Aug. 4, 1959 L. W. SHUGER 2,897,733

TRAFFIC MARKER, MATERIAL, AND METHOD

Filed Dec. 22, 1955

Fig. 1.

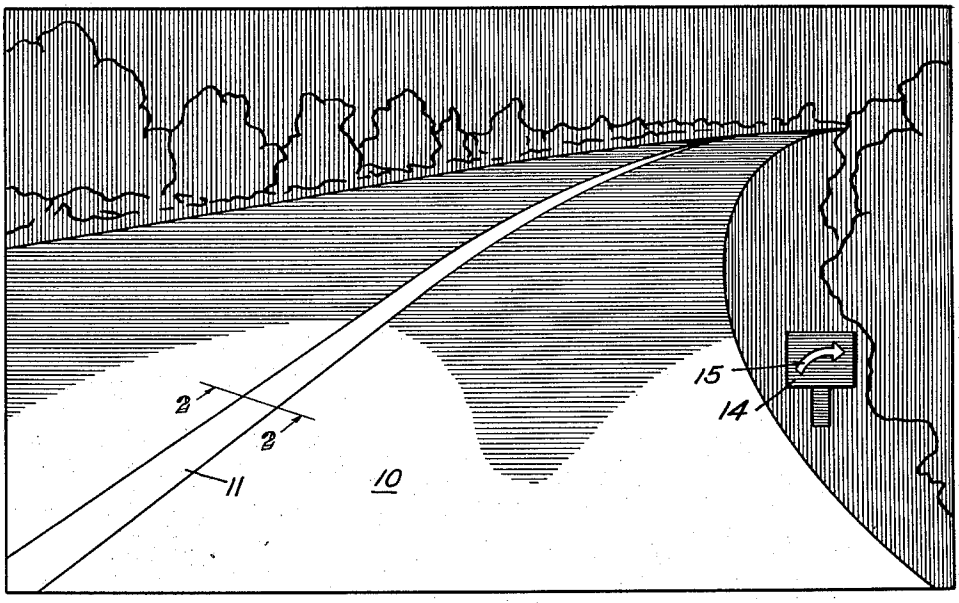


Fig. 2.

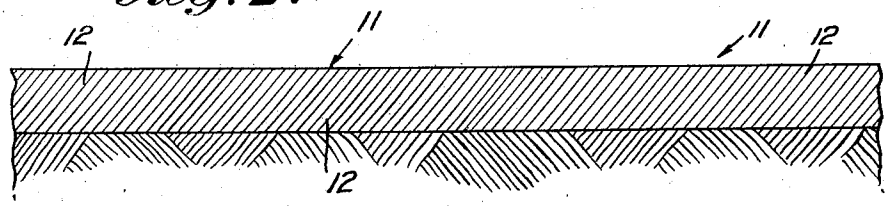


Fig. 3.

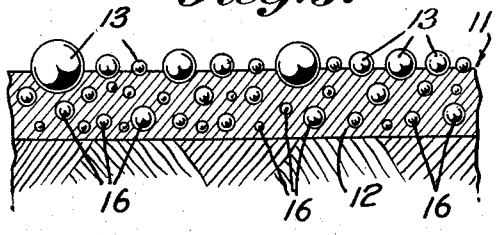
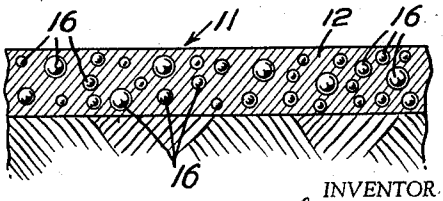


Fig. 4.



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United States Patent Office

2,897,733

Patented Aug. 4, 1959

2,897,733

TRAFFIC MARKER, MATERIAL, AND METHOD

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Application December 22, 1955, Serial No. 554,871

10 Claims. (Cl. 94—1.5)

This invention relates to surface marking, and more particularly to markings embodying a quick drying traffic paint of increased film thicknesses, that have essentially the same wet and dry film thicknesses.

