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PROCESS OF MAKING BEADED COATINGS AND FILMS FROM GLASS BEADS TREATED WITH OLEOPHOBIC SIZING AGENT

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This invention relates to the utilization of glass beads (small transparent spheres) in the production of beaded coatings and films, as in the production of reflex-reflective ("retrodirective") signs and markers and reflex reflector sheeting employed in making signs and markers. Highway and vehicle signs and markers of the "reflex" light-reflective type have a high night-time visibility to the drivers of motor vehicles whose headlights illuminate the sign or markers, since the reflected light that returns toward the source is of much higher intensity than is the case with ordinary signs and markers which diffuse the reflected light in all directions, and this high visibility is obtained even though the incident light strikes the surface of the sign or marker at a substantial angle to the perpendicular. Beaded reflex light reflector sign products include a monolayer of minute transparent glass beads held in a binder layer or coating. There are usually many thousands of these beads per square inch (or square centimeter), which results in difficult problems in forming beaded structures so as to utilize the beads to best advantage.

It has been discovered that novel and improved results, both as to processes and resultant products, can be obtained by using beads that have previously been given an extremely thin (microthin) surface coating of an oleophobic fluorocarbon sizing agent. This provides an imperceptibly thin oleophobic fluorocarbon surfacing that renders the beads both oleophobic and hydrophobic, and yet does not prevent good bonding of the treated beads to the organic binder layer in which they are embedded.

The varieties of reflective products in this field have in common the use of a making procedure that includes the steps of forming a liquid organic binder coating layer on a permanent or temporary base, partially embedding a monolayer of glass beads in the coating while it is still liquid or plastic, and then solidifying the binder to a solid bead-retaining state. In some cases a binder containing reflective pigment is used. In other cases a transparent binder is used. In the latter situation, the transparent binder coating may be formed on a reflective base; or it may be formed on a removable support from which, after drying, the beaded film is stripped and may subsequently be applied to a reflective base or be given a reflective coating or plating. Another expedient is to employ silvered glass beads and to remove the exposed silvering after a beaded coating or film has been produced, thereby optically exposing the unembedded glass surfaces of the beads. Still another expedient is to employ hemispherically silvered beads. In all such cases a reflex-reflecting (retrodirective) characteristic is obtained in the final products by an appropriate catadioptric combination of the transparent beads (serving as small spherulenses) and the associated underlying reflective means. Cf., U.S. Patents Nos. 2,326,634 (Aug. 10, 1943), 2,354,018 (July 18, 1944), 2,354,048 (July 18, 1944), 2,354,049 (July 18, 1944), 2,407,680 (Sept. 17, 1946), which describe a variety of reflex-reflective beaded products and making procedures that illustrate the above points.

A monolayer of the present fluorocarbon-surfaced beads (unlike ordinary beads) can be "floated" in the liquid binder layer (when it is of sufficient thickness and

fluidity) so as to be approximately half-submerged, and without the binder crawling upwards on the beads by capillarity; and this floated relationship of the beads is retained in the product during solidification of the binder to result in a uniform close-packed well-bonded surface layer of beads.

Glass is both hydrophilic and oleophilic as demonstrated by the fact that drops of water, drops of oil, and drops of common organic solvents and diluents used in varnishes and paints, when placed on a dry clean glass plate will all wet the glass surface and spread out to a thin film.

Ordinary untreated glass beads when dropped on rolled onto a layer of liquid binder coating, tend to submerge or "drown" owing to their higher density and also to the tendency of the coating material to spread on the glass and crawl up toward the tips of the beads. Hence the liquid binder coating must be applied upon the base surface in a carefully controlled thickness and must have a proper consistency at the time when the beads are applied, so that the beads will not settle too far nor be covered too much. If the binder contacts a bead surface to more than about 45° above its equator (due to excessive submergence or to crawling of the wet binder toward the tip of the bead), the resulting substantial decrease of the optical lens aperture seriously reduces the amount of reflex-reflected light which the bead can provide. If the binder coating is too thin or includes too much volatile vehicle, a "starved" binder results upon drying which cannot properly anchor the beads.

