sand	22.85
1/64" (0.4 mm) glass flakes	2.00
Glass beads 20/30 mesh (FLEXOLITE BT-3)	20.00
Titanium dioxide	3.50
Defoamer	0.10
Polymer	1.20
Melamine	0.35
Silica flour (140 mesh silica sand)	10.00
White Type I Cement	40.00
	100.00

Percentage Water (by weight)	18.0
Consistency	patching
Mix time four (4) minutes	

The mix is flowable until the last 3.5 minutes of mix time, at which time it then stiffens. A composite beam is cast from the following concrete mix, with a coating of ¼ inch (6.4 mm) thickness over the fresh concrete, approximately 30 minutes after mixing of the marking material formulation with water.

Concrete Mix	Weight Percent
Medusa Type I Cement	14.67
Concrete sand	37.46
Concrete stone ½" (12.5 mm)	47.87
Water/cement ratio	0.40
Slump	2 inches (5.1 cm)

The compressive strength value of the cementitious, integrated marking material is set forth below.

Compressive Strength (ASTM C-109)

	1-Day	7 Days	14 Days	28 Days
psi	3067	5573	6285	7300
MPa	21.1	38.4	43.3	50.3

Example 5

Samples of dry formulation cementitious marking material mixtures are prepared with the incorporation of VISABEAD (trade mark) L-511 and VISABEAD E-16 retroreflective glass beads obtained from Potters Industries, Inc. VISABEAD L-511 beads are surface treated with an adhesion promoter, namely a silane with amino and vinyl functionalities. These permit it to crosslink with cementitious formulation components. Both the VISABEAD E-16 and VISABEAD L-511 beads behave similarly in the cementitious mixture, except that the topsize of the VISABEAD E-16 bead is larger.

Marking Material Formulation	Weight Percent Mix 1	Mix 2
Silica sand	13.35	13.35
1/8“ (3.2 mm) glass flakes	2.00	2.00
16-18 mesh glass beads (VISABEAD L-511)	30.00	--.—
14-16 mesh glass beads (VISABEAD E-16)	--.--	30.00
Titanium dioxide	3.50	3.50
Defoamer	0.15	0.15
Acrylic Polymer	0.70	0.70
Melamine water reducer	0.30	0.30
Silica flour (140 mesh silica sand)	10.00	10.00
White Type I cement	40.00	40.00
	100.00	100.00
Percentage of Water Added	16.0	16.0
Consistency	flowable	flowable

Mix time was three (3) minutes for each.

Mix 2 remained flowable longer than Mix 1. Composite beams were cast over the concrete mixtures described below, approximately 30 minutes after mixing the concrete. The longer workability observed with Mix 2 is thought to be caused by a surface area effect.

Concrete Mix	Weight Percent
Medusa Type I	14.67
Concrete sand	37.46
Concrete stone	47.87
Water/cement ratio	0.41

Example 6

Samples of dry formulation cementitious marking materials having incorporated retroreflective glass beads are cast in petri dishes, and the surface is stamped to create a ridged, textured profile.

Marking Material Formulation	Weight Percent Mix 1	Mix 2
Silica Sand (30/50 mesh)	13.85	13.85
1/8“ (3.2 mm) glass flakes	1.50	1.50
16-18 mesh glass beads (VISABEAD L-511)	30.00	--.—
Titanium dioxide	3.50	3.50
Acrylic Polymer	0.70	0.70
Defoamer	0.15	0.15
Melamine water reducer	0.30	0.30
Silica flour	10.00	10.00
20/30 mesh glass beads (FLEXOLITE BT-3)	--.--	30.00
White Type I cement	40.00	40.00
	100.00	100.00
Percentage Water	16.0	17.0
Consistency	flowable	flowable

Mix time was three (3) minutes for each.

Stamping Procedure

Approximately 30 minutes after mixing, the surface of the petri dish samples are stamped using a square pattern branding pad to create a textured surface. After stamping the surface, a 1/16 inch (1.6 mm) ridge is created.

The surface of each stamped sample is screened using a 120 mesh carbide screen to expose the incorporated integral glass beads as on a worn roadway. The samples are checked qualitatively for retroreflection using a standard flashlight. Samples are placed on the floor in a dark room and the light is projected on to the surface. The areas where the beads are exposed exhibited retroreflection on contact with light. The reflectivity is similar to the STAMARK L380I notched tape from 3M, but not quite as pronounced.

