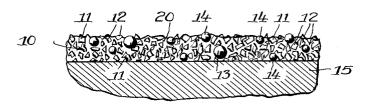
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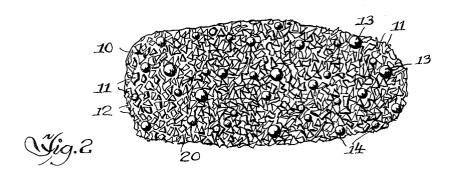
J. F. WYNN ET AL ROAD MARKING PAINT

YNN ET AL 3,005,790

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Inventors, James F. Wynn Harry N. Huntzicker, By: Schneider Dressler, Goldsmith & Element, Attys. 3,005,790
ROAD MARKING PAINT
James F. Wynn, Marietta, Ohio, and Harry N. Huntzicker,
Evanston, Ill., assignors to American-Marietta Company, a corporation of Illinois
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9 Claims. (Cl. 260—22)

The present invention relates to highway marking paint. More particularly, it relates to highway marking paints adapted to be sprayed, rolled or brushed on highway surfaces subject to vehicular traffic to provide reflex light-reflective traffic markers, e.g., centerlines, having high night-time visibility to motorists. The highway marking paints of the invention are particularly characterized by enhanced durability under normal conditions of abrasive vehicular wear and are further characterized in that they can be produced at lower cost, loaded with reflex reflecting elements to a greater extent and with improved suspension characteristics and provide greater resistance to skid than conventional reflective highway marking paints.

To the present time, the production of commercially suitable reflex reflective traffic markers has always been considered to require as an essential feature thereof, the use of spheres or beads to provide the reflex reflective action. Customarily, a paint composition was applied to the previously laid and partially dried paint. The reflective traffic markers so formed provided adequate initial reflex reflective qualities. However, the reflex reflective quality was short lived and not durable. Also, the two-stage application procedure was slow and laborious and added to the cost of producing the traffic marker.

In the United States patent to Heltzer, No. 2,574,971, dated November 13, 1951, "Highway Marking Paint Containing Glass Beads," the glass spheres or beads were incorporated in the paint and the paint and the glass spheres applied together in a single stage. The paint film above the beads of this composition is worn away to expose the tops of the beads and in this manner a reflex reflective surface is developed through wear. The durability of the reflex reflective action, although somewhat improved, does not provide the high standards of night-time visibility for adequately long periods of time.

When only a small proportion of the top of a given bead is exposed, the reflex reflective action is poor. When a larger proportion of the bead is exposed, the bead becomes easily dislodged and the surrounding paint is subjected to heavy wear. Thus, the reflex reflective action is limited by these two factors. When the beads become sufficiently exposed to participate effectively in the reflex reflective action, they tend to become easily dislodged. The effectiveness and durability of the traffic marker is thus substantially impaired.

When the marking paint is applied to the highway itself, the dislodged beads do more than reduce the reflective quality and durability of the marker, for these dislodged beads act as ball bearing surfaces to increase the tendency of dangerous skids by vehicles, especially under wet traffic conditions.

There is a further disadvantage to spheres which has escaped attention heretofore. Spheres or beads have been believed to be the best reflecting media, particularly when the viewing angle is of the order of 90° removed from the line of light directed at the beads. On the 65 highway, however, the driver never is in a position to view the reflected light at an angle of 90° because the headlights are forward of his position and do not light

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the beads at a point giving the driver a viewing angle even approaching 90°. At night, the light source, i.e. the automobile headlights, project a beam at an angle of incidence, even less than the angle at which the driver observes the reflected scattered light from a traffic paint marking on a road surface.

The present invention is based upon the discovery that reflex reflective qualities can be obtained using in a road marking paint, a combination of glass spheres and glass fragments of a nonspherical surface configuration, constituted by a multiplicity of angularly related planar surfaces. Glass fragments and glass beads combine to attain a high degree of light reflection as hereinafter explained and do not diffuse and dissipate the light to the detriment of visibility as would be expected from the random orientation of reflecting surfaces. This combination of reflex reflective glass material provides excellent visibility and a wider effective viewing angle.