Conventional markers heretofore extensively used are made from paints which utilize solvents, which must evaporate off to yield a dry film of the paint. It has been common practice to lay small glass spheres onto the paint when the latter is in a semi-dry or tacky condition to reflectorize the marker.

It has now been found most desirable to secure the maximum wet film thickness practicable, in order to obtain the maximum dry film thickness for greater durability.

Conventional traffic paints now in use, particularly if they are used with the glass beads for surface dressing, are recommended for application with a wet film thickness of 15 mils. Anything less than this usually gives bad bead retention. If the wet film thickness were increased above 15 mils, the conventional paint film would not dry in the required time for efficient usage. A conventional paint which would normally dry in three-quarters of an hour, when applied at 15 mils wet film thickness, would require approximately three hours or more to dry if applied at 30 mils wet film thickness.

It has not been easy in the past to obtain increased wet film thicknesses above 15 mils because at such increased film thicknesses the paint would flow over the edges, and the edges are not sharp.

An important consideration is the dry film thickness of such conventional traffic paints that actually remains on the road. After the solvent has evaporated and the remaining dry ingredients undergo some shrinkage, the dry film thickness of conventional paint is approximately 44–70% of the wet film thickness. In other words, when conventional traffic paints are applied at 15 mils wet film thickness, the dry film is approximately 6.6–10.5 mils thick.

The need has long existed for a marker of greater film thickness that could be conveniently applied to the roadway, that would be durable and adherent to glass spheres.

It is therefore an object of the present invention to provide a marker wherein the reflecting paint is of such a peculiar and critical nature that it has essentially the same wet and dry film thickness, is quick drying and will yield markers of greater film thickness.

It is a further object of the present invention to provide a marker including a reflecting paint and a series of auto-collimating units wherein the reflecting paint is of such a nature as to have essentially the same wet and dry film thicknesses and as to tenaciously hold the auto-collimating units to the marker.

It is a still further object of the present invention to provide an improved traffic paint that may be applied in greater film thicknesses and yet is quick drying.

It is a still further object of the present invention to provide an improved traffic paint that has essentially the same wet and dry film thicknesses.

It is a still further object of the present invention to provide an improved traffic paint wherein the use of solvents is substantially eliminated to yield a quick drying paint having essentially the same wet and dry film thicknesses.

Another object of the present invention is to provide an improved traffic paint having essentially the same wet and dry film thicknesses that can be applied to road surfaces utilizing essentially conventional line striping equipment.

Another object of the present invention is to provide a quick drying traffic paint that is highly adherent to glass spheres dropped onto the wet surface thereof.

A still further object of the present invention is to provide an improved marker that is an inert chemically resistant film impervious to weathering and having great durability.

Other objects and the nature and advantages of the invention will be apparent from the following description taken in conjunction with the accompanying drawings, wherein:

Fig. 1 is a view in perspective of a highway and a pair of markers associated therewith in accordance with the invention;

Fig. 2 is a view in section taken along the line 2—2 of Fig. 1 and looking in the direction of the arrows of a marker without the glass beads;

Fig. 3 is a similar view of a marker having glass beads embedded therein with some of the beads completely embedded and some of the beads partially exposed; and

Fig. 4 is a similar view of a marker having glass beads embedded therein with all of the beads completely embedded.

Referring to the drawings, a road surface **10** has a center line **11** applied thereto fabricated of a binder or paint **12** including ingredients such as specified later in detail. Fig. 2 shows a cross-section of the marker having no glass spheres therein. Fig. 3 shows a cross-section of a marker having a plurality of glass spheres **16** completely embedded therein and a plurality of glass spheres **13** partially embedded with their upper surfaces exposed. Fig. 4 shows a marker with the completely embedded spheres **16** only. At the side of the road is located a vertical sign **14** bearing a curved arrow insignia **15** indicating a turn in the road. The insignia **15** includes a binder or paint and a series of more or less embedded auto-collimating units such as, for example, relatively small glass spheres.