Example 7

An integrated cementitious marking material formulation is prepared with an increased polymer level, to determine if improved surface integrity would result.

Marking Material Formulation	Mix Weight Percent
Silica Sand (30/50 mesh)	10.50
1/8“ (3.2 mm) glass flakes	2.00
16-18 mesh glass beads(VISABEAD L-511)	30.00
Titanium dioxide	5.00
Acrylic Polymer	4.00
Melamine water reducer	0.30
Silica flour	8.00
Defoamer	0.20
White Type I cement	40.00
	100.00
Percentage Water	17.0
Consistency	flowable

Mix time was three (3) minutes.

The surface of the cast petri dish pat is hard. Screening is difficult due to improved density and hardness of the surface. The carbide screen (120 mesh) used, is able to abrade the surface more easily after the initial layer of paste is removed. The increased polymer level improves the surface quality. A sample is cast in a petri dish with a surface retarder applied at stiffening produces a good exposure of the beads. The use of a surface retarder as a chemical texturizer retards the hydration of cement at the surface to obtain the desired exposure of the profile of the beads. This could optionally be employed to enhance reflection.

Example 8

An expansive agent is incorporated in the mix to compensate for shrinkage, and an air entrainer for freeze-thaw resistance. Samples are prepared and tested for retroreflectivity.

Marking Material Formulation	Weight Percents Mix 1	Mix 2	Mix 3	Mix 4
Silica sand	16.34	19.34	14.34	18.84
140 mesh Silica Sand	10.00	10.00	10.00	10.00
Defoamer	0.10	0.10	0.10	0.10
Melamine water reducer	0.30	0.30	0.30	0.30
Acrylic Polymer	1.75	1.75	1.75	1.75
16-18 mesh glass beads (VISABEAD L-511)	30.00	30.00	30.00	30.00
Calcium oxide	2.50	2.50	2.50	--.--
Air entrainer	0.01	0.01	0.01	0.01
1/64“ (0.4 mm) glass flakes	--.--	--.--	--.--	
Titanium dioxide	4.00	--.--	--.--	4.00
Black iron oxide	--.--	--.--	6.00	--.—
Yellow pigment	--.--	1.00	--.--	--.—
White Type I cement	35.00	35.00	--.--	35.00
Gray Type I cement	--.--	--.--	35.00	--.—
	100.00	100.00	100.00	100.00
Percentage Water Consistency	14.0 leveling	14.0 leveling	17.0 patching	15.0 screedable

Mix time is four (4) minutes for each

Composite Beams

Marking material from each mix is cast over concrete beams at ¼ inch (6.4 mm) thickness approximately 30 to 60 minutes after screeding the concrete. The surface of the concrete is raked prior to application of the marking material. Concrete beams are cast in a 2“x2“x10“ (5.1x5.1x25.4 cm) length change mold from the concrete mix set forth below. Approximately 5 to 10 minutes after placing the coating over the concrete, a layer of the glass beads is applied by broadcasting the beads on to the surface of the coating from each mix at a rate of approximately 0.02 pounds per linear foot (approx. 3kg/m^2).

N.B. The “linear foot” assumes a standard U.S. stripe width of 4 inches. Thus, a linear foot represents an area of 0.33 sq.ft. (0.03/m^2).

Concrete Mix	Weight Percent
Medusa Type I	14.67
Concrete sand	37.46
Concrete stone	47.87
Water/cement ratio	0.385

A retroreflection test conducted with a standard flashlight exhibits good retroreflection of the light beam. The depth of bead penetration determines the degree of retroreflection. The more the beads are exposed, the greater the entrance of light that is permitted and the greater the subsequent retroreflection that is exhibited.

Example 9

An integrated cementitious marking material is prepared, incorporating an expansive agent and an air entraining agent. Silica flour is replaced with 100 mesh silica sand.