If it is sought to minimize these difficulties by employing a binder coating of a more viscous or plastic initial consistency, or by waiting to apply the beads until the initial binder coating has dried to a more viscous state, the beads may not penetrate sufficiently by impact or gravity action and the layer of beads then has to be given a carefully controlled rolling or pressing. The problem of forming an optically efficient monolayer of properly anchored beads is most acute when making reflective sheeting and sign products with minute beads in the 25-100 micron diameter range; these beads being of flour-like fineness and a mass of such beads containing millions per cubic inch or cubic centimeter.

Baking is generally employed in making beaded signs and this further complicates the problem when ordinary beads are used, since the binder coating temporarily becomes fluid when the sign is subjected to baking conditions.

The difficulties are compounded by the fact that a mass of beads of any given screen-graded size is a random mixture of beads of varying individual sizes which thus differ considerably in weight and diameter and in their response to the factors mentioned above. When such beads are dropped or otherwise impelled against the wet binder coating, the variations in size and momentum cause considerable variation in the degree of penetration, and it is impossible to obtain in the dried product a layer of beads whose centers are substantially coplanar or substantially equidistant from the underlying back surface of the binder layer or the base surface on which it was coated. This variability also makes more difficult the problem of correctly spacing beads, held in a transparent binder coating or film, from an underlying reflector surface or coating, to obtain an end product having desired reflex reflecting optical properties.

These problems seriously complicate the beading of binder coatings or films with minute beads and necessitate a great deal of skill and care if one wishes to produce reflex-reflective products of high optical efficiency coupled with high durability and freedom from loss of beads during handling and outdoor exposure usage.

Factory production of continuous webs of reflex-reflective sheeting of uniform acceptable quality lengthwise and crosswise of the web requires the use of special expedients and careful control on account of these problems.

It has been discovered that use of the aforesaid novel oleophobic fluorocarbon-surfaced beads has notable value in overcoming these difficulties and has further advantages. This utility depends in part on obtaining effective bead-to-binder bonding, which is apparently contradicted by the following considerations:

Fluorocarbon polymer films and coatings (e.g., films or coatings of polytetrafluoroethylene, sold by Du Pont under the trademark "Teflon") are notoriously inert. A fluorocarbon surface formed of completely fluorinated or highly fluorinated carbon chains (such as that of a "Teflon" film) is both oleophobic (oil-repellent) and hydrophobic (water-repellent) and is therefore incompatible with both oil-soluble and water-soluble organic materials employed in coating and adhesive compositions. Drops of oil, water, solvents or thinners, when placed on the fluorocarbon surface, do not wet the surface and spread, but remain indefinitely and roll off if the surface slants or is tilted. The surface will not adhere or bond to the usual organic coating materials or adhesives. In fact, fluorocarbon polymer films, and coatings of fluorocarbon-type sizing agents, are widely employed to provide nonadherent, antistick or release surfaces. It might be expected therefore, that if glass beads (small smooth glass spheres) were treated so as to be given an exposed oleophobic and hydrophobic fluorocarbon type of surface, the resultant beads could not be adequately adhesively bonded to a coating in which they are embedded. A liquid binder coating in which a fluorocarbon-surfaced bead is partially embedded is unable to crawl up on the bead surface to provide an adequate mechanical socket. Thus it might be concluded that the treatment of glass beads to provide a fluorocarbon surfacing would render them unsuitable for commercial usage in the field of present concern.

Surprisingly, it has been discovered that it is possible to provide fluorocarbon-surfaced glass beads which are oleophobic and hydrophobic and which nevertheless become firmly adherently bonded to binder layers in which they are embedded. This phenomenon is related to the microthinness of the fluorocarbon coating employed (less than 1 micron), which is formed from an oleophobic fluorocarbon sizing agent applied in extremely minute amount to the surface of the bead. This fluorocarbon surfacing is imperceptibly thin and does not interfere with the desired optical properties of the sphere-lens bead, and it is tightly adsorbed on the glass surface. It is thick enough to provide an oleophobic and hydrophobic surfacing but thin enough to permit of bead-to-binder bonding.