The marker in accordance with this invention may be fabricated by applying to the surface to be marked at approximately atmospheric temperature a binder or paint, which application may be made by spraying, brushing, dipping or otherwise coating. When auto-collimating units are dropped in for reflectivity, while the marker is in a wet, semi-wet, or tacky condition, the auto-collimating units are distributed over the surface thereof, either by hand or with a mechanical dispenser. The paint is then permitted to dry and hold the auto-collimating units. Those units which are partially exposed will serve to effect the reflection of light back to the source emanating light thereto.

The quick drying, resistant, adherent and durable film is obtained by using a traffic paint which contains practically no solvent, that is, contains 97–100% solids, and therefore has essentially the same wet and dry film thicknesses, and can be applied at thicknesses in the order of 10–30 mils.

The traffic paints in accordance with this invention are believed to be more or less permanent and not subject to abrasion or wear under normal traffic conditions. Such a paint and the method of application provide a

marking of far greater durability than those obtained with the use of conventional traffic paints.

The new traffic paints are essentially synthetic resins in combination with additives, pigments and fillers which may be applied either hot or cold, depending upon the particular synthetic resin used, to yield a reflecting, long-lasting marking that is quick drying and strongly adherent to glass spheres that may be dropped onto the marking prior to completion of the drying of the marking. These synthetic resins are curable and are not entirely thermoplastic; that is, they set up by oxidation or polymerization. These synthetic resins include polyesters, epoxy resins, alkyd resins, and the like. There are many different formulations containing these synthetic resins that will meet the above conditions, and all such formulations are intended to be included as a part of this invention.

The following specific examples are illustrative only and should not be construed as limiting the scope of the invention.

Example 1

The following formula is for a traffic paint that is liquid and may be applied at atmospheric temperatures:

	Parts by wt.
Modified polyester resin	773.0
Vinyl toluene	77.3
6% cobalt naphthenate	8.7
Titanium dioxide (rutile)	96.5
Mica	96.5
	[1] 1052
Lupersol DDM	19.3

[1] Equals 100 gals.

The term modified polyester resin as used in this specification refers to reaction products of dihydric alcohols, such as glycols, and dibasic acids; one of the dibasic acids must be ethylenically unsaturated, usually introduced as maleic or fumaric acid. The unsaturated polyester reaction products are mixed with an unsaturated reactive monomer, such as styrene, vinyl toluene, vinyl acetate, methyl methacrylate, alpha and para methyl styrene, divinyl benzene, ethylacrylate, acrylonitrile, diallyl phthalate, and many others, or other unsaturated reactive materials that are compatible with the polyester.

The modified polyester resins described above will copolymerize under the influence of heat and/or a peroxide catalyst, with the monomer or other material cross linking the unsaturated polyester to make a thermosetting solid.

The properties of the modified polyester resins can be modified through the use of various dibasic acids, different glycols, and several monomers, each in varying ratio to the others, permitting preparation of end products with almost any desired properties. These modified polyester resins are mobile liquids and can be converted quickly to solids. They are 100% reactive and evolve no gas or liquid during curing. A specific example of a suitable modified polyester resin found suitable is the reaction product of

	Pounds
Propylene glycol	974
Phthalic anhydride	888
Maleic anhydride	588

Approximately 2200 lbs. of unsaturated polyester reaction product is obtained to which is added 1083 lbs. styrene, or a ratio of 2 parts reaction product to 1 part styrene. Approximately 0.3 lb. hydroquinone and 0.1 lb. butylcatechol is added to act as a stabilizer, and antioxidant, to improve the shelf life of the product.

Expressed in mol percent, approximately 5 to 50% of reactive monomer or other material can be added, and the mol percent of glycol is usually greater than the combined mol percents of the acids used.