	Weight Percent	
Marking Material Formulation	Mix 1 - white	Mix 2 - yellow
Silica sand	20.94	23.44
100 mesh Silica Sand	10.00	10.00
16-18 mesh glass beads(VISABEAD L-511)	26.00	26.00
Titanium dioxide	3.50	--.—
Defoamer	0.10	0.10
Acrylic Polymer	1.75	1.75
Air entrainer (SILIPON (trade mark) RN6031)	0.01	0.01
Melamine water reducer	0.20	0.20
Calcium oxide	2.50	2.50
White Type I cement	35.00	35.00
Yellow pigment (HANSA DCC1103)	--.--	1.00
	100.00	100.00
Percentage of Water Added	13.0	16.8
ASTMC 230 Percentage Flow (5 drops)	73.0	74.0
Unit Weight	135 lb/ft^3 (2162.5 kg/m^3)	130 lb/ft^3 (2082.4 kg/m^3)
Consistency	patching	patching

Concrete Mix	Weight Percent
Medusa Type I	14.67
Concrete sand	37.46
Concrete stone	47.87
Water/cement ratio	0.409

The above concrete mix is cast into 4“x16“x3“ (10.2x40.6x7.6 cm) molds half hour prior to mixing cementitious marking topping. The surface of the concrete

is raked in crossed sections. The topping is placed and screeded to approximately 1/8 inch (3.2 mm) thickness. Both mixes stiffened more than usual, less flow was obtained. Glass beads, 16-18 mesh (VISABEAD L-511), are broadcast on the surface of each beam at a rate of 0.10 pounds per linear foot (approx. 1.5 kg/m^2). Because of the stiffer consistency, the samples are vibrated to facilitate bead penetration.

A retroreflection test conducted with light shown from a standard flashlight exhibits good retroreflectivity of the light beam. Retroreflectivity is equal to or better than retroreflectivity of the corresponding color of 3M STAMARK L420 plain tape, and 3M STAMARK L380I notched tape.

The compressive strength of the resulting topping is tested by ASTM-C109 at seven (7) days, with the results as shown below.

Compressive Strength at 7 days	Mix 1	Mix 2
psi	7605	5916
MPa	52.5	40.8

Example 10

Samples of integrated marking material, having both incorporated and surface broadcast retroreflective beads, are prepared for retroreflectivity testing.

	Weight Percent		
Marking Material Formulation	Mix 1 (white)	Mix 2 (white)	Mix 3 (yellow)
Silica sand	16.84	16.84	19.34
100 mesh Silica Sand	10.00	10.00	10.00
16-18 mesh glass beads(VISABEAD L-511)	30.00	30.00	30.00
Titanium dioxide	3.50	3.50	--.—
Defoamer	0.10	0.10	0.10
Acrylic Polymer	1.75	1.75	1.75
Air entrainer (SILIPON RN6031)	0.01	0.01	0.01
Melamine water reducer	0.30	0.30	0.30
Calcium oxide	2.50	2.50	2.50
White Type I cement	35.00	35.00	35.00
Yellow pigment (HANSA DCC1103)	--.--	--.--	1.00
	100.00	100.00	100.00
Percentage Water Added	14.0	13.0	17.0
Flow, inches (2 inch by 4 inch (5.1x10.2 cm) cylinder)	10.5	10.0	3.0

Mix time was three (3) minutes for each mix.

Sample preparations

The marking material is poured into petri dishes. Additional glass beads, 16-18 mesh (VISABEAD L-511), are broadcast on the surface of each pat at a rate of 0.10 pounds per linear foot (approx. 1.5 kg/m^2). The degree to which the beads sunk into the cementitious material is found to be based on consistency of the cementitious mix.

Mix 1 – beads sunk approximately 90% into mix.

Mix 2 – beads sunk approximately 75% into mix.

Mix 3 – beads sunk approximately 75% into mix.

Retroreflection tested with a standard flashlight confirms that the depth of penetration of the broadcast layer of beads determines the level of retroreflection. Mix 2 exhibits higher reflectivity (visually) as compared to Mix 1. However, even the 90% sunk sample of Mix 1 shows acceptable reflectivity compared to the corresponding color of 3M STAMARK L420 plain tape and 3M STAMARK L380I notched tape.

Example 11

Additional samples of cementitious marking material having both incorporated and broadcast retroreflective beads, are prepared for retroreflectivity testing.

	Weight Percent		
Marking Material Formulation	Mix 1 (white)	Mix 2 (yellow)	Mix 3 (black)
Silica Sand	16.94	19.39	16.24
140 mesh Silica Sand	10.00	10.00	10.00
16-18 mesh glass beads(VISABEAD L-511)	30.00	30.00	30.00
Defoamer	0.10	0.10	0.10
Black iron oxide pigment	--.--	--.--	4.00
Air entrainer	0.01	0.01	0.01
Melamine water reducer	0.20	0.25	0.40
Calcium oxide	2.50	2.50	2.50
Yellow pigment (HANSA DCC1103)	--.--	1.00	--.--
Acrylic Polymer	1.75	1.75	1.75
White Type I cement	35.00	35.00	--.--
Type II cement	--.--	--.--	35.00
Titanium dioxide	3.50	--.--	--.--
	100.00	100.00	100.00
Percent Water	15.0	16.0	18.0
Flow, inches (cm)	7.5 (19.05)	9.125 (23.2)	7.0 (17.8)

Mix time was four (4) minutes for each mix.

