

PAVEMENT MARKING COMPRISING A MIXTURE OF OPTICAL COMPONENTS

TECHNICAL FIELD

[001] The present invention relates to pavement markings comprising a mixture of optical components and methods of making a pavement marking.

BACKGROUND ART

[002] Pavement markings have been a ubiquitous feature of vehicular roads and have played an essential role in ensuring road safety by using materials that enhance its visibility throughout the day. Pavement markings that include glass beads for enhancing the reflection of light are described, for example, in U.S. Patent No. 2,574,971. Glass beads used in pavement markings to reflect light from vehicular headlights back to the driver work well when the pavement marking is freshly set and the road surface is dry, but over a period of time, the retroreflective quality of the pavement marking deteriorates because the impact of tyres and pedestrians walking on the optical components inevitably causes the optical components to be crushed, broken and dislodged. For busy roadways where there is a high volume of traffic, or a high frequency of start-stop traffic such as in urban areas, or highspeed traffic such as highways, the deterioration of a pavement marking occurs more quickly than on average roads.

[003] Standards established by government departments typically specify a minimum retroreflective performance after a specified duration. For example, the Singapore Standard SS 589 “Specification for hot-applied thermoplastic road marking materials” specifies for white markings a minimum coefficient of retro-reflected luminance R_L (mcd/m²/lx) of at least 300 under dry conditions when new and at least 150 after 5 months.

[004] In order to meet these stringent requirements, there is a need to provide an improved pavement marking composition that overcomes or at least ameliorates the disadvantages described above.

SUMMARY

[005] In an aspect, embodiments of the present disclosure relate to a pavement marking comprising a binder and a mixture of optical components at least partially embedded on the surface of the binder, the optical components comprising: retroreflective elements each comprising a core and a plurality of particles bonded to the core, a first group of glass microspheres having a mean diameter falling within a first size gradation, and a second group of glass microspheres having a mean diameter falling within a second size gradation, the second group of glass microspheres having a smaller mean diameter and a higher refractive index than the first group of glass microspheres.

[006] Advantageously, a pavement marking as described herein comprises glass microspheres with tiered sizing. Different populations of glass microspheres each having a selected size range enables the glass microspheres to be progressively exposed to the physical impact of traffic. The smaller sized glass microspheres are shielded from mechanical damage until the larger sized glass microspheres are worn out.

[007] In addition, the smaller sized glass microspheres are selected to have a higher refractive index than the larger sized glass microspheres. This enables the second group of glass beads to help maintain retroreflective performance of the pavement marking after the larger first group of glass microspheres are worn out or damaged.

[008] In another aspect, there is provided a method of forming a pavement marking, comprising: applying a liquid pavement marking composition comprising a curable binder onto a pavement surface, dropping a mixture of optical components onto the liquid pavement marking composition, the optical components comprising: retroreflective elements each comprising a core and a plurality of particles bonded to the core, said retroreflective elements having a mean diameter falling within a first range, a first group of glass microspheres having a mean diameter falling within the first range, and a second group of glass microspheres having a mean diameter falling within a second range, wherein the second group of glass microspheres has a smaller mean diameter and a higher refractive index than the first group of glass microspheres; and then allowing the liquid pavement marking composition to cure.

BRIEF DESCRIPTION OF DRAWINGS

[009] The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

[0010] Fig. 1 is a schematic view of an embodiment of a pavement marking comprising two different sizes of glass microspheres.

[0011] Fig. 2 is a schematic view of an embodiment of a pavement marking comprising three different sizes of glass microspheres.

[0012] Fig. 3 shows a photograph of the surface of Sample A (conventional) in accordance with Example 1.

[0013] Fig. 4 shows a photograph of the surface of Sample B in accordance with the invention as described in Example 1.

[0014] Fig. 5 shows the initial retroreflective performance of the invention compared to a conventional sample.

[0015] Fig. 6 shows the dry retroreflective performance of the invention compared to a conventional sample.

[0016] Fig. 7 shows the wet retroreflective performance of the invention compared to a conventional sample.