It has further been discovered that these minute oleophobic fluorocarbon-surfaced glass beads will "float" in an organic liquid binder coating layer so as to become approximately half-submerged, the layer of course being of sufficient thickness and fluidity to permit of this. It has also been discovered that this floated relationship will be retained as the binder layer dries or hardens to a solid bead-retaining state, even though subjected to baking temperatures. It has been found that this flotation phenomenon may be utilized to practical advantage to improve the production of beaded reflex-reflective products.

These organic liquid binder coating compositions usually comprise a varnish solution of a film-forming resin or polymer material which is dissolved in a volatile organic liquid vehicle that generally includes in major or total amount a hydrocarbon-type solvent or thinner, such as a hydrocarbon liquid or an alcohol, and which may or may not contain dispersed pigment depending upon whether a transparent or a reflective binder coating is desired. Some are air-drying types and some are baked

after initial drying to effect a curing reaction or polymerization. Such compositions are designated as varnishes, lacquers or paints. Use may also be made of liquid coating compositions which do not depend upon evaporation of a volatile vehicle for solidification. Thus use can be made of solventless liquid systems of monomers or low polymers which can be set up or cured to a solid state after being coated and beaded.

The oleophobic and hydrophobic surface characteristics of the present beads are each of importance in assuring flotation in wet liquid layers of such coatings, although the oleophobic property is the one that is most essential owing to the oil-soluble types of liquid ingredients commonly present. However, liquid ingredients that are water-soluble (such as alcohols) are often present. The hydrophobic property also prevents any water or moisture which might be present from wetting the bead surface and interfering with the flotation effect or with the establishment of the bead-to-binder bond.

When a mass of the present beads is distributed onto a wet binder coating, and the surplus beads removed as by tilting, a highly packed and uniform monolayer of partially embedded beads is left. The present beads do not tend to clump or agglomerate and a uniform and closely packed layer of the beads over the area results. This in itself is an important feature. Irrespective of variations in size, all of the beads come to float in an approximately half-submerged state, assuming of course that the binder coating is of sufficient thickness and liquidity. Beads which initially sink somewhat too far due to impact momentum (as when beads are dropped on) can rise to normal floating position. There is no capillarity effect and hence no cupping of the liquid binder between the beads, and there is no crawling of the liquid binder upon the beads. These geometrical or physical relationships are retained during drying or setting of the binder to a solid bead-retaining state and make possible reflex-reflective products of greater optical efficiency; resulting in improved visibility and brilliancy and uniformity of appearance.

The beads generally assume a floating position such that a little more than half of each bead is submerged, the liquid binder contacting the embedded beads only up to 5 to 30° above their equators. This is true despite wide variations in viscosity and eliminates the need of careful viscosity control, and it permits of using types of binder coatings that cannot be employed when ordinary beads are used. This positional relationship assists the anchoring of the beads in the ultimate dried binder coating. Each bead is adequately exposed and provides a sphere-lens having a large optical aperture relative to its size so as to permit of efficient reflex-reflection. During drying involving evaporation of volatile vehicle there is some shrinkage of the binder film and consequential cupping, but the beads remain bonded to the contacting binder so as to be firmly held in the dried coating or film by a combination of mechanical and adhesive actions. In the final dried product the centers of these "floated" beads are still approximately coplanar, the centers being approximately equidistant from the underlying back surface of the binder layer or the top surface of the base.

The glass beads have a density or specific gravity several times greater than that of the liquid binder coating. This density ranges from about 2.5 in the case of ordinary glass beads having a refractive index of about 1.5, up to about 3.5 for "high index" beads of about 1.9 refractive index, and up to about 5 or higher for "super high index" beads having a refractive index of 2.2 or higher. Thus the buoyancy effect of the liquid binder layer (density of less than unity) is a minor factor, especially as to beads of high refractive index. Flotation of the present beads is primarily due to an interfacial surface tension effect, and the ability of the treated beads to provide this effect is indicated by the high contact

angle between the fluorocarbon surface and the organic liquid binder. This high contact angle prevents capillarity and crawling of the liquid binder.

