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REFLECTIVE COATING COMPOSITIONS CONTAINING GLASS BEADS, METAL FLAKE PIGMENT AND BINDER

Alfred H. Nellessen, Roseville, Minn., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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This application is a continuation-in-part of my application Serial No. 591,305, filed June 14, 1956 (now abandoned).

This invention relates to new and useful liquid reflective coating compositions containing admixed glass beads, which can be used to provide a reflective coating in one step in making highway signs and markers that have brilliant long-range visibility when viewed at night by motorists owing to the inherently reflex-reflecting property of the coating, the reflection efficiency being much greater than in the case of ordinary painted signs and markers.

Compositions are provided which can be applied to desired base surfaces by brush, knife coat, screen process and spray methods, similarly to the application of conventional paints, to provide reflex-reflecting letters, symbols, designs, stripes, or backgrounds, employed exclusively or in combination with reflective or non-reflective areas of other kinds, in fabricating complete signs and markers.

The inherently reflex-reflecting characteristic of the dried coating on the sign or marker is due to the conjoint optical properties of an optically exposed surface layer of minute glass beads (transparent glass microspheres) in combination with finely divided metal flake reflective pigment particles associated with the back surfaces of the beads, this structure being held together and bonded to the underlying surface by a transparent varnish binder in which the beads and metal pigment are completely embedded. The microspheres serve as sphere lenses and refract the light rays impinging on the reflective area, both before and after reflection from the underlying metal pigment particles, in such a way that a brillaint cone of light is reflected back toward the source of light. This is true even when the sign or marker is illuminated by a beam of light which strikes it at a substantial angle away from the perpendicular, as is commonly the case when a roadside sign or marker is illuminated at night by the headlight beam of a vehicle moving along the road. The result is that the sign or marker appears much brighter to the occupants of the vehicle than does a conventional sign or marker which lacks this reflex-reflecting characteristic. The sign or marker attracts greater attention and is readily visible at much greater distances.

A well known way of making reflex-reflecting sign areas is to coat the base with reflective paint and, while it is still in a soft and tacky state, apply suitable glass beads to the surface so as to form a layer of beads partially embedded in the paint. Thus see Gebhard, Heltzer, Clarke and Davis Patent No. 2,326,634 (Aug. 10, 1943). This procedure requires two steps and requires care and skill to obtain an optically efficient, durable sign product. The paint coating must be applied in an accurate thickness relative to the size of the beads. If a quick-drying paint is employed, the viscosity and adhesion properties of the coating film rapidly change as it dries, so that the beads must be applied in just the right way to become securely bonded and properly positioned. If a slower-drying paint is employed, the beads may sink in too far during the drying period, and moreover there is delay in finishing the sign-making operation. In either case, the beads are applied against the surface of the wet or partially dried paint film. Its surface properties and viscosity, which alter during drying, affect the nature of the bead-paint bond and the force of capillarity which determines the way in which the wet paint crawls up on the beads and the resultant physical structure. In order to provide uniform durable sign surfaces it has been common practice to employ prefabricated reflex-reflecting beaded sheeting manufactured under controlled factory conditions, which the sign maker cuts and affixes to the sign base.

So far as I am aware, during the many years that these prior procedures have been known and practiced, no one has provided or proposed a premixed beaded paint comprised of a liquid binder vehicle containing a mixture of reflective pigment and glass beads, which could be applied by the sign maker to produce in one step an efficient inherently reflex-reflecting coating bonded to the sign base, ready to function as such immediately upon drying.

The natural expectation would be that this result could not be obtained because in the applied paint coating the beads would be surrounded by the opaque reflective pigment, producing external surface reflection and scattering of light rays so that the beads and underlying pigment would have no opportunity to function in the manner required for obtaining reflex-reflection. This was my own view of the matter during many years and it was only recently that I unexpectedly discovered the possibility of formulating compositions of the present type.