This formula results in a fluid product and requires no special processing. The pigment and filler is dispersed in the modified polyester resin using conventional equipment, preferably a pebble mill. To the pigment-resin paste is added the balance of the resin, vinyl toluene, and cobalt naphthenate and the mixture is mixed well for at least thirty minutes. The Lupersol is the curing catalyst, and is not added to the paint until the time of application.

The paint is preferably applied by spraying, using a catalyst type gun similar to those manufactured by Binks and De Vilbiss companies. Using this type of gun, the catalyst is introduced into the formula outside of the spray gun. The coating can be applied at a wet film thickness of 10 to 30 mils and dries to allow traffic to proceed in from ten to twenty-five minutes, depending upon the temperature. Such films have been applied up to 70 mils thick. Raising the temperature of the coating to 100–120° F. just prior to application decreases the cure time considerably. The dry film thickness of this marker is approximately the same as the wet film thickness, except for the minor shrinkage due to the curing of the resin. Glass spheres may be applied to the surface of the marker prior to completion of the curing of the resin.

The pigment is used to impart reflection to the marker as well as color and opacity, and the fillers impart structural strength to the film. To produce a white marker, it is necessary to have a prime pigment, such as the rutile titanium dioxide, to furnish the necessary whiteness and opacity. In place of the rutile titanium dioxide, anatase titanium dioxide can be substituted. The titanium dioxide can be extended with barium sulphate, calcium sulphate, magnesium silicate, zinc sulphide and normal or high strength lithopones to produce a white marker. For colored markers other than white, the following pigments are suitable: lead chromates, zinc chromates, siennas, umbers, iron oxides, inorganic or organic reds. Fillers or extenders, which may be used, are, for example: Asbestine (magnesium silicate), diatomaceous silica, amorphous and crystalline silica, micaceous materials, barium sulphate, whiting, wollastonite and pumices.

The vinyl toluene in Example 1 acts to adjust the viscosity of the mixture; however, unlike the solvents in conventional paints, the vinyl toluene copolymerizes with the unsaturated polyester resin to maintain close to 100% solids. The vinyl toluene may be replaced with other unsaturated monomers such as: vinyl acetate, styrene, methylmethacrylate, alpha and para methyl-styrene, divinyl benzene, ethyl acrylate, acrylonitrile, diallyl phthalate, diallyl esters, and others, or other unsaturated reactive materials that are compatible with the polyester.

The cobalt naphthenate is 6% metal and acts as an initiator to speed the reaction. The cobalt naphthenate can be replaced with alkyl mercaptan.

The Lupersol DDM acts as the catalyst to catalyze the polymerization of the modified polyester resin in the final dry film. Lupersol DDM is 60% methyl ethyl ketone peroxide in dimethyl phthalate. Other peroxide type catalysts may be substituted such as benzoyl peroxide and tertiary butyl hydro peroxide.

Example 2

	Parts by wt.
Modified polyester resin (Vibrin 114)	890
Cobalt naphthenate	8.5
Titanium dioxide	71.0
Magnesium silicate	43.5
Diatomaceous silica	22.0
	[1] 1035.0
Peroxide catalyst	2 gals. 10 liq. oz.

[1] Equals 100 gals.

Vibrin 114 is made by Naugatuck Chemical Co. and is believed to be a polyester of a glycol, phthalic anhydride and maleic anhydride mixed with styrene.

This formula can be applied in the cold, is a 100% solids formula and requires no special heating in the method of manufacture and can be shipped as conventional paints. The catalyst is, of course, shipped separately. This paint is highly adherent to the glass spheres when used to produce reflectorization.

Example 3

The material of Examples 1 and 2 may include 4½ lbs. of No. 70 mesh glass spheres incorporated into each gallon to provide a premix compound. The glass spheres can also be used as a surface dressing with this formula or any of the other described herein, utilizing the drop-on or drop-in process reflectorization.