DETAILED DESCRIPTION

[0017] The inventors of the present disclosure have found that the use of two or more populations of optical components with tiered sizes and tiered refractive index levels can effectively prolong the retroreflective performance of a pavement marking. This is achieved by pavement markings comprising glass microspheres of at least two different size gradations, i.e. a first and a second group of glass microspheres wherein the second group of glass microspheres has a smaller mean diameter than the first group. In addition, the second group of smaller-sized glass microspheres have a higher refractive index. Without being limited by theory, it is thought that a tiered size selection of

optical components will enable the optical components in the pavement marking to be exposed to traffic in stages over time. In other words, the larger sized glass microspheres will be exposed to traffic first while it shields smaller sized glass microspheres and retroreflective elements from mechanical damage during an initial period of traffic exposure. When the larger sized glass microspheres become gradually worn out, either being reduced in height, or crushed or dislodged, then the initially obscured and smaller sized second group of glass microspheres become exposed to traffic as well as in vehicular light. In this regard, consider the observation angle of a light beam from a vehicle. The light beam initially falls incident on the larger sized glass microspheres because of its greater height than surrounding smaller microspheres. As the larger sized glass microspheres get worn out, light from vehicles starts to fall incident onto the smaller glass microspheres and similarly get retroreflected back to the vehicle, notwithstanding the loss of retroreflectivity from the damaged larger sized glass microspheres. In addition, the selection of a higher refractive index for the smaller sized second group of glass microspheres helps to offset the loss of retroreflectivity from the wearing out of the first group of glass microspheres as well as the accumulation of dirt during the initial period of traffic exposure.

[0018] In this document, the following words and terms used herein shall have the following meaning:

[0019] The terms "beads" and "microspheres" are used interchangeably and refer to particulate material of any shape, such as spherical, ellipsoidal or cuboidal shapes.

[0020] The term "glass microspheres" refer to microspheres that are made of glass and/or glass-ceramic materials. Glass-ceramic materials refer to materials such as silica, alumina and zirconia.

[0021] The term "retroreflective" as used herein refers to the attribute of reflecting an incident light ray in a direction generally antiparallel to its incident direction such that it returns to the light source or the immediate vicinity thereof.

[0022] The recitation of all numerical ranges by endpoint is meant to include all numbers subsumed within the range (i.e., the range 1 to 10 includes, for example, 1, 1.5, 3.33, and 10).

[0023] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0024] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[0025] As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

[0026] Throughout this disclosure, certain embodiments may be disclosed in a range format. The description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[0027] Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether the excised material is specifically recited herein.

[0028] The pavement marking described herein comprise a binder and a mixture of optical components at least partially embedded on the surface of the binder. The mixture of optical components comprise bonded core retroreflective elements comprising microcrystalline particles bonded to a centre core. It also comprises glass microspheres

wherein a first group thereof is of a first size gradation, and a second group thereof is of a second, smaller size gradation and having a higher refractive index than the first group of glass microspheres.

[0029] Bonded core retroreflective elements refer to retroreflective elements that are in a bonded core construction, in which small microcrystalline particles are bonded to or partially embedded at the surface of a larger-sized, centre core. The retroreflective properties of bonded core retroreflective elements remain intact even after continued application of external forces and stresses. Examples of microcrystalline particles include reflective particles derived from high refractive index materials. In an exemplary embodiment, the particles comprise microcrystalline ceramic particles such as glass or glass-ceramic particles. Advantageously, microcrystalline ceramic particles are characterised by internal microcrystalline structure which prevents cracks from starting and propagating, resulting in improved toughness. The core may comprise materials such as glass, ceramic, organic polymers, metal-polymer nanocomposite, or an oxide such as silicon dioxide. Some exemplary cores are described in, for example, U.S. Patent Nos. 5,774,265; 5,942,280; 7,513,941, and WO2017/044418 all of which are incorporated herein by reference. One exemplary type of core is a sand core, which is described generally in U.S. Patent Publication No. 2005/0100709. In some embodiments, the core is selected from a sand core, sand, glass, polymer, or ceramic. An exemplary form of durable retroreflective elements is one in which the core comprises an ionic copolymer, as described in WO2017044425A1 and is incorporated herein in its entirety. The term "ionic copolymer" refers to materials that include a fraction of ionized units covalently bonded to a polymer backbone as pendant group moieties. In some embodiments, the ionic copolymer is a thermoplastic, which enables processing using an extruder as compared to thermoset or highly crosslinked materials, like epoxy. In one embodiment, the ionic copolymer has a Shore D hardness between 36 and 68. In one embodiment, the ionic copolymer has a Shore D hardness of 66.