It has been found that glass spheres and glass fragments both preferably graded to possess a range of particle sizes, form effective reflex reflective elements when incorporated in a conventional reflective traffic paint. The reflex reflective elements may be incorporated in the conventional traffic paint in amounts ranging from about 0.5 to 9 lbs. of glass material per gallon of glass-free paint.

When utilizing the combination of nonspherical planar glass fragments and glass spheres, the reflex reflective action is greatly improved and visibility is maintained for greatly extended periods of time. Intermingling of glass beads and glass fragments provides a longer lasting paint because securely anchored, dimensionally irregular glass fragments extending above the paint vehicle provide a retarding action to the wearing away of the paint vehicle between glass particles. With a paint vehicle of longer life, the rate at which glass beads become dislodged from the paint layers is markedly less than when the glass beads are used alone.

The nonspherical planar and angular glass fragments of the combination of fragments and spheres by virtue of their dimensional irregularity, and adjacent and overlapping positioning in the paint layer tend to be more securely keyed into the paint layer and are not dislodged as readily as beads by vehicular wear. This resistance to dislodgement is maintained despite the fact that a large portion of the upper surface of the fragment becomes exposed at the time when the fragment exhibits effective reflex reflective action. Beads or spheres on the other hand, have the paint worn from the surface thereof quicker than glass fragments to establish reflex reflective action more quickly after deposition of the paint on a pavement. By the use of the combination of two types of glass particles, the durability of the paint layer is greatly improved because the beads are protected against dislodgement through the presence of closely associated glass fragments solidly keyed in the paint layer and acceptable standards of night visibility are maintained for greatly extended periods of time.

The invention will now be described in greater detail with reference to the accompanying drawings in which:

FIGURE 1 is a diagrammatic sectional view taken through a reflex reflective highway marking paint constructed in accordance with the invention, said paint having been freshly painted on a highway;

FIGURE 2 is a fragmentary top plan view of the reflex reflective highway marking paint after the passage of vehicular traffic has abraded the upper surface of the paint to expose the upper portion of many of the reflex reflective elements incorporated therein.

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Referring more particularly to the drawing, the glass particles in FIGURE 1 are generically designated by the numeral 10 and, in accordance with preferred practice of the invention, a plurality of differently sized and shaped particles are present. Thus, the numeral 11 designates some of the larger sized fragments, the numeral 12 designates some of the smaller size fragments. The numeral 13 designates large glass spheres or beads and the numeral 14 designates smaller glass spheres.

The glass particles 11, 12, 13 and 14 are, as is ap- 10 parent from the drawings, and in the embodiment shown, made up of a plurality of non-spherical particles and a minor proportion of glass spheres embedded in a paint vehicle 20 overlaying a cement pavement 15. The various surfaces reflect light in an irregular manner and 15 are angularly interrelated.

While it has generally been assumed that such a combination of spherical and nonspherical particles would cause widespread dispersion of incident light, it has surprisingly been found that improved reflex reflective action 20 is achieved.

The beam of a motorist's headlights has a small angle of incidence with regard to the reflective particles. At a motorist's viewing angle of 2 to 12°, the reflective paint reflects back light fully satisfying rigid highway standards of brilliance. Moreover, adequate visibility is achieved at a range of angularities to permit a centerline to reveal a curve or sweep on the road ahead.

FIGURE 2 clearly shows the manner in which the paint layer 20 is worn away to expose a large portion of the upper surface of the glass fragments 10. As will be evident, a considerable portion of the fragments 10 are exposed and vehicular traffic cannot further wear away the paint layer 20 until the fragments 10 are dislodged.

The invention will be more fully understood by reference to the following examples which are given without any intention that the invention be limited thereto.