Mix 1 stiffens approximately 10 minutes after mixing. Mix 2 remains workable for several hours.

Samples of the cementitious marking materials are cast in petri dishes, and glass beads, 16-18 mesh (VISABEAD L-511), are broadcast on the surface of each pat at a rate of 0.10 pounds per linear foot (approx. 1.5 kg/m^2).

Example 12

Formulations of yellow and white cementitious marking coating materials with water proofing properties are prepared and tested, with broadcast glass flakes and glass beads.

Marking Material Coating Formulation	Mix 1 (white)	Mix 2 (yellow)
50 mesh white Silica Sand	16.925	18.30
100 mesh Silica Sand	16.925	18.30
Sodium oleate	0.25	0.25
Mixed stearates	0.50	0.50
Defoamer	0.35	0.35
Acrylic Polymer	6.00	6.00
Hydrophobic aluminum silicate	2.75	2.75
Melamine water reducer	0.80	0.80
Calcium carbonate	10.50	10.50
Yellow pigment (HANSA DCC1103)	--.--	1.25
Titanium dioxide	4.00	--.—
White Type I cement	40.00	40.00
Wollastonite fibers (NYAD G fibers)	1.00	1.00
	100.00	100.00
Percent Water Added	24.0	24.0
Percent Flow (5 drops) – ASTM C230	108.0	120.0
Flow, inches (2 inch (5.1 cm) by 7/8 inch (2.2 cm) cylinder)	6.0	6.25

Mix time was four (4) minutes for each mix.

The consistencies of Mix 1 and Mix 2 are good; however, white patches and unmixed stearates are present in Mix 2. As mixed stearates are an optional component of the coating material, they need not be used in either white or yellow formulations.

Samples of each mix are placed over precast concrete at a thickness coating of 1/32 inch (0.8 mm). The hardened precast concrete slab is lightly sandblasted and pre-wetted before application of the coating. One half of the coated section of both the yellow and white stripes are seeded with glass flakes (1/8“ (3.2 mm)) and the other with glass beads. Coverage for the beads and flakes is approximately 0.01 pounds per linear foot (approx. 1.5 kg/m^2). The glass beads are easy to apply and the effect of their reflective properties results in higher visibility than is obtained by using the glass flakes.

Example 13

Formulation	Weight Percent Mix 1	Mix 2
50 mesh silica sand	17.76	20.67
100 mesh silica sand	10.00	10.00
16-18 mesh glass beads (Visa Bead L-511)	30.00	30.00
Defoamer	0.06	0.08
Titanium Dioxide	4.00	--.--
Hansa Yellow, DCC 1165	--.--	1.00
Melamine water reducer	0.18	--.—
Sodium naphthalene sulfonate water reducer	--.--	0.15
Sodium carbonate	0.15	0.20
Calcium oxide	0.50	0.50
Acrylic redispersible polymer	1.75	1.75
Neopentyl glycol	0.50	0.50
White calcium aluminate cement	0.10	0.15
White type 1 cement	35.00	35.00
Percentage water added	11.04	11.34
Mixing time	4 mins.	4 mins.
Flow, inches (2"x4" (5.1x10.2 cm) cylinder)	7.75	7.125
Unit Weight	131 lb/ft^3 (2098.4 kg/m^3)	135 lb/ft^3 (2162.5 kg/m^3)
Stiffening rate	1 hr. 35 min.	1 hr. 19 min.
Initial set	1 hr. 55 min.	1 hr. 39 min.
Final set	3 hrs. 20 min.	2 hrs. 24 min.

The performance of certain integrated cementitious marking materials prepared in the foregoing examples is evaluated for compressive and flexural strength, splitting tensile strength and pull-off bond reported in pounds per square inch (psi) and parenthetically in megapascals (MPa) in Table I below. Dry shrinkage of the material is tested by ASTM C-157 (modified) and reported as percent change in Table I. Specimens are moist cured for one day, then air cured for the remainder of the test. The ASTM test protocols followed for each measurement are also listed in the Table.