[0030] Examples of glass or glass ceramic particles are described in U.S. Patent Nos. 3,493,403; 3,709,706; 4,564,556; 6,245,700 and 7,524,779, all of which are incorporated herein in their entirety. In some embodiments, the glass or glass ceramic particles include at least one or more of, for example, a lanthanide series oxide, Al_2O_3 , TiO_2 , BaO , SiO_2 , or ZrO_2 . Examples of commercially available bonded core

retroreflective elements include, for example, Reflective Elements and All Weather Elements made by 3M Company of St. Paul, MN, USA.

[0031] Retroreflective elements may have a size distribution anywhere between several hundred microns to several thousand microns. In exemplary embodiments, such as in bonded core elements, they may have a size distribution of between 500 μm and 2000 μm , or more particularly 600 μm and 1700 μm . Within this size distribution, the mean diameter of the retroreflective elements may be between 1180 and 1410 μm . This corresponds to US Mesh (ASTM D1214) size 16 and 14. In another embodiment, the mean diameter of the retroreflective elements may be between 1000 μm and 1180 μm . This corresponds to US Mesh (ASTM D1214) size 18 and 16. In another embodiment, small elements may have a mean diameter of between 850 μm to 1180 μm and large elements may have a mean diameter of between 1000 μm to 1140 μm .

[0032] By using high refractive index particles, the bonded core retroreflective particle construction achieves a correspondingly high refractive index, generally being 1.9 and above, or preferably above 2.1, or in some cases above 2.4. High refractive index particles may comprise high refractive index glass or glass-ceramic particles. In some embodiments, the glass or glass ceramic particles have refractive indices of between about 1.5 and about 2.6. In some embodiments, the glass or glass ceramic particles have refractive indices of between about 1.8 and about 2.3. In some embodiments, the glass or glass ceramic beads have a mean refractive index of between about 1.8 and about 2.3. In some embodiments, the glass or glass ceramic particles have a refractive index of between about 1.9 and about 2.2. In some embodiments, the glass or glass ceramic particles have a refractive index of about 1.9. In some embodiments, the glass or glass ceramic particles have a refractive index of about 2.2.

[0033] In some embodiments, the glass or glass ceramic particles have mean or average diameters of 30-200 microns. In some embodiments, the glass or glass ceramic particles have mean or average diameters of 50 - 100 microns. In some embodiments, the glass or glass ceramic particles have mean or average diameters of 60 - 80 microns.

[0034] Another type of optical component used in conjunction with the retroreflective elements are glass microspheres, which are a lower cost material than retroreflective elements and is more prone to deterioration but has similar retroreflective characteristics.

Therefore, by selecting a complementary size and refractive index for the glass microspheres, one can enhance the behaviour of the pavement marking while reducing the total costs. In this case, two or more groups of glass microspheres are used to achieve a tiered, large-small glass microsphere sizing in the binder in order to achieve the sequential exposure of the glass microspheres to traffic. The first group of glass microspheres has a comparable size, preferably a larger size than, or a similar size to, the retroreflective elements. The second group of glass microspheres has a smaller size than the first group of glass microspheres. Current industrial production methods yield glass microsphere sizes that are typically spread over a range of sizes rather than being of a uniform size. In some cases, the sizes are distributed in a bell-shaped curve where the distribution peaks around a mean diameter. Accordingly, one way to characterise the size of the glass microspheres is by specifying its size gradation. The first and second groups of glass microspheres are selected from different size gradations. In one embodiment, the first group of glass microspheres are selected from a first size gradation of between about 600 μm to about 1700 μm . For example, the first group of glass microspheres are selected from a size gradation of between 710 μm to about 1700 μm . Such glass microspheres may comprise British Standard (B.S.) 6088-1981 Class A or AASHTO M247 type 3 or 4 glass beads. This corresponds to US Mesh (ASTM D1214) size 30 to 12. In another embodiment, the second group of glass microspheres are selected from a second size gradation of between about 150 μm to about 850 μm . Such glass microspheres may comprise B.S. 6088-1981 Class B or AASHTO M247 type 1 or 2 glass beads. This corresponds to US Mesh (ASTM D1214) size 100 to 20. In a further embodiment, the pavement marking further comprises a third group of glass microspheres of a smaller size gradation and a higher refractive index than the second group of glass microspheres.