Example I

This example illustrates the types of glass particles which are usable in accordance with the invention. Fragments should be made from a glass composition having a high index of refraction, preferably approximately 1.5 or higher. The glass should be transparent, although the degree of transparency may vary within rather wide limits. Preferably, the glass is clear and colorless, and free from milkiness, dark particles and air. Since in use the fragments are exposed to the elements, the glass used should be resistant to the action 50 of water and should be capable of withstanding refluxing with distilled water in a Soxhlet extractor for 90 hours without noticeable surface dulling and not more than 2.5% loss in weight. The glass fragments also exhibit no tendency toward decomposition, including sur- 55 face etching, when exposed to the atmosphere, moisture, dilute acids and alkalies and paint constituents. Preferred glass compositions are as follows:

A. Soda lime glass.—66% SiO₂; 16% Na₂O; 9% CaO; 9% mixture of metallic oxides consisting of barium, 60 aluminum, iron, magnesium and potassium.

B. Crown optical glass.—74.6% SiO₂; 9% Na₂O; 11% K₂O; 5% CaO.

The above compositions are crushed to produce fragments suitable for use in accordance with the invention. 65 Thus, glass flake ½ mil in thickness is crushed so that all particles will have at least two reflective surfaces. Fragments are graded to the correct size by separating with vibrating screens of the desired mesh.

It has been found that fragments retained by a 270 70 mesh sieve prossess considerable reflex reflective properties and particles which pass through a 270 mesh sieve can be remelted and recrushed. It is preferred to incorporate a range of differently sized glass particles in a highway marking paint in accordance with the inven-75

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tion. A particularly preferred mixture of nonspherical particles is as follows:

Sieve size:	Percent of m passing the	
U.S. Standard	No. 60 sieve	100
	No. 80 sieve	
U.S. Standard	No. 140 sieve	15–30
U.S. Standard	No. 230 sieve	0-10
U.S. Standard	No. 270 sieve	0

The mixture above set forth is pictured in a highway marking paint in the drawings where it is incorporated in a layer of paint having a thickness of approximately 5 to 6 mils. A paint including this mixture is adapted to be sprayed with conventional spray equipment.

It is desired to point out that the invention is not limited to the specific glass compositions A and B of Example 1. Thus, another and a preferred illustrative composition is as follows:

C. Silicate glass.—SiO₂, 70.6%; Na₂O, 17.0%; MgO, 0.1%; CaO, 10.6%; Al₂O₃, 0.8%.

This glass in flakes approximately ½ mil in thickness is crushed to the desired particle size by hammer-milling. The desired particles are then separated by U.S. standard sieves to recover particles passing through a No. 60 screen and retained on a No. 270 screen.

The mixture of nonspherical particles above set forth is combined with spherical particles of the following description.

The glass bead content may be made up as follows, in proportion by weight:

		Percent
	No. 10 beads, diameter 5.9 mils	20
	No. 12 beads, diameter 4.7 mils	
_	No. 13 beads, diameter 3.9 mils	25

It will be understood that the diameters listed represent an average value only. No. 10 beads, for example, may vary in size from 9.4 to 4.2 mils in diameter although most of the beads will fall within the limits of 6.6 to 5.2 mils in diameter. The glass utilized in the preparation of such beads may have a refrective index varying from about 1.3 to about 1.6.

The size and density of the beads must be taken into account on producing stable paint compositions and long wearing paint films. Large beads or beads of high density are more inclined to settle out from fluid compositions due to their higher ratio of weight to surface. Large beads are also less firmly bonded in the dried film, and show a greater tendency to scuff loose under the impact of traffic. On the other hand, extremely fine beads have such enormous surface area in relation to their weight that they unduly extend the paint which then requires excessive dilution and results in lower bonding power. It is preferred to use for the purposes of this invention, beads in the size range between about 3 and about 10 mils average diameter.

Where transparent beads are employed for their reflectorizing effect as well as their resistance to wear they may be made of glass having any desired reflective index as long as suitable properties of weather resistance and the like are maintained.

Glass particles, useful in this road marking paint, i.e., beads or fragments may be surface treated if desired, either to provide improved adhesion between glass surface and binder, or to provide a colored or reflective or protective surface, or for any other purpose.

The above described nonspherical and spherical particles may be combined in ratios by weight varying from about 8:1 to about 1:2 and preferably vary from about 3:1 to about 1:1.