The spheres may be incorporated in these formulas as a premix at a ratio of up to 8 lbs. of spheres per gallon of paint. The glass spheres are primarily incorporated to obtain greater structural strength and elasticity of the marker. Due to the permanency of the markers in accordance with this invention, it is not believed that the upper surface of the films will abrade off, certainly not as rapidly as in conventional paints used heretofore. Thus, the surface of the embedded spheres will not rapidly become reflective, and the addition of the partially exposed glass spheres may be desirable to provide reflectorization. Up to 14 lbs. of glass spheres may be utilized for 100 square feet of surface of the marker.

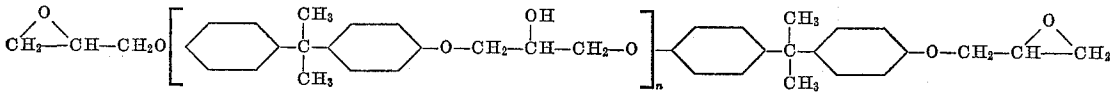
Example 4

The following formula is for a traffic paint that is solid at atmospheric temperatures and may be applied by spraying or the like after heating the material:

	Pounds
Epon 1001	445
Epon 828	445
Titanium dioxide	415
[1]	1305
Diethylenetriamine (curing agent)	53

[1] Yields 100 gals.

The Epons are epoxy-resins based upon epichlorhydrin and bisphenol-A and have the following formula:



The commercial resins are mixtures of polymers wherein *n* varies between 0 and 10, indicating molecular weights of 400 to approximately 8000. These products contain both epoxide and hydroxyl groups capable of further reaction. It is the combination of these groups with the curing agent that results in the cured resin systems incorporating the pigments that possess the excellent properties. Various amines, acid anhydrides, dibasic acids and resins, such as polyamides, are typical curing agents.

Epon 828 is made by Shell Chemical Corp. and has a melting point of 8–12° C., and an epoxide equivalent of 190–210. Epon 1001 has a melting point of 64–76° C. and an epoxide equivalent of 450–525.

In preparing this material, the Epon 828 is heated to 250–300° F. and the Epon 1001 is added gradually until it is dissolved in the hot Epon 828. When the solution is uniform, the pigment is added gradually and mixed, keeping the temperature constant. The material is permitted to cool to room temperature. At room temperature, the formula is a sticky, almost solid mass.

To apply, the formulation is heated to 220–230° F. and the curing agent is added just prior to application. Within five minutes after addition of the curing agent, the marker will dry to a hard porcelain-like film.

The marking is applied by a jacket heated tank to provide the necessary heat, using a catalyst type gun for spraying, wherein the catalyst is introduced into the formula outside of the spray gun.

The glass spheres are applied to the top surface of the marker prior to completion of the cure where reflectivity is desired.

Up to 8 lbs. per gallon of No. 70 mesh glass spheres can be incorporated into the plant to provide a premix. Up to 14 lbs. of glass spheres per 100 square foot of surface can also be dropped in for reflectivity.

Example 5

Another example of a hot mix formula utilizing a curing agent is as follows:

	Pounds
Epon 1001	377
Epon 828	377
Alkyd resin (94.5% solids)	158
Titanium dioxide	350
[1]	1262
Diethylenetriamine (curing agent)	45

[1] Yields 100 gals.

The alkyd resin used was Glyptal 2477 manufactured by General Electric Co., which is furnished at 65% solids. It was evaporated to 94.5% solids. This alkyd resin is included to serve as a plasticizer to increase the elasticity of the marker. Glyptal 2477 is a non-drying alkyd resin of the glycerol-phthalic type modified by castor oil, a non-drying oil.

This formulation is mixed and applied similarly to Example 4 and results in a more flexible marker, but the drying time is somewhat longer.