[0035] Another way to characterise the glass microspheres is by specifying its mean diameter. In a preferred embodiment, the first group of glass microspheres has a mean diameter of between 600 μm to 1400 μm . The second group of glass microspheres has a mean diameter of between 300 μm and 850 μm . In certain embodiments, the second group of glass microspheres has a mean diameter that is generally between 40% to 70% of the mean diameter of the first group of glass microspheres. In exemplary embodiments, the first group of glass microspheres may comprise European Standard (EN) 1423 Type 3, 4 or 5 glass microspheres, and have a refractive index of about 1.5.

The second group of glass microspheres may comprise European Standard (EN) 1423 Type 1, 2 or 3 glass microspheres and have a refractive index higher than the first group of glass microspheres, being at least 1.6, preferably 1.9 or 2.1, and above.

[0036] The glass microspheres may have a generally spherical, cuboidal, oval or ellipsoidal shape, or in some cases an irregular shape, although a spherical shape is preferable for providing good retroreflectivity. The glass in the glass microspheres may be derived from virgin glass or recycled glass. In other embodiments, glass microspheres may also comprise glass-ceramic materials including Al_2O_3 , TiO_2 , BaO , SiO_2 , ZrO_2 and lanthanide series oxides. In certain embodiments, a mixture of glass and glass ceramic microspheres may also be used.

[0037] The binder affixes the optical components to a pavement surface. Pavement surfaces are typically substantially solid and typically include a major portion of inorganic materials. Exemplary pavement surfaces include asphalt, concrete, and the like. The binder is typically, for example, a paint, a thermoplastic material, thermoset material, or other curable material. In an embodiment, the binder is selected from an alkyd resin, high build acrylic paint and thermoplastic resin. Common binder materials include polyacrylates, methacrylates, polyolefins, polyurethanes, polyepoxide resins, phenolic resins, and polyesters. For reflective pavement marking paints, the binder may include reflective pigment. In one embodiment, the binder comprises a 7% to 80% ethylene vinyl acetate (EVA) and are described in WO2015/123625. In another embodiment, the pavement marking comprises a 5-carbon (C5) hydrocarbon resin. The binder may be formed with a thickness of above 15 mils, 20 mils, 40 mils, or in the case of certain alkyd or thermoplastic resins, the binder has a thickness of 60 mils, and above.

[0038] The pavement marking described in this document generally has a night time initial coefficient of retroreflected luminance (R_L) of above 300, 500, 600, or 800 $\text{mcd/m}^2/\text{lx}$ under dry conditions, and above 200, 300, or 350 $\text{mcd/m}^2/\text{lux}$ under wet conditions.

[0039] Fig. 1 shows a schematic view of an embodiment of a pavement marking described herein. Pavement marking 100 is arranged on a surface 101, such as a road surface, and comprises a binder 110 and optical components 120 arranged on its surface. Optical components comprise retroreflective elements 130, and two types of glass

microspheres 140, 150. Retroreflective elements 130 comprise a core 133, and has retroreflective particles 135 bonded to the periphery of the core 133. Glass microsphere 140 is of a larger or comparable size to the retroreflective elements 130, and glass microsphere 150 is of a smaller size than glass microsphere 140 but has a higher refractive index.

[0040] Fig. 2 shows a schematic view of another embodiment in which three types of glass microspheres 240, 250 and 260 are used. Glass microsphere 260 is larger than the rest of the optical components, while glass microsphere 240 is of a comparable size to retroreflective element 230, and glass microsphere 250 is the smallest optical component present.