The test results demonstrate that the integrated cementitious marking materials of the present invention are suitable for use in roads and highways, as well as other paved surfaces such as airfield runways, parking lots, parking decks and garages, and

the like. It should be understood that the examples are provided for illustrative purposes only, as further exemplification of how to make and use the marking materials of the present invention. Integrated marking materials according to the present invention can be formulated according to techniques known in the art to meet performance criteria required for specific applications.

Table I

Integrated Marking Material Performance

	1 Day		28 Days
Ex 13 Mix 1 (White)	psi (MPa)		psi (MPa)
Compressive Strength ASTM C-109	2940 (20.3)		6727 (46.4)
Flexural Strength ASTM C-348	657(4.53)		878(6.0)
Splitting Tensile ASTM C-496	341(2.35)		479(3.3)
Pull-off Bond ASTM D-4541	208(1.4)		233(1.6)
Drying Shrinkage (% change)	3-Days	7-Days	
ASTM C157/ICRI (modified)	-0.031	-0.058	-0.095
Ex 13 Mix 2 (Yellow) Compressive Strength ASTM C-109	3832(26.4)		8838(61.0)
Flexural Strength ASTM C-348	742(5.1)		1116(7.7)
Splitting Tensile ASTM C-496	360(2.5)		706(4.9)
Pull-Off Bond ASTM D-4541	200(1.4)		283(2.0)
Drying Shrinkage (% change)	3-Days	7-Days	
ASTM C157/ICRI (modified)	-0.023	-0.047	-0.091

Example 14

Eight samples of horizontal retroreflective coatings are evaluated for retroreflective luminance according to ASTM D-4061 93b.

Five samples are selected from cementitious marking materials containing the retroreflective agent and polymeric cement modifier according to the present invention, in white, yellow and black, to be compared against 3M STAMARK L420 white and 3M STAMARK L421 yellow highway marking tapes, and a black highway marking tape from Stimsonite.

Table II below shows the retroreflected luminance data obtained for both white and yellow light sources.

The evaluation is run according to ASTM D-4061 93b. Data was obtained using Photoresearch Division of Macbeth Kollmorgen, PR-703 Spectraradiometer. Two light sources are used to generate the data. The "white or standard" lamp is a Sylvania H4703 Halogen low beam lamp. The "yellow or fog" lamp is a Blazer International C 1075K8M Halogen Fog lamp.

The samples are run at a geometry maintained at an 86° entrance angle and 0.2° observer angle geometry per the ASTM D-4061 method. Checks during measurement show no significant variance at a constant observation angle. The final converted units are in English (millicandelas per square foot per foot-candle) or in Metric (millicandelas per square meter per lux). Numerically the results are the same.

The data in Table II present values that compare the total reflected luminance at the test conditions with each lamp type. The last two columns apply the correction factor for size ratio by dividing the result to the left of the normalized area factor by the factor and reporting in these two columns. There is no correction applied to the reference samples since it would be 1.0 as a factor.

Based on white auto lamp source retroreflection testing Sample 1 has one half the retroreflectance of Sample 2. Compared to the 3M reference tape the Sample 2 retroreflects better. Sample 1 reflects less. Sample 1 has the broadcast retroreflective beads embedded approximately 90%, while Sample 2 has the broadcast retroreflective beads embedded approximately 50%.

The two white test samples are also different. Sample 3 has about one half the reflectance of Sample 4. Uncorrected Sample 4 is less retroreflective than the 3M reference tape sample. With the area correction factor applied, Sample 4 reflects better than the 3M reference tape sample. The black Sample 5 is larger than the Stimsonite sample evaluated. The uncorrected value of the retroreflected luminance of Sample 5 is significantly greater than the black reference tape, and corrected values are approximately equal.

Based on yellow auto fog lamp source retroreflection testing, the two yellow samples are nearly equal (Sample 1) and greater (Sample 2) than the yellow 3M reference tape sample retroreflectance coefficient. The rationalized values, modified for difference in area, are equal (Sample 1) and better (Sample 2) than the 3M yellow reference tape. The two white samples are one-half (Sample 3) of the other (Sample 4) in retroreflection. Sample 4 (with no area adjustment) is equivalent to the 3M white reference tape sample. The unadjusted black sample (#5) is better than the Stimsonite sample. Adjusted for area, the two samples are equal.