Beads having diameters in the size range of about 25 to 1000 microns (1 to 40 mils) are employed in making beaded reflex-reflective products of various kinds and these can all be employed for present purposes. (In fact ordinary glass beads as large as 2000 microns (80 mils) in diameter have been successfully floated in reflective binder coatings when treated according to the present invention.) The larger beads in this range are mostly utilized for the beading of highway paint lines, such as centerline marker stripes, by the "drop-on" procedure; the beads being sprinkled onto the paint line on the highway surface while it is still wet and tacky. The smaller beads are utilized in making signs and in manufacturing reflective sheeting and other reflective articles.

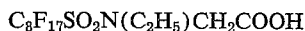
Among the advantages of using the present fluorocarbon-surfaced beads is the fact that even the smaller beads in this range (having a diameter of about 25 to 150 microns or 1 to 6 mils) can be employed, using simple application techniques, to obtain a close-packed uniform well-bonded bead layer that results in substantially greater reflex reflection brilliancy and durability to outdoor exposure. Use of these very small beads is highly advantageous for a number of reasons. Thus these minute floated beads provide a relatively "smooth" beaded surface and one that has good "printability" for designs that are applied by screen process printing. A given weight of beads provides a greater reflective sign area. Less paint is needed to bond the beads and a better mechanical anchorage is obtained.

A preferred treatment of the beads to impart the aforesaid fluorocarbon-surface properties involves mixing a mass of clean beads with a highly dilute solution of a fluorocarbon coordination complex of a polyvalent metal and a fluorocarbon monocarboxylic acid having an oleophobic fluorocarbon terminal chain ("tail") of 4 to 10 carbon atoms. The beads are then drained and dried. The metal coordination complex forms an insoluble polymeric film on the bead which is tightly bonded owing to the presence in the molecules of functional binding atoms (or groups of atoms) having an affinity for the substrate. The fluorocarbon chains (tails) of the molecules are inert and have no affinity for either the substrate bead surface or for the binder coating in which the beads are later embedded. The procedure results in an integral transparent surface film coating that is so extremely thin (less than 1 micron) that it is imperceptible. The fluorocarbon chains (tails) become oriented outwards to provide the bead with an external fluorocarbon surface that is both oleophobic and hydrophobic. However, the extreme thinness of the film apparently permits the binding atoms of the fluorocarbon compound to function in some way to effectuate an adherent bonding between the binder coating and the embedded bead during drying or curing, even though there is so little initial affinity between the bead surface and the wet binder that the latter does not spread or crawl on the surface of the floating bead.

Aqueous treating solutions of fluorocarbon chromium coordination complexes are preferred and are described in U.S. Patents Nos. 2,662,835 (Dec. 15, 1953) and 2,809,990 (Oct. 15, 1957) and 2,934,450 (April 26, 1960). The complex may be made by reacting chromyl chloride with a fluorocarbon monocarboxylic acid (having a highly fluorinated terminal chain or tail containing 4 to 10 carbon atoms) in an isopropanol vehicle which serves both as solvent and reducing agent, the chromium to acid mole ratio being in the range of 2:1 to 5:1. The resultant green-colored isopropanol solution of the complex is diluted with water at the time of use. The fluorocarbon acid preferably has 6 to 8 fully fluorinated (perfluorinated) carbon atoms in the terminal fluorocarbon chain or tail. A clean glass plate when treated with this com-

plex, exhibits a contact angle to xylene of about 80°, whereas the contact angle is less than 15° in the case of a clean dry untreated glass plate. Drops of xylene and other volatile hydrocarbon liquids, drops of mineral and vegetable oils, drops of common organic solvents, such as alcohols, and drops of water, when placed on the treated glass surface, remain without spreading and will roll when the plate is tilted.

A specific working example of a treating solution is one made from a chromium coordination complex of perfluorooctanoic acid ($C_7F_{15}COOH$), having a chromium to acid mole ratio of 3:1, prepared in isopropanol so as to result in a green-colored solution having a solids concentration of 28%. Equivalent use can be made of the fluorocarbon acid N-ethyl, N-perfluorooctanesulfonyl glycine, having the formula:



This solution is diluted at time of use by mixing one volume with 100 volumes of water. Mixing of the glass beads with this dilute aqueous solution, followed by draining, results in wet beads having an appropriate coating weight of the chromium complex to provide, on drying, beads having a suitably microthin and firmly bonded film coating. Another procedure is to mix the beads with just sufficient of the aqueous solution to wet the surfaces of all the beads, there being little if any surplus liquid to drain off. The wet beads can be air dried at normal temperature, but a more durable type of coating results from drying or curing the coating by heating with hot air circulated through the mass of beads, or by heating in trays in an oven, or by flowing the beads through a heating chamber; avoiding temperatures above about 150° C.

The optimum thickness of the dried fluorocarbon surfacing is one which is just sufficiently thick to impart the desired oleophobic and hydrophobic surface characteristic. Such a coating is so extremely thin as to be of the order of molecular dimensions and cannot be measured mechanically as its thickness is less than a tenth of a micron. Adequate treatment is readily demonstrated by the ability of the treated beads to float both on water and on hydrocarbon liquids (such as oils, heptane, xylene, etc.).

This treatment may be given to glass beads that have already been given a surface treatment or coating that provides a hydrophilic or electronegative type of surfacing that is the actual substrate surface upon which the fluorocarbon treating agent is applied. Mention has already been made of the use of silvered glass beads in producing reflex reflecting products. These can be treated as above described to provide oleophobic and hydrophobic silvered beads that will float on binder coatings. The treatment does not prevent subsequent acid etching to remove the silver from the portions of the beads protruding from the dried binder coating, so as to thereby expose the transparent glass beads to penetration by incident light rays. Beads that have been hemi-spherically silvered can also be treated; so as to provide reflective beads that can be floated on binder coatings to provide a combination of diffused and retrodirective reflection owing to the beads pointing every which way. Pretreatment of the beads is also desirable in some cases to provide a reactant on the surface of the beads that can react with a subsequently applied fluorocarbon sizing agent to form the ultimate insoluble fluorocarbon coating composition in situ.

It is only necessary that the fluorocarbon surface treatment of the beads be of a sufficiently durable nature to maintain an oleophobic and hydrophobic surface until it has served its purpose in floating the beads on the binder coating and until the binder has become dried to a sufficiently solid state to fix the beads in the floated relationship. In fact, elimination of the original fluorocarbon surfacing film as such, during the final drying or curing of the binder or upon continued contact (as by disintegration and migration into the binder) might well result

in establishing an even stronger bonding of the beads to the binder. Thus the class of useful fluorocarbon sizing agents is not limited to those that are employed in other arts for the durable coating or sizing of materials that are subjected to mechanical wearing, or washing or cleaning, or to weathering. The fluorocarbon compound need not provide a polymeric coating.

The only essential requirements of the oleophobic fluorocarbon sizing agent, are that it supply oleophobic fluorocarbon chains or "tails" and that it include functional atoms capable of binding a microthin coating thereof to the substrate surface of the bead and capable of developing an adherent bond to the dried binder in which the beads are embedded. The presence of such binding atoms in the molecular structure of the fluorocarbon treating compounds also provides functional atoms or groups that solubilize the compounds sufficiently to permit of making up dilute aqueous or organic solutions for treating glass beads.

Rather than to attempt to calculate or make a theoretical prediction as to whether a particular fluorocarbon compound will serve as an oleophobic fluorocarbon sizing agent to provide a desired oleophobic surfacing that permits of the aforesaid bead flotation effect in binder coatings, it is much easier and more reliable to treat a small sample mass of the beads that are to be employed, and then perform the test of seeing whether they float on the surface of xylene, a convenient test liquid. Experiments with a wide variety of fluorocarbon compound treating agents have shown this simple test to be effective. If the treated beads float on xylene so as to be approximately half-submerged (preferably to the extent of 10 to 20° above the equator), it may safely be assumed that they will properly float in liquid binder coatings. A confirmatory test can then be made using the type of binder coating that is to be employed. An oleophobic fluorocarbon surface is inherently also hydrophobic, as readily demonstrated by the ability of the treated beads to float on water. It is for this reason that it is not necessary to specify "oleophobic and hydrophobic" in characterizing the surface or the fluorocarbon, since the hydrophobic property necessarily accompanies the oleophobic property.

A wide variety of oleophobic fluorocarbon sizing agents are already well known. Fluorocarbon compounds of this type are commercially available from the Minnesota Mining and Manufacturing Company, Saint Paul, Minnesota. Included in this category are fluorocarbon acids, salts, amines, quaternary ammonium salts, metal coordination complexes of acids, alcohols, mercaptans, acrylate and methacrylate esters and polymers, vinyl esters and polymers, urethanes and urethane polymers, etc. Latex polymers dispersed in an aqueous vehicle may be used for coating the beads to provide a thin coherent film of fluorocarbon polymer particles that adhere to the glass upon drying and heating; an example being an acrylate polymer latex. Cf., U.S. Patents Nos. 2,567,011 (Sept. 4, 1951), 2,606,206 (Aug. 5, 1952), 2,642,416 (June 16, 1953), 2,666,797, (Jan. 19, 1954), 2,693,458 (Nov. 2, 1954), 2,706,733 (April 19, 1955), 2,727,923 (Dec. 20, 1955), 2,732,398 (Jan. 24, 1956), 2,759,019 (Aug. 14, 1956), 2,764,602 (Sept. 25, 1956), 2,803,615 (Aug. 20, 1957), 2,803,656 (Aug. 20, 1957), 2,809,990 (Oct. 15, 1957), 2,841,573 (July 1, 1958).

The following are specific illustrations:

One is a diluted latex emulsion of the homopolymer of the acrylate ester of N-propyl, N-ethanol perfluorooctanesulfonamide:



as described in U.S. Patent No. 2,803,615. Another is the fluorocarbon acid N-ethyl, N-perfluorooctanesulfonyl glycine:



or, preferably, its ammonium salt, which is applied to the

beads in dilute aqueous solution following pretreatment of the beads with a dilute aluminum chloride solution, to thereby forms on drying an insoluble coating of an aluminum complex of this acid. The acid is described in U.S. Patent No. 2,809,990. An equivalent acid for this purpose is perfluorooctanoic acid. Still another example of a treating agent is the fluorocarbon mercaptan compound:



As previously indicated, the presently preferred fluorocarbon bead-treating compounds are the chromium coordination complexes already described in detail. As these are quite satisfactory, there is no need for anyone to experiment with other compounds in order to commercially practice the present invention.

Although such fluorocarbon compounds are relatively expensive in comparison with ordinary industrial chemicals, the cost of treating glass beads as herein described is economically justified by the improved results; the fluorocarbon coating being of almost infinitesimal thickness and hence the ratio of its weight to the weight of the treated beads being extremely small.

The invention does not pertain to the chemistry of such compounds, nor is novelty asserted as to the mere general principle of coating glass therewith. This invention has to do with the specific novel idea of using the herein described fluorocarbon-surfaced glass beads, and with the empirical discovery that new and improved results can thereby be obtained in the production of beaded coatings or films such as are utilized in producing reflex-reflective products; making possible beaded reflex reflector signs, markers and sheeting of superior physical and optical qualities.

The following specific examples further illustrate the invention. In all these cases the fluorocarbon-surfaced beads had been treated with a chromium complex of a perfluorocarboxylic acid, as has been previously described in the working example thereof.

Example 1

A comparison was made in a commercial sign shop to demonstrate the improved results obtainable using fluorocarbon-surfaced glass beads (without any other change in the regular making procedure) in the production of beaded reflex-reflecting highway signs having an embossed metal base. Some signs were made with untreated beads and some with treated (fluorocarbon-surfaced) beads. The glass beads had diameters in the range of about 110 to 125 microns (120-130 U.S. Standard Mesh) and a refractive index of approximately 1.92.

In all instances the sign base (which had previously been given the usual white enamel primer coating) was given a second coating of a commercial white bead binder paint (a pigmented air-drying alkyd resin type dissolved in mineral spirits, thinned to a suitable viscosity). The sign blanks were sprayed with the paint, one at a time, and immediately coated with beads by the customary vertical drop method. The signs were then tilted and shaken to remove excess beads, and air-dried for four hours. The embossed legend of each sign was then roll-coated with black lettering paint and the signs were baked.

Comparison showed that the signs made with the treated beads had a much more uniform and a smoother beaded layer over the entire surface. Viewed under a microscope, it was evident that the treated beads were closely packed in the bead layer and there was an absence of unbeaded and sparsely beaded areas such as were present in the signs made with untreated beads. The signs made with treated beads were easily and uniformly lettered by the aforesaid roll-coating procedure, giving clean demarcation edges enhancing the appearance of the finished signs. Those made with untreated beads had rough demarcation edges, and many of the beads partially protruded through the applied paint coating due to nonuniformity of embedment in the base paint coating.

It was observed that the paint spraying operation was easily controlled when treated beads were used since it was only necessary that the wet film thickness be adequate to float the beads; whereas the paint film thickness was critical when untreated beads were used—if too thin, the beads sank into contact with the base surface and were weakly bonded, if too thick, the beads were drowned or the wet paint rose too near the tips due to capillarity.

The retrodirective brilliancy of the white beaded areas (measured under reflex-reflection conditions) of the treated-bead signs was 1.3 times greater than in the case of the best signs made with the untreated beads, and was 45 times greater than the brilliancy of a nonbeaded white painted sign surface. The treated beads were firmly and durably bonded.

Example 2

In the beading of motor vehicle license plates to impart reflex-reflectivity, using black iron embossed blanks which are coated with paint by dipping, it was found that two coats of paint are needed when untreated beads are used, the first coat being dried before the second is applied. Otherwise a large proportion of the beads will sink in the wet paint coating and come into substantial contact with the underlying black base surface which is non-reflective. Attempts to avoid this by using a single thicker paint coating results in difficulties in dipping operations (due to the higher viscosity requirement) and in the "drowning" of beads.

Use of the fluorocarbon-surfaced treated beads of this invention permitted the use of a single paint coating of a thickness readily obtainable by standard dipping procedures. Flotation of the beads resulted in the inner extremities of the beads being covered with reflective paint, so that the license plate had the desired color and reflex-reflection brilliancy at all viewing angles including dead-ahead viewing. Less paint is required than when untreated beads are used in conjunction with two coats of paint, and the beaded surface is smoother, more uniform and of enhanced visibility under night-time viewing conditions.

Comparative license plates were made using treated and untreated glass beads in the diameter range of about 70–85 microns, a wet coating thickness of white paint adequate for the treated beads, the beads being sifted onto the horizontally placed blanks immediately after dipping and draining, and the plates being baked and finished in the same way. The plates made with the treated beads had a reflex-reflection brilliancy in the beaded white areas that was 35 times as great as for nonbeaded white paint coatings; and 5 times as great as the white beaded areas of the plates made with the untreated beads, showing that a large proportion of the latter had sunk into contact or close proximity to the black base surface.

Example 3

Comparisons were made between beaded highway traffic marker lines using treated and untreated beads.

The same fast-drying white highway marker paint was used (an air-drying oil-modified phenol aldehyde type of resin base, pigmented with titanium dioxide and magnesium silicate and dispersed in a naphtha type solvent, thinned to a viscosity of 70–74 Krebs units). The paint was applied to a concrete highway surface by spraying so as to provide a wet film thickness of approximately 15 mils (275 microns). The beads were applied to the wet marker line by the usual drop-on method. The paint and beads were both applied by an applicator machine travelling at about 8 m.p.h.

Two different sizes of treated and untreated beads were used in making the comparative marker lines, all beads being of the ordinary glass type having a refractive index of approximately 1.5. The larger size was the usual size commonly employed in making beaded marker lines by the drop-on procedure; the beads randomly varying in diameter in the range of 250–800 microns. The

small size comprised beads varying in diameter in the range of 150–250 microns.

It was noted that in the cases of the untreated beads, a large proportion (the smaller beads of each size type) were drowned in the wet paint film or covered by capillarity, so that only the largest beads were exposed above the opaque paint surface in the dried marker line and capable of providing initial reflex-reflection. This is the usual result, reliance being placed on gradual dislodgement of larger beads and exposure of smaller beads, as traffic wear from the tires of motor vehicles progressively operates on the beaded line. In the cases of the treated beads, many of even the smaller beads of each size type had floated in the wet paint film so as to be initially exposed in the dried marker line. Even the largest beads, which were too large to float in the available thickness of the wet paint film, were better exposed to incident light rays owing to the absence of crawling of the wet paint toward the tips (in consequence of the oleophobic surfaces of these treated beads). Yet the treated beads were durably bonded.

The application of the treated beads to the wet paint film was less critical in respect to variations in the viscosity of the wet paint film at the instant of contact; the viscosity of the wet paint (which is of a fast-drying type) changing in the interval between spraying of the paint and dropping on of beads and the amount of change depending on the temperature and weather. When ordinary untreated beads are used, the drowning of the smaller beads is especially pronounced when the paint is too wet (too fluid) at the instant of contact.

After drying, the reflectivities of the various lines were compared with a Hill-Ecker photometer, a standard test procedure designed to indicate the relative visibilities of road markers to motorists under nighttime conditions. The following table gives the results in the units of this test, the relative values being significant here:

| Bead Size, microns | Untreated | Treated |
|--------------------|-----------|---------|
| 250-800 | 4.8 | 9.3 |
| 150-250 | 3.6 | 8.9 |

In other experiments it was found that treated 1.5 index beads of a size even as large as a 1600–2000 micron diameter range could be floated by the drop-on procedure in a wet paint layer when of adequate thickness.

The invention is not limited to reflex-reflective products. Thus, beaded light-diffusing coatings and films can be made by flotation of fluorocarbon-surfaced beads in transparent films and coatings while in an intermediate liquid state prior to drying or solidifying, to thereby provide a beaded surface layer in the film or coating.

We claim:

1. A process of making beaded coatings and films by forming a liquid organic binder coating layer on a base surface, partially embedding a layer of glass beads in the coating, and solidifying the binder to a solid bead-retaining state, characterized by using oleophobic fluorocarbon-surfaced glass beads having an imperceptibly thin surface coating of an oleophobic fluorocarbon sizing agent, and floating the beads in a sufficiently thick and fluid binder layer so that they are approximately half-submerged prior to and during solidification; said surface coating being of a nature which permits adherent bonding of the beads to the dried binder.

2. A process according to claim 1 wherein said fluorocarbon sizing agent is a metal coordination complex of a fluorocarbon monocarboxylic acid.

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3. A process according to claim 1 wherein beads having a density of at least about 3.5 are floated in the binder layer to provide a product having a uniform close-packed monolayer of beads contacted by the binder only up to 5 to 30° above their equators.

4. A process according to claim 1 wherein beads having a size in the range of about 25 to 150 microns diameter are floated in a pigmented reflective binder layer in uniform close-packed monolayer relation to provide a reflex-reflective area in which the reflective binder contacts the embedded beads only up to 5 to 30° above their equators.

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