[0041] In order to form a pavement marking as shown in Fig. 1 and Fig. 2, the optical components 120, 220 are either separately or in groups, dropped sequentially or concurrently onto a heated liquified binder 110, 210. As the binder cools, it solidifies and holds the optical components in place. A commonly used device for dispensing optical components is known as a “double-drop” machine which is used to drop two groups of optical materials, such as glass beads and optical elements onto a liquefied binder. Typically, a bag of glass beads and optical elements are separately loaded into the machine. In some embodiments, the ratio of the weight of retroreflective elements to the total weight of the glass microspheres is between about 1:1.5 to 1: 2.5. In another example, the ratio of the weight of the first group of glass microspheres to the second group of glass microspheres present is between about 2:1 to 4:1.

[0042] In an embodiment, three types of glass microspheres are used in which a third group thereof is of a third size gradation smaller than the second group, and has at least the same or higher refractive index than the second group. In order to accommodate 3 or more optical components into a double drop machine without increasing the number of drop cycles, the smaller sized, second group of glass microspheres may be pre-mixed with the retroreflective elements and placed into the double drop machine as a first drop, while the first group of glass microspheres are placed into the double drop machine as second drop, for example.

[0043] In some embodiments, it may be advantageous to provide a hydrophobic coating to the first and/or second group of glass microspheres. In order to prolong the

retroreflectivity of the glass microspheres,. In one embodiment, the first and/or second group of glass microspheres comprise a hydrophobic coating. The hydrophobic coating may be selected from the group consisting of silicones, silanes, siloxanes, polydimethylsiloxanes, and fluoropolymers.

[0044] The pavement marking may further comprise other ingredients, such as an inorganic filler, a rheology modifier, a plasticizer, and a colour pigment. In various embodiments, the inorganic filler comprises calcium carbonate; the rheology modifier comprises polyethylene and bentonite clay. Colour pigments may be included in the pavement marking, including colours such as white titanium dioxide and ultramarine blue pigment.

EXAMPLES

[0045] Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1

[0046] A conventional pavement marking with single size glass microsphere was prepared according to Table 1 (Sample A). Conventional Type 3 glass beads according to AASHTO M247 were used. A drop-on rate of 260 g/sqm was used, along with 3M® All Weather Elements White Series 90S (700-1400 um), with the drop rate of 230 g/sqm.

Material Description	Material Designation	Weight ratio
Intermix thermoplastic:		
Organic Binder	Hydrocarbon C5 Resin	18.00%
Inorganic Filler	Calcium Carbonate	50.00%
Rheology Modifier	PE Wax	3.00%
Plasticizer	White Oil	1.20%
Rheology Modifier	Bentonite Clay	2.72%
White Pigment	TiO ₂	7.00%
Color Correction Pigment	UltraMarine Blue	0.08%

Optical component 1	Conventional type 3 glass beads	15.00%
Optical component 2	3M All Weather Element 90S	3.00%
Total		100%
Drop-on Optical components:		
Optical component 1	Conventional type 3 glass beads	260 g/sqm
Optical component 2	3M All Weather Element 90S	230 g/sqm

Table 1: Sample A

[0047] For a comparative study, a pavement marking with tiered large-small sizing of glass microspheres according to the present disclosure (Sample B) was prepared according to Table 2.

Material Description	Material Designation	Weight ratio
Intermix thermoplastic:		
Organic Binder	Hydrocarbon C5 Resin	18.00%
Inorganic Filler	Calcium Carbonate	50.00%
Rheology Modifier	PE Wax	3.00%
Plasticizer	White Oil	1.20%
Rheology Modifier	Bentonite Clay	2.72%
White Pigment	TiO ₂	7.00%
Color Correction Pigment	UltraMarine Blue	0.08%
Optical component 1	Glass Microspheres T3 (850-1400 um)	10.00%
Optical component 2	Glass Microspheres CL. B (150-850 um)	5.00%
Optical component 3	3M All Weather Element White 90S (700-1400 um)	3.00%
Total		100%
Drop-on Optical components:		
Optical component 1	Glass Microspheres T3 (850-1400 um)	260 g/sqm
Optical component 2	Glass Microspheres CL. B (150-850 um)	60 g/sqm

	um)	
Optical component 3	3M All Weather Element White 90S (700-1400 um)	180 g/sqm

Table 2: Sample B

[0048] In Sample B, the first group of glass microspheres comprised Megalux 850-1400 um reflective glass beads from M. Swarco GmbH having refractive index of 1.5 Type 3 glass beads according to AASHTO M247. Drop rate for it was set at 260 g/sqm. The second group of glass microspheres comprised Solidplus100 180-850 um reflective glass beads also from M. Swarco GmbH having refractive index of 1.6 Class A according to BS 6088 Class B. Drop rate for it was set at about 60 g/sqm, which is about 4 to 5 times less than Optical component 1. The bonded core retroreflective elements used comprised 3M All Weather Element White 90S (size 850-1400 μm) having refractive index of 1.90 for Dry and 2.4 for Wet. The drop rate for it was set at 180 g/sqm, 50 g/sqm less than sample A.

[0049] **Retroreflectivity and Luminance.** After a period of 1-week exposure to a simulated traffic environment, the pavement marking samples were inspected. Fig. 3 shows a photograph of the surface of Sample A while Fig. 4 shows that of Sample B. Both retroreflectivity and luminance of the two pavement marking samples were measured. Table 3 shows the conventional pavement marking's dry and wet night visibility coefficient of retroreflected luminance (RL), as well as luminance coefficient under diffuse illumination for day visibility (Qd). Table 4 shows the measurements for Sample B.

NO.	R _i (dry)	R _i (wet)	Qd
1	896	296	182
2	703	337	194
3	926	322	180
4	645	273	193
5	937	245	183
6	449	345	203
7	416	350	189
8	620	299	190
9	645	319	187
Ave	693.0	309.6	189.0

Table 3

NO.	RL(dry)	RL(wet)	<u>Qd</u>
1	809	415	189
2	849	354	192
3	818	395	192
4	880	365	189
5	848	401	187
6	970	445	189
7	898	395	192
8	859	387	188
Ave	866.4	394.6	189.8

Table 4

[0050] It is observed that nighttime dry retroreflective performance is roughly 25% higher in sample B than in Sample A, increasing from 693 to 866.4 (~25% +). Wet retroreflective performance increases from 309.6 to 394.6 (~25% +). Daytime visibility remained comparable (189 vs. 189.8) with the conventional Sample A. These data are plotted in Fig. 5 along with the deviation. The data shows a much smaller deviation range in the nighttime dry retroreflection (R_L Dry) readings for Sample B, which indicates lower variability in the retroreflective performance behavior of Sample B as compared to Sample A.

[0051] The performance of pavement marking samples A and B were subsequently inspected continuously within a trial period of 65 weeks under 5000 annual average daily traffic (AADT). Fig. 6 shows dry retroreflective performance of both samples and Fig. 7 shows that of Sample B. From both figures, sample B demonstrates superior brightness than sample A for the entire service and inspection period. For instance, sample B final dry retroreflectivity is approximately 336 mcd/m²/lux after 65 weeks, +58% higher than sample A's 211.8 mcd/m²/lux.

Example 2

[0052] Other synthesis examples were prepared. In this example, a first group of glass microspheres comprised Megalux 850-1400 μ m reflective glass beads from M. Swarco GmbH having refractive index of 1.5 Type 4 glass beads according to

AASHTO M247. Drop rate was 230 g/sqm. A second group of glass microspheres comprised Solidplus100 180-850 um reflective glass beads also from M. Swarco GmbH having refractive index of 1.6 Class A according to BS 6088 Class B. Drop rate was about 50 g/sqm, which is about 4 to 5 times less than Optical component 1. Bonded core retroreflective elements comprised 3M All Weather Element White CR90 850-2000 um having refractive index of 1.90 for Dry and 2.4 for Wet. The elements' drop rate 150 g/sqm.

Material Description	Material Designation	Weight ratio
Intermix thermoplastic:		
Organic Binder	Hydrocarbon C5 Resin	18.00%
Inorganic Filler	Calcium Carbonate	50.00%
Rheology Modifier	PE Wax	3.00%
Plasticizer	White Oil	1.20%
Rheology Modifier	Bentonite Clay	2.72%
White Pigment	TiO ₂	7.00%
Color Correction Pigment	UltraMarine Blue	0.08%
Optical component 1	Glass Microspheres T4 (1000-1700 um)	10.00%
Optical component 2	Glass Microspheres CL B (150-850 um)	5.00%
Optical component 3	3M All Weather Element White CR90 (900-2000 um)	3.00%
Total		100%
Drop-on Optical components:		
Optical component 1	Glass Microspheres T4 (1000-1700 um)	230 g/sqm
Optical component 2	Glass Microspheres (150-850 um)	50 g/sqm
Optical component 3	3M All Weather Element White CR90	150 g/sqm

	(900-2000 um)	
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Table 5

Example 3

[0053] A further synthesis example was prepared. In this example, a first group of glass microspheres comprised Megalux 850-1400 um reflective glass beads from M. Swarco GmbH having refractive index of 1.5 Type 3 glass beads according to AASHTO M247. Drop rate was 230 g/sqm. A second group of glass microspheres comprised comprised Solidplus100 180-850 um reflective glass beads also from M. Swarco GmbH having refractive index of 1.6 Class A according to BS 6088 Class B. Drop rate was about 50 g/sqm, which is about 4 to 5 times less than Optical component 1. Bonded core retroreflective elements used comprised 3M All Weather Element White D-SEC with 700-1400 um having refractive index of 1.90 for Dry and 2.4 for Wet. The elements' drop rate 150 g/sqm.

Material Description	Material Designation	Weight ratio
Intermix thermoplastic:		
Organic Binder	Alkyd Resin	18.00%
Inorganic Filler	Calcium Carbonate	50.00%
Rheology Modifier	PE Wax	2.00%
Plasticizer	DOTP-168	1.46%
Rheology Modifier	Bentonite Clay	2.50%
White Pigment	TiO ₂	8.00%
Color Correction Pigment	UltraMarine Blue	0.04%
Optical component 1	Glass Microspheres T3 (850-1400 um)	10.00%
Optical component 2	Glass Microspheres CL B (150-850 um)	5.00%
Optical component 3	3M All Weather Element White D-SCE (700-1400 um)	3.00%
Total		100%
Drop-on Optical components:		

Optical component 1	Glass Microspheres T3 (850-1400 um)	230 g/sqm
Optical component 2	Glass Microspheres (150-850 um)	50 g/sqm
Optical component 3	3M All Weather Element White D-SCE (700-1400 um)	150 g/sqm

Table 6

Example 4

[0054] In this example, a first group of glass microspheres comprised Megalux 850-1400 um reflective glass beads from M. Swarco GmbH having refractive index of 1.5 Type 3 glass beads according to AASHTO M247. Drop rate was 200 g/sqm. A second group of glass microspheres comprised Solidplus100 180-850 um reflective glass beads also from M. Swarco GmbH having refractive index of 1.6 Class A according to BS 6088 Class B. Drop rate was about 100 g/sqm, which is about 4 to 5 times less than Optical component 1. Bonded core retroreflective elements used comprised 3M All Weather Element Yellow CR91 with 900-2000 um having refractive index of 1.90 for Dry and 2.4 for Wet. The elements' drop rate 100 g/sqm.

Material Description	Material Designation	Weight ratio
Intermix thermoplastic:		
Organic Binder	Hydrocarbon C5 Resin	18.00%
Inorganic Filler	Calcium Carbonate	56.00%
Rheology Modifier	PE Wax	3.00%
Plasticizer	White Oil	1.50%
Rheology Modifier	Bentonite Clay	2.00%
Yellow Pigment	PY83	1.50%
Optical component 1	Glass Microspheres T4 (1000-1700 um)	10.00%
Optical component 2	Glass Microspheres CL. B (150-850 um)	5.00%
Optical component 3	3M All Weather Element Yellow CR91	3.00%

	(900-2000 um)	
Total		100%
Drop-on Optical components:		
Optical component 1	Glass Microspheres T4 (1000-1700 um)	200 g/sqm
Optical component 2	Glass Microspheres CL. B (150-850 um)	100 g/sqm
Optical component 3	3M All Weather Element Yellow CR91 (900-2000 um)	100 g/sqm

Table 7

Industrial Applicability

[0055] The pavement marking may be useful as a road marking, for example as white, yellow and red lines for roads. The composition may be useful as markings for substrates other than roads, including in shipyards, factories with lane marking requirements and sporting venues.

[0056] It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A pavement marking comprising a binder and a mixture of optical components at least partially embedded on the surface of the binder, the mixture of optical components comprising:

bonded core retroreflective elements comprising microcrystalline particles bonded to a centre core, and

glass microspheres wherein a first group thereof is of a first size gradation, and a second group thereof is of a second, smaller size gradation and having a higher refractive index than the first group of glass microspheres.
2. The pavement marking of Claim 1, wherein the first size gradation is between about 710 μm to about 1700 μm .
3. The pavement marking of Claim 2, wherein the first group of glass microspheres comprise BS 6088 Class A or AASHTO M247 Type 3 or Type 4 glass beads, or a mixture thereof.
4. The pavement marking of any of the preceding claims, wherein the second size gradation is between about 150 to about 850 μm .
5. The pavement marking of Claim 3 and 4, wherein the second group of glass microspheres comprise BS 6088 Class B or AASHTO M247 Type 1 or Type 2 glass beads, or a mixture thereof.
6. The pavement marking of any of the preceding claims, wherein the first group of glass microspheres has a refractive index of about 1.5.
7. The pavement marking of any of the preceding claims, wherein the second group of glass microspheres has a refractive index of at least 1.6.
8. The pavement marking of any of the preceding claims, wherein the bonded core retroreflective elements have a mean diameter falling within the first size gradation.
9. The pavement marking of Claim 8, wherein the bonded core retroreflective elements have a mean diameter of between about 700 μm to about 2000 μm .
10. The pavement marking of any of the preceding claims, further comprising a third group of glass microspheres of a smaller size gradation and a higher refractive index than the second group of glass microspheres.

11. The pavement marking of any of the preceding claims, wherein the ratio of the weight of retroreflective elements to the total weight of the first and second group of glass microspheres is between about 1:1.5 to 1: 2.5.
12. The pavement marking of any of the preceding claims, wherein the weight ratio of the first group of glass microspheres to second group of glass microspheres is between about 2:1 to 4:1.
13. The pavement marking of any of the preceding claims, wherein the pavement marking has night time initial coefficient of retroreflected luminance (R_L) of above 800 mcd/m²/lux under dry conditions, and above 350 mcd/m²/lux under wet conditions.
14. A method of forming a pavement marking, comprising:

 applying a liquid pavement marking composition comprising a curable binder onto a pavement surface,

 dropping a mixture of optical components onto the liquid pavement marking composition, the optical components comprising:
 bonded core retroreflective elements comprising microcrystalline particles bonded to a centre core, and
 glass microspheres wherein a first group thereof is of a first size gradation, and a second group thereof is of a second, smaller size gradation and having a higher refractive index than the first group of glass microspheres;

 and allowing the liquid pavement marking composition to cure.
15. The method of Claim 14, wherein a mixture of the bonded core retroreflective elements and the second group of glass microspheres is dropped onto the binder simultaneously in a first step, and the first group of glass microspheres is dropped onto the binder in a second step.
16. The method of Claim 14, wherein the retroreflective elements are dropped onto the binder in a first step, and a mixture of the first and second groups of glass microspheres is dropped onto the binder in a second step.
17. The method of any of Claims 14 to 16, wherein a portion of the optical components is pre-mixed with the liquid pavement marking composition prior to its application on the pavement surface.
18. The method of any of Claims 14 to 17, wherein the retroreflective elements are dropped at a rate of about 80 g/m² to about 280 g/m².

19. The method of Claim 18, wherein the ratio of the weight of retroreflective elements to the total weight of the first and second group of glass microspheres is between about 1:1.5 to 1:2.5.
20. The method of any of Claims 14 to 19, wherein the weight ratio of the first group of glass microspheres to second group of glass microspheres is between about 2:1 to 5:1.