Surprisingly, I found that liquid coating compositions can be made which are essentially a mixture of minute glass beads (transparent glass microspheres), finely divided metal flake reflective pigment, and varnish solution containing volatile solvent, that can be applied to the base surface to produce in one step an efficient reflex-reflecting coating ready to function as such immediately upon drying. Upon application, the glass beads flow out to form a mono-layer containing tens of thousands per square inch or per square centimeter. The varnish drains from the glass beads during evaporation of the solvent. The dried varnish film forms a thin transparent skin over the tops of the beads so that the outer surface has a corresponding spherulate or lenticular contour exposed to the atmosphere. The proportion of varnish binder solids is, however, sufficient to provide secure anchorage of the beads to the base surface. During the drying period and while the varnish solution is still fluid, a rather amazing motion of the metal flake pigment particles occurs. These flakes are smaller than the beads. The flakes which initially overlie the beads slide off the front hemispherical surfaces of the beads, thereby optically exposing the beads to incident light rays. Efficient reflection is provided by flakes which move into position to face toward the back hemispherical surfaces of the beads, in contact therewith or in close proximity, thereby providing each bead with a concentric concave metallic reflector contiguous to its back surface. The flakes are secured in the necessary relationship to the beads by the time the varnish has become too viscous to permit of movement. The result is that incident light rays can pass to and through the beads to the associated metal flakes serving as back reflectors and be reflected back through the beads toward the source of light, so that the dried coating has an efficient inherently reflex-reflecting characteristic. This effect is obtained regardless of whether the coating composition is applied to a vertical or to a horizontal surface or even to the underside of a horizontal base (such as a ceiling).

My compositions are clearly distinguishable from the beaded highway marking paints which have been employed for over ten years and were described by Heltzer in his application filed in 1945, since issued as Patent No. 2,574,971 (Nov. 13, 1951), and in a court opinion concerning that patent, reported in 132 F.S. 640, 105 USPQ 416. That paint, as is well known, provides a marker on the highway surface that is not reflex-reflecting in its initial dried state, the beads being covered over by an opaque reflective paint film that optically masks the beads. The paint contains diffusing-type pigments such as titanium dioxide. Reflex-reflection does not occur until the action of weathering and traffic wear has removed the paint sufficently from the tips of the beads to expose them so they can function as lens elements, which ordinarily requires several weeks before efficient reflex-reflection is developed.

The present result is not obtainable with non-metallic diffusing-type pigments such as the non-shiny metal oxide pigments commonly employed in paints, including the beaded highway paint of the above-mentioned Heltzer patent. Nor is it obtainable with any and all mixtures of beads, reflective metal flakes, and varnishes. A proper selection and proportioning is needed in accord with principles hereinafter indicated, in order that each ingredient function in harmony with the other ingredients to produce the desired result.

The optimum size of the glass beads to obtain good functional efficiency, coatability, and dispersion and suspension in the varnish vehicle, is in the range of about 25 to 75 microns diameter. A micron is a thousandth of a millimeter. (There are 25 microns in a mil, which is a thousandth of an inch, so this range is about 1 to 3 mils.)

The beads must have a refractive index of at least about 1.8. The optimum value is about 1.9 to obtain efficient reflex-reflection when the above-mentioned coating procedure results in a spherulate varnish surface exposed to the atmosphere for viewing under normal dry conditions. The optimum value is about 2.5 if the surface is covered with water under viewing conditions. A composition containing a mixture of beads of about 1.9 index and of about 2.5 index has advantages when used for coating outdoor surfaces exposed to wetting by water or rain (as in the case of marker buoys and bridge abutments) since the two types have optimum reflex-reflecting efficiencies when the spherulate surface contacts air or water, respectively. Beads of such high refractive indices are to be distinguished from ordinary glass beads, which have a refractive index of about 1.5 and cannot be used for present purposes.

The metal flake pigment must provide efficient metallic (shiny) reflection. The particle size must be substantially less than the particle size of the beads. The flakes permit of pigment leafing. Aluminum powder leafing pigments, preferably extremely fine, are desirable because of relative low cost in relation to high efficiency, but other metal flake pigments can be used such as bronze powder, copper flake, tin flake, German silver flake, nickel flake, and even gold and silver leaf although too expensive for ordinary usage. The optimum proportion is one that suffices to provide complete reflective areas at the backs of the beads without substantial excess of pigment serving no useful purpose, and this will vary depending upon the particular pigment and size of beads, etc., but can readily be determined by trial in any given case. In general, it has been found that the optimum value lies in the range of one part by weight of pigment to about 5 to 50 parts by weight of glass beads. A useful formula for estimating the approximate maximum ratio for efficient reflection has been found to be:

$$R=0.1(A)(D)(d)$$

where R is the weight ratio of glass beads to pigment, A is the surface area in square centimeters covered by 1 gram of leafed out metal flake pigment, D is the density of the glass beads, and d is the mean diameter of the beads in centimeters.

Another factor to be considered is the "bead volume concentration" (BVC) by which is meant the percent ratio of the volume of the glass beads to the summation of the volume of glass beads plus the volume of pigment plus the volume of vehicle solids (varnish solids on dry basis). The volume of the beads means the actual volume of the beads themselves, and not the bulk volume of a mass. The volume per unit weight of each of the materials can readily be determined so as to facilitate making the BVC computation from weight data. The BVC value should be in the range of about 40 to 85%. Too low a value results in inadequate flow-off of binder and pigment from the bead tops. Too high a value results in a dried coating that is too weak or is punky or brittle. If the composiion is to be applied to porous base surfaces that will absorb appreciable binder solids from the wet applied coating, thereby materially reducing the proportion of binder solids in the coating proper and unduly increasing the BVC value thereof, allowance must be made for this in compounding the coating composition by including a correspondingly greater proportion of binder solids. In this situation it is preferable to employ a varnish having a gelatinous body so as to prevent or minimize absorption by porous base surfaces.

The composition must include sufficient volatile solvent to provide adequate fluidity when applied. The proportion depends upon the nature of the particular composition and the application procedure to be employed, and can best be determined by trial in any given case. In general, varnish solutions formulated so as to contain nonvolatile binder solids in the weight range of about 10 to 40% (and, correspondingly, 90 to 60% of volatile solvent material) have proved useful, as illustrated by the working examples hereinafter described.

The term "varnish" is employed herein in its broad sense and includes not only oil and spirit resin varnishes but lacquers as well, which provide adequately durable transparent film coatings when coated and dried. A liquid varnish vehicle is a mixture of non-volatile film-forming binder material (commonly referred to as the varnish solids) and of volatile solvent material which imparts the desired degree of fluidity and which evaporates during drying of the coating. Alkyd resin varnishes have been employed by me in obtaining reflective coatings having prolonged resistance to outdoor exposure including resistance to darkening by the sun's rays. For temporary signs, nitrocellulose lacquer formulations have proved satisfactory. The varnish solution is thixotropic, having a "false body," which appears to assist the process of relocation of the metal flake pigment particles in the applied coating as previously described, and also serves to retard settling of the beads and pigment during storage of the composition. The inclusion of a small proportion (preferably a fraction of a percent) of a colloidal suspending agent in the liquid coating composition is advantageous in producing a more stable and thixotropic suspension of beads and pigment, and in preventing clumping together of pigment particles, thereby improving the shelf life. Illustrations of such additives are the organic derivatives of bentonite sold under the trademark "Bentone" by the Baroid Division of the National Lead Company. Even when prolonged storage has resulted in marked settling of beads and pigment, they can be redispersed before use of the composition by vigorous agitation or stirring, as by using a paint shaker or a propeller mixer.

When clear (colorless) glass beads and binder are used, the light reflected from the coating will have the color of the reflective metal pigment. Thus silvery reflection is obtained when aluminum pigment is employed. In such case the day appearance will be dull, viewing being by diffused daylight; thus the sign area will have a dull gray daytime appearance when aluminum pigment is used. This is not objectionable in many situations, but attractive color effects both by day and night can readily be obtained by compounding the coating compositions so as to include material that will have a color filter effect without impairing the transparency of the elements of the coating that must transmit light rays. Thus colored glass beads can be utilized, made from transparent colored glass, or provided with concentric transparent colored coatings. Transparent color pigment (such as phthalocyanine pigment) can be included so as to produce coloration of the binder, this pigment having approximately the same refractive index as the binder so as not to materially interfere with transparency, or a dye can be employed.

The dried coating of the present type provides a reflective area upon the base surface having a vast number of reflex-reflecting spots per square inch or square centimeter, each consisting of a minute glass bead having a metal flake reflector concavely shaped to be contiguous to the back surface, forming a reflex-reflecting catadioptric combination. The human eye cannot distinguish between the light rays emanating from adjacent individual spots, and so the reflective area appears to the viewer of the sign or marker as a uniform continuous area. The viewer's reaction under reflex-reflecting viewing conditions is that the area is coated with an extraordinarily brilliant paint. This is true even when the incidence of the illuminating light beam is at a substantial angle away from the perpendicular, when the sign is viewed by persons located near the axis of the incident light, and hence the signs have what is known as good reflex-reflection "angularity," also known as "wide-angle" reflex reflection. This means that highway signs and markers have good night time visibility to motorists even when they do not face substantially directly toward the observer, and even when they have a curved surface (as in the case of posters tacked on telephone poles and in the case of reflectorized tree trunks).

In contrast, a mirror type of sign or marker provides specular reflection and returns reflected rays toward the source only when the angle of incidence is zero (i.e., when the rays impinge perpendicularly to the surface of the mirror). A surface coated with a conventional aluminum paint (dried varnish containing leafed-out aluminum flakes) provides semi-specular reflection and visibility is poor for persons located near the axis of an angularly incident beam of light. Signs and markers of these types must be viewed from approximately dead ahead to have good visibility. This prevents general utility for roadside signs and markers, since they are ordinarily so located that they can be viewed from dead ahead (if at all) for only an instant from a rapidly moving vehicle.

An ordinary painted or enamelled sign surface provides non-specular or diffused reflection, owing to the reflection characteristic of the jagged pigment particles which causes a beam of light to be reflected in all directions. Some light rays are reflected in the direction of the source of an angularly incident beam of light, but most of the light is scattered in other directions. A glossy enamelled surface exhibits specular surface reflection in addition to the diffused reflection provided by the pigment particles, which further reduces visibility to persons located near the axis of an angularly incident beam of light.

The following table illustrates the relative reflection intensities for various samples as measured by a photometer located close to the beam of incident light, the di-

vergence angle being ⅓° and being representative of the average divergence angle encountered in typical highway viewing conditions. (The divergence angle is the angle subtended between straight lines connecting the light source to the reflective area and connecting the reflective area to the viewing eye or photometer.) The reflection intensities are shown for angles of incidence of 10°, 20°, 30° and 40°. (The angle of incidence is the angle subtended between a straight line connecting the source to the reflective area and a line perpendicular to the plane of the reflective area.) The same light beam source was used for all measurements. In each instance the value given is the ratio of the photometer reading for the sample being tested to the reading for a typical glossy white enamelled sign surface (used as a comparison standard), both having the same area and being measured at the same angle of incidence.

Reflective surface	Relative reflection intensities at designated angles of incidence			
	10°	20°	30°	40°
White sign enamel (diffused reflection)	1	1	1	1
Aluminum paint (semi-specular reflection)	0	0	0	0
This invention (reflex-reflection)	125	125	115	100

In this table the "zero" values for the aluminum paint sample signify values which are very small compared to those for the white enamel sample. The former type has a dark gray appearance when visual comparison is made at the designated angles, and has a brilliant silvery appearance only when viewed from substantially dead ahead (i.e., when the angle of incidence is zero or quite small).

The above-noted sample prepared with the reflective coating composition of this invention was made by screen process coating a white showcard stock with the composition of Example A (given hereafter) using glass beads of 1.9 refractive index having diameters in the range of 20–45 microns. These are representative of values obtainable with a variety of compositions, and even higher values have been obtained with some of my compositions.

The invention makes possible highly effective reflective coating compositions that can be utilized in aerosol "bomb" or "spray-can" applicators from which the composition can be sprayed on any desired surface. The pressure is provided by a volatile propellant liquid having a high vapor pressure that is included in the vessel. For example, the reflective coating composition can be readily sprayed on bridge abutments, concrete curbings, posts, tree trunks, etc., to provide reflectorization that has a brilliant visibility at night to motorists and serves as a guide or as a warning of a hazard. The daytime appearance is not materially changed owing to the inconspicuousness of the coating except when viewed under reflex-reflecting conditions. A highway patrolman can carry a small applicator in his car or motorcycle and can conveniently stop and reflectorize any object that appears in need of greater nighttime visibility. The compositions can also be sprayed from a spray-gun.

Temporary highway safety markers and signs can be easily prepared. There is also a market for temporary advertising signs that are inexpensive and have high visibility at night to motorists. Examples are signs advertising special sales, and posters used during political campaigns. These can readily be made in quantity, as by spraying the reflective coating composition on inexpensive cardboard backings (such as showcard stock) using a stencil procedure, or by screen process printing.

The invention also permits of obtaining reflex-reflecting coating structures having a smooth flat outer surface instead of the spherulate or lenticular exposed surface resulting when only the one-step procedures as previously described has been employed. This can be accomplished by first providing a coating of the beaded reflective composition and allowing it to dry, and then coating the spherulate surface with a transparent varnish, colored or clear, which covers the protrusions and provides, when dry, a flat outer surface. In this situation, the theoretical optimum effective refractive index of the beads is about 2.8 but a lower value can be used with good results. As is known in the art, the effective refractive index of a bead can be increased by providing the bead with a concentric transparent coating having a lower refractive index, so that the focal relationship of the bead and back reflector in the final coating structure is altered to produce a reflection characteristic similar to that obtainable with a uniform sphere lens of higher refractive index, thus avoiding the need of glass of very high refractive index.

The following examples provide illustrations of presently preferred varieties of reflective coating compositions of this invention.

Example A

The following formulation is well-adapted for application by screen process and knife coating procedures on various paper and metal base surfaces in making signs and markers.

	Percent by weight
Glass beads of 1.9 refractive index (diameter range of 20–45 microns)	59.00
Nitrocellulose mixture (5000 second viscosity type wet with 35% ethanol)	1.90
Oil-modified alkyd varnish resin solution (50% solution of alkyd resin in xylol)	6.45
Dibutyl phthalate (plasticizer)	0.23
Aluminum pigment paste (fine lining aluminum flake milled with 60% butyl lactate)	5.87
Butyl lactate	13.85
Xylol	11.30
Butanol	1.40

A preferred type of alkyd resin solution for this purpose is available under the trademark "Beckosol 1307" from Reichhold Chemicals, Inc., and is a solution of meduim oil length, soya-modified, phthalic alkyd resin (drying type) in 50% of xylol solvent.

A preferred type of aluminum pigment is an extremely fine aluminum leafing powder, also known as fine lining aluminum flake, of which 1 gram covers a surface area of 25,000 sq. cm. The paste is prepared by ball milling the aluminum pigment with the butyl lactate for 16 hours or longer.

The composition is prepared by charging the butanol and xylol solvents to a mixing vessel. The nitrocellulose (wet with ethanol) is added and the mixture is stirred until the nitrocellulose is thoroughly wetted and pulped. The butyl lactate solvent is slowly added with stirring which is continued until a clear solution is obtained, after which the dibutyl phthalate and the alkyd resin solution are added with continued stirring. The aluminum pigment paste and the glass beads are successively added with thorough mixing to obtain a good dispersion. The product is then ready for packaging.

The weight and volume percentages on a dry solids basis (disregarding all voltatile components) are the same as in a dried coating and are as follows:

	Percent weight	Percent volume
Glass beads	89.3	77.8
Aluminum pigment	3.6	4.2
Varnish solids	7.1	18.0

Thus it is evident that the bead volume concentration (BVC), as previously defined, is approximately 78%, and that the total volume concentration of beads and pigment is 82%. The weight ratio of glass beads to pigment is 25:1. In the liquid coating composition the varnish vehicle (exclusive of beads and pigment) is comprised of 13.3% non-volatile plasticized binder solids (nitrocellulose, oil-modified alkyd resin and dibutyl phthalate) and 86.7% volatiles (ethanol, butanol, xylol and butyl lactate) by weight.

Example B

The following abbreviated formulation is similiar to that of the preceding example except that an organic derivative of bentonite is included to improve thixotropic and suspension properties, producing a more stable product. A preferred example of such compound is available under the trademark "Bentone 18–C" from the Baroid Division of the National Lead Company and is believed to be identifiable as an alkyl ammonium montmorillonite.

	Percent by weight
Glass beads	55.00
Nitrocellulose mixture	1.90
Oil-modified alkyd resin solution	6.70
Dibutyl phthalate	0.23
Aluminum pigment paste	4.55
Bentonite derivative paste (75% ethyleneglycol monoethylether)	2.00
Butyl lactate	16.35
Xylol	11.80
Butanol	1.47

The bentonite derivative paste is prepared by mixing the bentonite derivative and the ethyleneglycol monoethylether in 25:75 ratio and then working twice through a three-roll paint mill to form a fairly stiff lump-free paste.

The composition is compounded as described in the preceding example except that just prior to admixing the glass beads, the bentonite derivative paste is stirred in and the batch is heated to 120–130° F. with continued stirring until smooth and free from lumps.

Example C

The following formulation employs an air-drying alkyd resin varnish base as distinguished from the nitrocellulose lacquer type varnishes of the preceding examples. It provides an excellent suspension of the glass beads and it can be brushed or sprayed on many types of surfaces, including metal, wood, paper and concrete, to provide dried coatings having excellent reflex-reflection properties. This composition lends itself to use in aerosol spray containers, which can be loaded with this composition and an equal amount of fluorinated propellant (such as a mixture of equal parts of "Freon 11" and "Freon 12") together with a steel ball so that shaking of the container will ensure a good dispersion at time of use.

	Percent by weight
Glass beads	62.75
Polyamide modified alkyd resin (gelled with 60% mineral spirits)	19.56
Fine lining aluminum flake	1.97
Naphtha (V.M. & P.)	12.90
Mineral spirits (thinner)	2.54
Metal naphthenate drier (50% solution)	0.23
Anti-skinning agent	0.05

A preferred polyamide modified alkyd resin, which is desirable because of its thixotropic properties, is available under the trademark "Burnok" from the T. F. Washburn Company, Chicago, Illinois, and is believed to be disclosed in U.S. Patent No. 2,663,649 issued to that company. Metal naphthenate varnish driers are well known to the art (e.g., a mixture of cobalt, manganese and lead naphthenates). Anti-skinning agents are also well known in the varnish art and prevent or minimize the formation of a surface skin upon exposure to the atmosphere.

The composition is prepared by charging the alkyd resin gel to a mixing kettle and vigorously agitating. The naphtha and mineral spirits are slowly added with mixing and heating to 100° F. to obtain a smooth mixture. Then the aluminum flake pigment, metal naphthenate drier and anti-skinning agent are added and worked in. As the batch cools and becomes more viscous the glass beads are stirred in and dispersed.

Example D

The following formulation illustrates the use of a synthetic rubber type base. It is useful in screen process printing on cloth to provide reflex-reflecting designs thereon that are highly flexible, as on warning flags, tarpaulins and clothing, and it can also be employed on rubber, leather and plastic articles.

	Percent by weight
Glass beads	39.0
Phenolic varnish resin (heat-advancing oil-reactive 100% phenol-aldehyde resin)	4.6
Cumarone resin	1.5
Neoprene rubber mix (100 parts polychloroprene rubber milled with 5 parts ZnO, 4 parts calcined MgO, 1½ parts sodium acetate and 2 parts anti-oxidant)	6.2
Aluminum pigment paste (milled with 60% butyl lactate)	4.7
Ethanol	0.5
Toluene	29.0
Butyl lactate	14.5

The ethanol and half of the toluene are charged to a mixing vessel. The phenolic resin and the cumarone resin (such as Cumar W) are mixed in, and then the neoprene rubber mix is added with continued stirring until a smooth mixture is obtained. The remaining toluene and the butyl lactate are added, following which the aluminum pigment paste and the glass beads are incorporated.

Example E

The following formulation utilizes a high-viscosity type of cellulose-derivative lacquer and has excellent shelf stability. It is particularly useful for application by screen process printing and knife coating techniques upon metals, hard plastics, paper and wood, and forms coatings which are brilliantly reflex-reflecting and superior to the coatings of the Example A formulation for which test data was given in the preceding table of reflection intensities.

	Percent by weight
Glass beads (1.93 refractive index, 3.65 density (grams/cc.), diameter range of 20–45 microns)	60.75
Cellulose acetate butyrate (high viscosity type)	3.40
Hard acrylic ester resin	0.75
Silicone resin leveling agent solution (60% solution in toluene)	1.30
Di(2-ethylhexyl) phthalate (plasticizer)	0.95
Ethylene glycol monoethyl ether acetate	8.25
Diacetone alcohol	8.25
Methyl-ethyl benzene solvent (petroleum distillate solvent mixture of approx. 100° F. flash point)	7.65
Aluminum pigment paste (37% fine lining aluminum flake pigment of minus 400 mesh, ball milled with 3% amorphous silica adsorbent and 60% butyl lactate)	6.95
Butyl lactate	1.75
	100.00

The above formulation, exclusive of the glass beads and pigment, contains 16.2% solids and 83.8% volatiles, by weight.

The weight and volume percentages on a dry solids basis (disregarding all volatile components) are the same as in a dried coating and are as follows:

	Percent by weight	Percent by volume
Glass beads	87.5	72.7
Aluminum pigment	3.7	4.4
Silica adsorbent	0.3	0.4
Varnish solids	8.5	22.5

The BVC value is 72.7%.

The above-mentioned aluminum pigment is so fine that 1 gram will cover a surface area of approximately 25,000 sq. cm. The flakes range in size down to a few microns and it is estimated that the average size is no greater than about one-fourth the average bead diameter.

A preferred high viscosity cellulose acetate butyrate (which in combination with the hard acrylic ester resin provides the film-forming lacquer or varnish binder solids) is a 20-second viscosity type with approximately 38% combined butyryl (C_4H_7O) content and 13% combined acetyl, the remainder being combined cellulose residue containing 2% free hydroxyl groups. A commercially available example is Eastman's "EAB 381–20."

An example of silicone resin leveling agent is Dow Corning's "DC–840." The acrylic ester resin is illustrated by a hard methyl methacrylate lacquer resin, and may be the "Acryloid B–72" sold by Rohm & Haas Co. The amorphous silica adsorbent may be the "Syloid Al–1," sold by Davison Chem. Div. of W. R. Grace & Co.

The coating composition may be prepared from the above ingredients by charging a mixing vessel with the solvents, then adding the lacquer polymer solids and stirring until dissolved. The plasticizer and the silicone resin are added with continued mixing until a clear solution is obtained. The aluminum pigment paste and the glass beads are added with thorough mixing to obtain a good dispersion. The final viscosity of the composition is adjusted to the desired value by the addition of the butyl lactate in whatever small amount is required, permitting of obtaining a uniform batch-to-batch viscosity. For the formulation of this example, a preferred viscosity range is 12,000 to 14,000 centipoises as measured at 77° F. on a Brookfield viscometer. The product is now ready for packaging.

I claim:

1. A liquid reflective coating composition of the character described and consisting essentially of a mixture of fluid thixotropic transparent bead-binder varnish solution containing sufficient volatile solvent to produce adequate coating fluidity and the formation of the type of coating hereinafter specified, transparent glass beads having a refractive index of at least about 1.8 and a diameter in the range of about 25 to 75 microns, and finely divided metal flake reflective pigment particles of a size substantially less than the size of the beads, the weight proportion of said metal pigment being in the range of one part to about 5 to 50 parts of said glass beads and the glass beads being present in a bead volume concentration in the range of about 40 to 85%; the ingredients and proportions being such that upon application of the coating composition to a base surface the glass beads flow out to form a lenticular varnish-bonded monolayer thereof wherein the metal flake pigment particles become positioned so as to optically expose the varnish-coated front surfaces of the beads to incident light rays and so as to provide the back surfaces of the beads with contiguous concentric metallic reflectors, forming a beaded reflective coating which when dried is already inherently and brilliantly reflex-reflecting.

2. A coating composition according to claim 1 where-

in the weight ratio of the glass beads to the metal flake pigement is approximately equal to

$$0.1(A)(D)(d)$$

where (A) is the surface area in square centimeters covered by one gram of leafed out metal flake pigment, (D) is the density of the glass beads, and (d) is the mean diameter of the beads in centimeters.

3. A coating composition according to claim **2** wherein the bead-binder solids of the varnish solution consists mainly of a high-viscosity cellulose-derivative lacquer.

4. A coating composition according to claim **3** wherein said cellulose-derivative is cellulose acetate butyrate.

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JOSEPH L. SCHOFER, *Primary Examiner.*

JOHN H. MACK, LEON J. BERCOVITZ, *Examiners.*

A. LIEBERMAN, J. A. SEIDLECK, *Assistant Examiners.*