It is to be noted that larger particles may be used i.e., fragments which will not pass through a No. 60 sieve and beads that are larger than No. 10 beads. However, these larger glass particles are not adapted to a paint intended to be sprayed using conventional spray equipment

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although paints containing these larger particles can be applied in other ways e.g., by brushing or by the use of spreaders. Particles of nonspherical configuration and smaller than that retained by a No. 270 U.S. standard screen are preferably excluded from the paint because 5 these particles thicken the paint and provide little reflec-

Example 2

A typical varnish base coating is as follows:

Phenolic modified pentaerythritol ester of 119

Hydrocarbon resin (Piccopale 100)___lbs__ Chinawood oil_____gal__ 11.89 15 Bodied linseed oil_____gal__ 11.89 VM&P naphtha_____gal__ 57.80

In the above varnish base, the phenolic modified pentaerythritol ester of rosin is desirably the product "Pentalyn" 802A manufactured by Hercules Powder Co. and having the following specification:

Softening point	165°–170° C.	
Color	K	
Acid number	15–22.	
Viscosity at 25° C.: (a) Linseed oil disper-		
(a) Linseed oil disper-		2.00
sion	400+20 poises (r	ninimu

ստ). Viscosity ____ 600+20 poises (maximum). 40% resin/60% oil.

(b) 50% solids_____ C (minimum). Toluol (G.H.)___ G (maximum).

The hydrocarbon resin in the above varnish base is desirably of polymerized unsaturated petroleum monomers consisting essentially of diene and reactive olefins and having an average molecular weight of 90. These unsaturated monomers are polymerized to form a hard solid having an average molecular weight of 1100. Such a hydrocarbon resin is manufactured by Pennsylvania 40 Industrial Chemical Company as "Piccopale" 100 having the following specification:

Softening point	
Specific gravity at 25° C	.970975.
Color	13 Gardner-Holdt scale.
Acid number	Less than 1.
Saponification number	Less than 2.
Iodine value (WIJS)	120.
Bromine number	7.3.

The varnish base above specified is prepared by heating the admixed "Pentalyn" 802A, "Piccopale" 100, China-wood oil and 8 gallons of linseed oil in a kettle at 560° F. for 45 minutes. The heated mixture is then chilled by the addition of 3.89 gallons of linseed oil and 55 allowed to cool to 350° F. whereupon the naphtha is added to the mixture. This varnish is employed in a paint composition as follows:

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Varnish	368.5
Titanium dioxide pigment	247.0
Magnesium silicate	126.0
Crushed glass	265.0
Glass beads	135.0
Toluene	91.0
VM&P naphtha	25.0
6% cobalt drier	
24% lead drier	

oxide and the magnesium silicate with 144.6 lbs. of varnish and the mixture is ground on a paint mill. The driers are then added and the remainder of the varnish and the glass particles mixed thoroughly into the mixture.

This alkyd is sold by American-Marietta Company
The toluene and naphtha thinners are then added. This under No. "SV-141-B7."

paint had a viscosity of 75 Krebs Units and a total solids content of 77%. The weight proportions of this paint are as follows:

		Percent
Pigment	 	_ 29.62
Vehicle solids	 	_ 15.8
Glass	 	_ 31.78
Thinner and drier_		22.8
Immer and area-	 	

The glass particles used were the crushed glass and 10 glass beads of Example 1.

The finished paint can be applied with spray, brush or roller. Small amounts of naphtha may be used to compensate for individual application technique. If long storage is contemplated, small amounts of antisettling agents, such as calcium linoleate, may be used for suspension.

It has been found that the crushed glass fragments, perhaps due to their geometrical angularity, are more satisfactorily maintained in satisfactory suspsension than spherical beads. This is particularly true for the heavier particles, e.g., those retained by a 60 mesh screen and this is of particular value in paints adapted for brush, roller or spreader application as contrasted with spray application.

Example 3

The following illustrates a paint composition employing as the vehicle a phthalic alkyd containing 30% phthalic anhydride having a soya modification of 55%, the alkyd being prepared using glycerin as the polyhydric alcohol and having the following characteristics in a 60% petroleum spirits solution:

	Solids	60%.
_	Viscosity Color (Hallico)	Z1-Z3 Gardner-Holdt.
5	Color (Hellige)	1–3.
	Acid number	4–6.
	Pounds per gallon	7.8.
	Phthalic anhydride	30% (on resin solids).
	Oil acid content	50% (on resin solids).
,	Type of oil	Soya.

An alkyd of the above composition and having the characteristics stated is sold by General Electric Company under the trademark "Glyptal" 2475.

Paint composition:	Lt
aint composition: Titanium dioxide	22
Phthalic alkyd (50% solids)	40
Calcium carbonate	1
Crushed glass	20
Glass beads	1
VM&P naphtha	
Cobalt drier	
Lead drier	1

This paint was prepared by adding the titanium dioxide and calcium carbonate to 300 lbs. of the phthalic alkyd vehicle. This mixture was ground on a paint mill and the remainder of the vehicle added. The glass particles (as 60 specified in Example 1) were then stirred in thoroughly and the naphtha and driers added.

Example 3 is modified by using as the vehicle for the paint, a 30% phthalic pentaerythritol alkyd modified with 54% of an oil consisting of equal parts by volume of linseed oil and soya oil having the following characteristics: 65

Solvent 50% VM&P naphtha. 50% Mineral spirits. This paint is compounded by mixing the titanium di- 70 Acid number 10.2. Color_____ 7 (Gardner Holdt). Pounds per gallon_____ 7.50. Viscosity_____ V-W (Gardner Holdt).

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Example 4

The reflectorized paint may also be of the emulstion type as is illustrated by the following:

Pigment grind:	Lbs.
Water	20.0
Tetrasodium pyrophosphate decahydrate, 10% aqueous solution	10.0
"Emulphor" EL-719 dispersing and wetting	2.0
"Polyglycol" P-1200 polypropylene glycol	2.0
"Carbitol"—diethylene glycol monoethyl ether	25.0
Dibutyl phthalate	
ASP-400 clay	
Titanium dioxide	
Reduction:	
Water	130.0
"Methocel" 4000 methyl cellulose, 2.0% aqueous	
solution	260.0
Du Pont "Elvacet" 81-900 polyvinyl acetate	
emulsion	320.0
Crushed glass (as specified in Example 1)	
mt m m	

The Du Pont "Elvacet 81–900" polyvinyl acetate resin emulsion is a dispersion of polyvinyl acetate resin and water. The polyvinyl acetate resin is a thermoplastic, water-insoluble, colorless, odorless material having density at 20 degrees C. of approximately 1.2 and a refractive index of approximately 1.467. Specifications are:

Solidspercent	55
Pounds per gallon	9.2
Viscosity at 25 degrees Ccentipoises 800-	000
pH	
PII	

"Emulphor EL-719" is a polyoxyethylated vegetable oil which is used to promote wetting and stabilize the emulsion.

The "Polyglycol P 1200" is a polypropylene glycol with an approximate molecular weight of 1200. It is formed by the addition of propylene oxide to propylene glycol. P 1200 acts as an antifoaming agent for the emulsion.

Example 5

Resin solution types, either synthetic or natural, can be used, giving a quick drying paint resistant to wear. Typical example:

	LUU.
Titanium dioxide	200.0
Resin solution (50% manila resin-alcohol)	400.0
Magnesium silicate	125.0
Crushed glass	200.0
Glass beads	200.0
Ethyl alcohol	116.0

When synthetic resins are used, the thinner is simply varied to give optimum results. These reflectorized center line paints dry quickly by evaporation although in 55 general they are not as tough as resinous paints.

Example 6

The following is a specific illustration of a graded mixture of crushed glass fragments containing fragments which are retained by a #60 mesh screen. These larger particles prevent sprayability in ordinary spray equipment because they tend to clog conventional spray equipment, but they may be used advantageously in producing paints for roller application. In such paints, up to about 50% by weight of particles which pass through a #40 mesh screen but are retained by a #60 mesh screen may be used. Particles retained by a #40 mesh screen but not by a #20 mesh screen may also be used in an amount not exceeding about 20% by weight. The use of still roll larger particles is not recommended, although up to 5% by weight of slightly larger particles can be tolerated.

These larger particles, when incorporated in a highway marker paint formulation, provide enhanced brilliance of night visibility and are of great value in speed-75

ing the initiation of the reflex reflective action upon vehicular abrasion of the traffic marker.

Preferred graded mixtures for roller application contain from 5-25% of particles which pass through a #40 mesh screen but which are retained by a #60 mesh screen and 10-30% of particles which pass through a #60 mesh screen and not a #80 mesh screen. Thus, a particularly preferred mixture of nonspherical glass fragments including a proportion of heavier glass particles, e.g., those retained by a #60 mesh screen, is as follows:

10	•		
		Percent of r	nixture
	Sieve size:	passing t	hrough
	U.S. Standard No	. 40 sieve	100
		. 60 sieve	
15		. 80 sieve	
		. 140 sieve	
		. 230 sieve	
	• D	. 270 sieve	

The glass used in the above set forth mixture may be of any of the glass compositions A, B and C which are more fully set forth in Example 1. This mixture may be incorporated in any of the reflective paint compositions set forth in Examples 2, 3, 4 and 5 together with the specified glass beads to provide an effective highway marking paint having great durability and enhanced brilliance of night visibility in comparison with the use of the mixture of differently sized glass fragments set forth in Example 1.

It is desired to emphasize that the presence of a substantial proportion of glass fragments or particles which are retained by a #60 mesh screen and beads larger than #8 causes the highway marking paint containing these glass particles to clog conventional spray equipment. Hence, and as a practical matter, these latter highway marking paints, including large sized incorporated glass particles, are not amenable to spray application. However, these paints may be applied efficiently to highways in many manners other than spraying as, for example, roller coating, in which instance the presence of the larger size particles or fragments does not prevent effective application of the paint incorporating the glass fragments.

Under abrasion, due to wear by vehicular traffic, the surface of the above exemplary paints wears away to expose the glass particles for their reflex reflective function.

FIGURES 1 and 2 pictorially distinguish between fragments and beads by showing the fragments as having flat angular surfaces and irregular nonspherical shapes whereas the glass beads are shown as spheres. The presence of the combination of fragments and spheres is of paramount importance, Light is reflected from the surface or surfaces of fragments and spheres in directions dependent upon the angle of incidence of the light. Light reflected in a direction other than toward the vehicle driver when using the combination of spheres and fragments is not entirely diffused and lost. Reflection by random oriented faces of glass fragments of at least some of the light reflected from beads in a direction other than toward the vehicle driver or reflection by spheres of light directed thereto by reflection from fragments, is at least partially converted to reflected light thus maintaining adequate visibility and brilliance under widely varying and rapidly changing conditions of lighting.

We claim:

1. A reflective highway marking paint comprising a paint vehicle containing between about 0.5 lb. and about 8 lbs. of a suspended mixture of glass particles per gallon of glass-free paint, said glass particles being a mixture of transparent glass beads having an average diameter of the order of about 3 to about 10 mils and glass fragments being of a size to be retained by a U.S. Standard No. 270 mesh screen and being constituted by a plurality of angularly intersecting substantially planar light reflecting faces, the ratio of said glass beads to glass fragments being in the range between 2:1 and 1:8, and said fragments being present in sufficient concentration such that when applied

to a highway as a marking paint the fragments provide with the binder a keying action whereby dislodgements of fragments and spheres is resisted.

2. A reflective highway marking paint comprising a drying oil-base varnish vehicle containing between about 5 0.5 lb, and about 8 lbs, of a suspended mixture of glass particles per gallon of glass-free paint, said glass particles being a mixture of transparent glass beads having an average diameter of the order of about 3 to about 10 mils and glass fragments being of a size to be retained by a 10 U.S. Standard No. 270 mesh screen and being constituted by a plurality of angularly intersecting substantially planar light reflecting faces the ratio of said glass beads to glass fragments being in the range between 2:1 and 1:8, and said fragments being present in sufficient concentration 15 such that when applied to a highway as a marking paint the fragments provide with the binder a keying action whereby dislodgements of fragments and spheres is resisted.

3. A reflective highway marking paint comprising a paint vehicle containing between about 0.5 lb. and about 8 lbs. of a suspended mixture of glass particles per gallon of glass-free paint, said glass particles being a mixture of transparent glass beads having an average diameter of the order of about 3 to about 10 mils and glass fragments of a particle size passing through a U.S. Standard No. 270 mesh screen and being constituted by a plurality of angularly intersecting planar light reflecting faces, the ratio of said glass beads to glass fragments being in the range between 1:1 and 1:3, and said fragments being present in sufficient concentration such that when applied to a highway as a marking paint the fragments provide with the binder a keying action whereby dislodgements of fragments and spheres is resisted.

4. A paint as claimed in claim 2 wherein said varnish vehicle is a vegetable oil modified alkyd resin of phthalic anhydride and glycerin which is dispersed in an organic

solvent.

5. A paint as claimed in claim 2 wherein said glass fragments have a refractive index of at least 1.5.

6. A reflective highway marking paint comprising a paint vehicle containing a reflective pigment dispersed therein and between about 0.5 lb. and about 8 lbs. of a suspended admixture of glass particles per gallon of glassfree paint, said glass particles being a mixture of transparent glass beads having an average diameter of the order of about 3 to about 10 mils and light reflecting glass fragments of a size to pass through a U.S. Standard No. 60 mesh screen and to be retained on a U.S. Standard No. 270 mesh screen, the ratio of said glass beads to glass fragments being in the range between about 2:1 and 1:8,

and said fragments being present in sufficient concentration such that when applied to a highway as a marking paint the fragments provide with the binder a keying action whereby dislodgements of fragments and spheres is resisted.

7. A paint as claimed in claim 6 wherein said reflective

pigment includes titanium dioxide.

8. A reflective highway marking paint comprising a paint vehicle containing between 0.5 lb. and about 8 lbs. of a suspended admixture of glass particles per gallon of glass-free paint, said glass particles being a mixture of transparent glass beads having an average diameter of the order of about 3 to about 10 mils and glass fragments sufficiently large to be retained by a U.S. Standard No. 270 mesh screen and being constituted by a plurality of angularly intersecting substantially planar light reflecting faces, said glass fragments comprising up to about 50% by weight fragments retained by a U.S. Standard No. 60 mesh screen and passing through a U.S. Standard No. 40 mesh screen, and said fragments being present in sufficient concentration such that when applied to a highway as a marking paint the fragments provide with the binder a keying action whereby dislodgements of fragments and spheres is resisted.

9. A reflective highway marking paint comprising a paint vehicle containing between about 0.5 lb. and about 8 lbs. of a suspended mixture of glass particles per gallon of glass-free paint, said glass particles being a mixture of transparent glass beads having an average diameter of the order of about 3 to about 10 mils and glass fragments being of a size to be retained by a U.S. Standard No. 270 mesh screen and being constituted by a plurality of angularly intersecting substantially planar light reflecting faces the ratio of said glass beads to glass fragments being in the range between 2:1 and 1:8, the glass particle loaded paint being adapted to be sprayed on highway surfaces subject to vehicular traffic to provide nighttime visibility to motorists, and said fragments being present in sufficient concentration such that when applied to a highway as a marking paint the fragments provide with the binder a keying action whereby dislodgements of frag-

ments and spheres is resisted.

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UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,005,790

October 24, 196

James F. Wynn et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 21, after "conventional" insert -- reflex --; column 3, line 71, for "prossess" read -- possess --; column 4, line 41, for "refrective" read -- refraction --; column 7, line 2, for "emulstion" read -- emulsion --; column 10, line 47, for the patent number "2,354,108" read -- 2,354,018 --.

Signed and sealed this 24th day of April 1962.

(SEAL)

Attest:

ESTON G. JOHNSON

Attesting Officer

DAVID L. LADD

Commissioner of Pate