Example 6

Another modification of a hot mix formula utilizing a curing agent is as follows:

	Pounds
Epon 1001	317
Epon 828	317
Styrene oxide	63
Titanium dioxide	90
Mica (60 mesh)	180
Glass spheres (70 mesh and smaller)	435
[1]	1402
Diethylenetriamine (curing agent)	38

[1] Yields 100 gals.

This formula is mixed and applied similarly to Example 4. The styrene oxide is not a plasticizer but is added as

a viscosity modifier that enters into the reaction. Drop-in glass spheres can also be applied to furnish reflectivity.

Example 7

This is a formula utilizing a hot mix but requiring no curing agent:

	Pounds
Alkyd resin A–35 (90% solids)	450
Lead naphthenate	9.5
Cobalt naphthenate	3.8
Titanium dioxide	580
Calcium carbonate	493
Magnesium silicate	210
	[1] 1746.3

[1] Yields 100 gals.

The alkyd resin A–35 is a glycerol phthalate resin modified with a drying oil such as soybean oil. The naphthenates are driers.

In manufacturing this material, the alkyd is heated to 350° F. and the pigment is added and mixed to uniform consistency. At room temperature this material is a hard solid mass.

The material is heated prior to application; however, a catalyst gun is not needed. The film is spread by a doctor blade spreader or by a heat jacket spray gun.

Glass spheres can be dropped in and where desired may be incorporated as a premix.

The paint formulas in accordance with this invention have an unusual adhesion to glass. When glass spheres are dropped into the film prior to curing, it would appear that the partially exposed beads would be lost after a short encounter with traffic; however, heavy trucks, after days of traffic, did not disclose the partially exposed spheres. Of course, the heavier film thickness of these markers permits greater embedment and even greater bead retention. The range of sizes of glass spheres useful in these markers is greater than could be used previously due to the greater film thickness. For premix purposes also, larger size spheres can be used due to the heavier film thickness applied, the only limitation being that the spheres must be of a size that will enable them to pass freely through a spray gun or other application means. Suitable sizes of spheres that can be used in the premix are S–45, which are 13 mils or smaller, S–70 which are 10 mils or smaller, or practically any size for the drop-in spheres.

It will be obvious to those skilled in the art that various changes may be made without departing from the spirit of the invention and therefore the invention is not limited to what is shown in the drawings and described in the specification but only as indicated in the appended claims.

What is claimed is:

1. A combined highway and surface marker comprising a road adapted to receive automotive traffic, the upper surface of which is coated with a reflecting pigmented composition, said coating having a thickness of 10 to 30 mils, said composition having 97–100% solids content and essentially the same wet and dry film thicknesses, said composition consisting substantially entirely of light reflecting pigment and a resin, said resin comprising a mixture of alkyd resins and epoxy resins catalyzed by a suitable catalytic agent to a thermoset solid, said epoxy resin comprising at least one glycidyl polyether of a dihydric phenol, said polyethers having a chain of alternating glyceryl and divalent aromatic radicals united by ether oxygen with glyceryl radicals in terminal position, said alkyd resin being a glycerol phthalate resin, the reaction involving the catalyst occurring on said road surface to form a solid incorporating the pigment adherent to said road surface and resistant to the abrasion of traffic.

2. A combined highway and surface marker in accordance with claim 1 wherein said composition includes a plurality of small glass spheres embedded therein having an average diameter up to 13 mils.

3. A combined highway and surface marker in accordance with claim 1 wherein said composition includes a plurality of small glass spheres partially embedded in the upper surface thereof, said spheres having an average diameter up to 30 mils.