Use of the integrated marking material of the present invention is more favorable than prior art tapes and paints in view of the equivalent optical performance achieved, in addition to the extended lifetime of the integrated marking material as compared to tapes and paints.

Table II

Retroreflected Luminance Evaluation

Sample	Color of Sample	Material Tested	Area sq. in.	Raw Data mCd/m^2	Raw Data mCd/m^2	Retroreflected Luminance mcd/m^2/Lx*	Retroreflected Luminance mcd/m^2/Lx*	Normalized Area Factor	Normalized Data Retroreflected Lumin. (rational) mcd/m^2/Lx	Normalized Data Retroreflected Lumin. (rational) mcd/m^2/Lx
				White Light	Yellow Light	White Light	Yellow Light		White Light	Yellow Light
1	Yellow	Ex#11 Mix#2	21.11	20310	6175	548	167	0.84	649	197
2	Yellow	Ex#10 Mix#3	20.53	40380	12160	1090	328	0.82	1327	400
3	White	Ex#10 Mix#2	18.25	26340	9156	711	247	0.75	951	331
4	White	Ex#11 Mix#1	17.98	54740	14990	1477	405	0.74	2006	549
5	Black	Ex#11 Mix#3	18.81	6224	1437	168	39	1.71	98	23
6	Yellow	3M Tape #L421	25.00	31520	7226	851	195		851	195
7	White	3M Tape #L420	25.42	65590	14850	1765	401		1765	401
8	Black	Stimsonite Tape	10.98	4150	854	112	23		112	23

* - Evaluated per ASTM D4061 with Photoresearch PR703 Spectraradiometer at Observation angle of 0.2° and Entrance angle of 86°

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Claims:

1. A dry formulation for an integrated retroreflective marking material for concrete or asphalt applications comprising a cementitious mixture including a hydraulic or cementitious binder, a redispersible polymeric cement modifier, a retroreflective agent filler, and optionally, a reflective agent filler.

2. The formulation of claim 1 wherein the retroreflective agent is selected from the group consisting of glass beads, glass bubbles, glass spheres, ceramic spheres, plastic beads, fluorescent glass beads, fluorescent plastic beads and mixtures thereof, wherein the retroreflective agent has an average topsize of at least about 600 μM.

3. The formulation of claim 1 wherein the reflective agent is selected from the group consisting of glass beads, glass bubbles, glass flakes, glass spheres, ceramic spheres, plastic beads, florescent glass beads, fluorescent plastic beads and mixtures thereof, wherein the reflective filler has an average particle topsize of less than about 600 μM.

4. The formulation of claim 1 wherein the redispersible polymeric cement modifier is a dry polymer selected from the group consisting of acrylates, methacrylates, ethylene vinyl acetate, styrene-acrylate, styrene-butadiene, polyvinyl acetate, acrylonitrite-butadiene, polychloroprene, vinyl chloride, vinyl laurate, vinyl versatate, vinyl acetate, and blends, copolymers, or terpolymers thereof.

5. An integrated, retroreflective marking material for pavement applications prepared substantially on-site from a mixture of water with a dry formulation as set forth in claim 1.

6. A dry formulation for a cementitious marking material for concrete or asphalt, compatibilized for accepting retroreflective agents, comprising a cementitious mixture including a hydraulic or cementitious binder and a redispersible polymeric cement modifier, the modifier being present to the extent of from 0.5-8% when the binder is portland cement and from 0.2-2% when the binder is a quick-setting cement.

7. A cementitious marking material for concrete or asphalt applications prepared substantially on-site from a mixture of water with a dry formulation comprising a cementitious mixture including a hydraulic or cementitious binder and a redispersible polymeric cement modifier, said marking material having retroreflective agents at least partially embedded in its surface.

8. A dry formulation for an integrated retroreflective marking material for concrete or asphalt applications comprising a mixture including a hydraulic binder of at least one of magnesium phosphate cement and magnesium potassium phosphate cement, a retroreflective agent filler, and optionally, a reflective agent filler.

9. An integrated retroreflective marking material for concrete or asphalt applications comprising a surface including a hydraulic binder of at least one of magnesium phosphate cement and magnesium potassium phosphate cement, having an at least partially embedded broadcast of retroreflective agent particles having a topsize of at least about 600 microns at the surface.

10. A process of marking a surface of concrete or asphalt, by applying thereto a liquid integrated retroreflective marking material according to claim 5.