4. A method of making a traffic marker which comprises applying a layer of a liquid reflecting pigmented composition to a road surface adapted to receive automotive traffic, said layer having a wet film thickness of 10 to 30 mils, said composition having 97–100% solids content and essentially the same wet and dry film thicknesses, said composition consisting substantially entirely of light reflecting pigment and a resin, said resin comprising a mixture of alkyd resins and epoxy resins capable of being converted to a thermoset solid by action of a suitable catalytic agent, said epoxy resin comprising at least one glycidyl polyether of a dihydric phenol, said polyethers having a chain of alternating glyceryl and divalent aromatic radicals united by ether oxygen with glyceryl radicals in terminal position, said alkyd resin being a glycerol phthalate resin, adding said catalytic agent to said composition immediately prior to the composition reaching said road surface, whereby said resin is catalyzed by said agent on said road surface to form a thermoset solid incorporating the pigment adherent to said road surface and resistant to the abrasion of traffic.

5. A method in accordance with claim 4 wherein said composition includes a plurality of small glass spheres embedded therein having an average diameter up to 13 mils.

6. A method in accordance with claim 4 wherein a plurality of small glass spheres are partially embedded in the upper surface of said layer prior to completion of the solidification, said spheres having an average diameter up to 30 mils.

7. A combined highway and surface marker comprising a road adapted to receive automotive traffic, the upper surface of which is coated with a reflecting pigmented composition, said composition having 97–100% solids content and essentially the same wet and dry film thicknesses, said composition consisting substantially entirely of light reflecting pigment and a resin, said resin comprising a mixture of alkyd resins and epoxy resins catalyzed by a suitable catalytic agent to a thermoset solid, said epoxy resin comprising at least one glycidyl polyether of a dihydric phenol, said polyethers having a chain of alternating glyceryl and divalent aromatic radicals united by ether oxygen with glyceryl radicals in terminal position, said alkyd resin being a glycerol phthalate resin, the reaction involving the catalyst occurring on said road surface to form a solid incorporating the pigment adherent to said road surface and resistant to the abrasion of traffic.

8. A combined highway and surface marker in accordance with claim 7 wherein said composition includes a plurality of small glass spheres embedded therein having an average diameter up to 13 mils.

9. A combined highway and surface marker in accordance with claim 7 wherein said composition includes a plurality of small glass spheres partially embedded in the upper surface thereof, said spheres having an average diameter up to 30 mils.

10. A method of making a traffic marker which comprises applying a layer of a liquid reflecting pigmented composition to a road surface adapted to receive automotive traffic, said composition having 97–100% solids content and essentially the same wet and dry film thicknesses, said composition consisting substantially entirely of light reflecting pigment and a resin, said resin comprising a mixture of alkyd resins and epoxy resins capable of being converted to a thermoset solid by action of a suitable catalytic agent, said epoxy resin comprising at least one

glycidyl polyether of a dihydric phenol, said polyethers having a chain of alternating glyceryl and divalent aromatic radicals united by ether oxygen with glyceryl radicals in terminal position, said alkyd resin being a glycerol phthalate resin, adding said catalytic agent to said composition immediately prior to the composition reaching said road surface, whereby said resin is catalyzed by said agent on said road surface to form a thermoset solid incorporating the pigment adherent to said road surface and resistant to the abrasion of traffic.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,897,733 August 4, 1959

Leroy W. Shuger

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

Column 3, line 26, for "Modified polyester resin" read -- Mixture of polyester resin and monomer --; line 36, strike out "term modified"; line 46, for "modified" read -- mixture of --; same line 46, for "resins" read -- resin and the vinylidene monomers copolymerizable therewith --; same column 3, line 51, for "modified polyester resins" read -- copolymerizable mixture --; lines 55 and 56, for "modified polyester resins" read -- copolymerizable mixtures --; column 3, line 60, and column 4, line 3, for "modified polyester resin", each occurrence, read -- copolymerizable mixture --; column 4, line 66, for "Modified polyester resin" read -- Mixture of polyester resin and reactive monomer --; column 6, line 15, for "plant" read -- paint --; column 7, line 21, for "soybean" read -- soyabean --.

Signed and sealed this 5th day of April 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents