Principles of Glass-Bead Reflectorization

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● IT HAS been estimated by Ashman (1) that the 48 states used nearly 2½ million gallons of traffic paint of all kinds in 1950. On the basis of returns from 33 states to the same author, nearly half of all white paint and two thirds of the yellow, totaling almost 1¼ million gallons, were reflectorized with glass beads in 1950. At normal application rates, this means a total consumption of more than 6 million pounds of beads for that year, and a most significant trend is revealed in the fact that these figures represent an increase over the previous year of 67 and 59 percent respectively in the amount of white and yellow paint so reflectorized. This is fairly big business, and its rapid growth in recent years gives definite notice that glass beads have become an important highway material whose functioning must be thoroughly understood and properties carefully evaluated in order to realize maximum benefits from their use.

It is the purpose of this paper to discuss some of the more important principles governing the use and performance of glass beads in traffic paint to serve as a basis for the design of adequate tests and interpretation of their significance. Fortunately, the application of theory to practice is so direct in most instances that laboratory tests can easily be devised to faithfully predict performance in service. Moreover, the intelligent application of these principles to the whole problem of bead reflectorization brings immediate and substantial dividends of a very practical nature.

The subject matter of the discussion which follows is divided among three major topics: (1) effect of chemical composition on properties of the glass; (2) effect of physical properties of the beads on performance; and (3) principles of application. The main object is to point out how the recognition and utilization of certain fundamental principles and physical laws can be made to advance the art of glass-bead reflectorization and thus serve the best interests of all concerned.

CHEMICAL COMPOSITION ON PROPERTIES OF GLASS

Glass has been defined by Morey (2)[1] as "an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of the substance, but which, as the result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid."

It is important to understand that glass is, in effect, an undercooled, highly viscous liquid. When properly compounded and processed, the melt solidifies on cooling to form an amorphous, vitreous solid in which crystallization has been inhibited or prevented by the high viscosity of the liquid at temperatures near the melting point. When crystallization, or devitrification, occurs on cooling, the glass is ruined. Devitrification is probably the most important factor which limits the range of composition of commercial glasses, and may be caused by errors in either composition or heat treatment. Other compositions, satisfactory with respect to devitrification, are unsuitable because of enormously high viscosities in the temperature range above the freezing point, which makes working extremely difficult.

Most glasses can be considered as composed of oxides, the acidic oxides most commonly used being silica, SiO_2; boric oxide, B_2O_3; and phosphorous pentocide, P_2O_5. Vanadium pentoxide, V_2O_5; arsenious oxide, As_2O_3; and germanium oxide, GeO_2, are also glass-forming but of limited use. Germanium oxide is ex-

[1]This standard work includes an extensive and thorough treatment of the effect of chemical composition on all of the important properties of glass Together with some of the more recent publications of the National Bureau of Standards, it constitutes the principal basis for the present discussion of glass chemistry

cellent, but too expensive. Phosphorus pentoxide does not have as marked glass-forming properties as either boric oxide or silica, and is not used much. Boric oxide is widely used, but only in silicate glasses, since when used alone or in too large amounts the resulting glass lacks chemical durability. Almost all commercial glasses contain silica, which has the essential qualities of chemical durability and freedom from devitrification to a marked degree; in fact, if it were not so difficult to melt and work, silica glass would be the best type for most ordinary uses. Such glasses have a relatively low refractive index, however, which handicaps their effectiveness in beads for pavement-stripe reflectorization.

Because of the difficulty and cost of making silica glass, and in order to secure glasses having certain special qualities, other oxides are added to flux the silica and make it workable. A great many different metallic oxides are used for this purpose, the particular ones selected depending on the properties desired in the glass. Most of the common ones will be mentioned in specific applications a little later. A point that should not be overlooked in interpreting the significance of chemical tests is that comparatively small amounts (less than 1 percent) of some of the constituent oxides may greatly affect the chemical and physical properties of the glass. Whether these small quantities are added deliberately, or whether introduced as an impurity in materials or by interaction of the glass with the refractory container during melting, they should be taken into account when attempting to relate composition with physical properties.

For the present purpose, properties of primary interest related to composition are chemical durability, refractive index, density, strength, and color. The discussion of these topics which follows will also include some remarks on the significance of applicable tests for glass beads.

Effect of Composition on Durability

Chemical durability, or resistance to attack by the atmosphere and corrosive solutions, is a matter of prime importance in the utilization of all glasses. Most optical glasses are exposed to air throughout their service life and are subject to the corrosive action of chemical constituents in the atmosphere, carried by the water which is always present. Even pure water may attack certain glasses more severely than many strongly acid or alkaline solutions.

Sodium oxide is the best flux for silica, but the resulting silicate is soluble in water, and other oxides must be added to give chemical durability. Lime is most commonly used for this purpose, and the resulting product is the familiar soda-lime-silica glass that makes up the bulk of commercial production. If too little lime is added, the glass melts easily but has poor chemical durability; if too much, the glass is hard to melt and sure to devitrify. The best composition for pure soda-lime-silica glass is in range: SiO_2, 73-74 percent; CaO, 7-13 percent; Na_2O, 13-20 percent.

Magnesia and zinc oxide can be advantageously substituted for part of the lime, and aluminum oxide, Al_2O_3, gives better chemical durability and freedom from devitrification, but too much makes the glass hard to melt and work. Potassium, barium, and boric oxides all increase chemical durability and prevent devitrification, but also increase viscosity. They are helpful in small amounts, but a large proportion of any one of them has some unfavorable effect.

Glasses containing a high percentage of the acidic oxides, such as silica and boric oxide, are resistant to acid solutions, but less so to water and alkalis. Conversely, glasses containing small amounts of these oxides are subject to considerable attack by acid solutions; in fact, some of the extra-heavy lead and barium glasses can be decomposed sufficiently for chemical analysis by digestion with hydrochloric or nitric acid.

Durability versus Serviceability

While the ability of a glass to maintain an optically clear and polished surface is a measure of its serviceability, it is also true that some optical glasses of relatively poor chemical durability give excellent service (3). It has long been known that the formation of films on optical glasses in certain cases actually improved performance by reducing external reflection, and the discovery of this fact was the basis for the present practice of lens coating (4). When water of aqueous solutions attack glass, the action is not one of ordinary solution, but rather one of progressive hydrolysis and hydration, resulting in a breakdown of the silicates and preferential solution of the reaction products, somewhat analagous to the hydration and leaching of portland cement. In certain glasses this preferential solution of alkali and other metal ions by water leaves a surface film rich in silica, which has a considerably lower refractive index than the base glass. Although this film is not as effective as one of controlled thickness and refractive index, it is sufficient to give noticeable improvement in transmittance and reduction of external reflection.[2]

The foregoing should not be construed to mean that all dull surfaces and evidences of poor durability are beneficial to optical performance. Etched, pitted, and otherwise damaged surfaces are in an entirely different category. It is intended to emphasize the fact that serviceability and chemical durability are not synonymous terms, but represent destinctly different properties. For this reason, a laboratory test for chemical durability based only on weight loss by extraction with water or apparent dulling of surface luster may wrongly condemn a perfectly satisfactory glass. Optical tests before and after exposure to attack are the only reliable method of distinguishing serviceable glass beads. In our own laboratory it has been observed that weight loss of a glass-bead sample by extraction bears no evident relation to dulling of surface luster, and neither criterion is an infallible indication of subsequent optical performance. In one case, reflectivity of the glass beads was improved after refluxing for 90 hr. with distilled water in spite of a substantial weight loss in the process.

Long life is not an essential quality of pavement marking beads. It is only necessary that the glass beads retain their reflective power through the effective life of the pavement stripe, which in turn is regulated chiefly by the performance of the paint. Chemical durability, then, is not as significant as serviceability in evaluating glass beads for pavement reflectorization. A test for hygroscopicity of glass as a measure of service-ability has been used and described by Hubbard (3), but photometric tests are more practical and direct for glass beads when equipment for making such tests is available.

Effect of Composition on Density and Refractive Index

Because of the nature of glass, its density is approximately an additive function of its composition, a relationship which is generally true of all liquids (2). Silica and boric oxide are the lowest in density, followed by the oxides of aluminum, sodium, potassium, magnesium, iron, calcium, zinc, barium, and lead. The factors used to compute the density of glass from percentages of its constituent oxides are not greatly different for the common ingredients of ordinary soda-lime-silica glass, so that the composition can vary within rather wide limits without greatly affecting density. Appreciable quantities of barium and lead in the heavier crown and flint glasses have a marked effect on density however.

Density is of interest largely for three reasons: (1) it determines the relative amount of reflective surface furnished per pound of beads of a given size; (2) it affects application procedures through its effect on the sedimentation rate of beads in paint; and (3) it is related closely to refractive index. As a general rule, the refractive index increases as the density increases, but the relationship is not linear. Refractive index is a very important property indeed, and its significance will be discussed in some detail a little later, in connection with the effect of physical properties on bead performance.

Effect of Composition on Crushing Strength

There is little published information on the relation of glass composition to crushing strength and still less on strength as determined in current methods of glass-bead testing. The results of compression tests by Gehloff and Thomas on a series

[2]For optimum results, the refractive index of the film should be the square root of that of the base glass, and its thickness one fourth the wave length of the incident light

of glasses derived from a two-component soda-silicate glass by the substitution of various metallic oxides for part of the silica are given by Morey (2). These tests were performed on very small glass prisms and indicated that the alkali oxides reduced strength most. The order of effect of the various oxides is given as: Al_2O_3, (SiO_2, MgO, ZnO), B_2O_3, Fe_2O_3, (BaO, CaO, PbO), Na_2O, K_2O, the oxides in parentheses having about the same effect. No correlation was found between crushing strength and tensile strength.

More recently, the work in Missouri reported by Lyon and Robinson (5) also shows generally greater strengths for the high-silica beads, but the effect of composition is clouded somewhat by considerable variation in physical characteristics, such as surface condition, internal milkiness, etc. Experience in testing beads from various sources in our own laboratory has given further evidence of the same general relationship between strength and silica content.

Effect of Composition on Color

When light enters glass, some of it is absorbed and some transmitted. If the absorption is small and uniform for all wavelengths of visible light, the glass appears clear and colorless. As the overall absorption increases, the glass becomes greyish in color. When the glass selectively absorbs light of any given wavelength, the hue of the transmitted light perceived by the eye is the composite of the remaining colors of the visible spectrum. In short, the apparent color of the glass is the complement of the absorbed color when the incident light possesses a continuous spectrum.

For the most part, colors encountered in beads for paint reflectorization are those incidental to the compounding of the glass and are not added intentionally. Iron oxide is usually present as an impurity in commercial glasses, giving either a greenish color or a weak yellow, depending on whether the oxide is ferrous or ferric. The addition of other oxides as so-called decolorizers masks or neutralizes the color but results in a reduction of transmission. High-grade optical glasses are produced with transmissions of more than 99 percent, but ordinary window glass has a transparency of only 85 to 90 percent. The presence of much lead or barium oxide in the optical glasses of higher refractive index also decreases the transparency. The two oxides of vanadium, V_2O_3 and V_2O_5, give colors similar to those of ferrous and ferric iron respectively.

There are two aspects to the problem of color in glass beads. One, of course, is the fact that selective absorption weakens the intensity of reflex-reflected light, since the incident beam must pass through the bead twice before being returned to the driver's eye. The other is the possibility of an objectionable color modification of the painted stripe by the beads. So far, the decision as to what constitutes objectionable color has been made on a purely subjective basis. There appears to be no necessity for a "water white" color specification, however, since a noticeable color of the beads in bulk may be totally imperceptible when they are applied to the paint in the required quantities. Some variation in color should be permitted as long as there is no appreciable alteration of the color of the paint stripe, and color specifications which are unnecessarily restrictive may hamper the development of glasses superior in other respects.

Eventually it may be feasible to use a yellow bead with yellow traffic paint. Such a practice may help prevent the washing out of the background color by the more brilliant beads, which is noticeable in most yellow-reflectorized signs of high specific intensity. The desirability of using colored beads will no doubt receive increasing consideration as the reflective efficiency of pavement stripes approaches that of present beaded highway signs.

PHYSICAL PROPERTIES OF THE BEADS ON PERFORMANCE

In the preceding section, the relation between chemical composition and certain significant properties of the glass was brought out, and it was shown how some of these properties, such as chemical durability and color, directly influence the service performance of the beads as such. The purpose of the discussion which now follows is to explain the influence of the important physical properties of the beads themselves, namely, refractive index, particle size, and flaws of various kinds, on performance in a reflectorized stripe.

While refractive index is not a property of the bead, but of the glass composing it, its significance is so intimately related to physical form that it may properly be included here for more detailed discussion.

Refractive Index on Distribution of Reflected Light

Refractive index is one of the most important properties of glass beads, since it determines to a large extent the amount and distribution of reflected light. The proportion of incident light reflected from the bead-paint interface is a function of the difference in index of the two materials, while the pattern of the reflected beam depends on the focal length of the bead lens, which is determined in turn by the refractive index of the glass. The subject of interrelation of beads and paint in reflex reflection will be taken up in a little more detail after first explaining the principles of geometric optics applicable to the performance of the beads themselves.

Reflection. When light is incident on an interface of two transparent media, it will generally be distributed in three ways: (1) a part of the light will be reflected from the surface of the second medium; (2) part will be transmitted; and (3) the remainder will be absorbed. The proportion of light reflected at the boundary surface is a function of both the angle of incidence and the refractive indices of the two media and is given by

$$R = 1/2\left(\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)},\right) \qquad (1)$$

where R is the fraction of incident light reflected, and i and r are the angles of incidence and refraction respectively. When one medium is air, the reflection at normal incidence is

$$R = \frac{(n-1)^2}{(n+1)^2}, \qquad (2)$$

where n is the ratio of the refractive index of the second medium to that of the first. The equation holds, and the reflection is the same, irrespective of which medium is traversed first.

In Figure 1, the Equation 1 has been plotted for three different glasses having refractive indices of 1.50, 1.75, and 2.00 respectively (in air). These graphs show that external reflection at normal incidence from a glass surface in air is almost tripled for an increase of 0.50 in the index of the glass and that reflection increases very rapidly at angles of incidence beyond about 50 deg., to total external reflection at 90 deg.

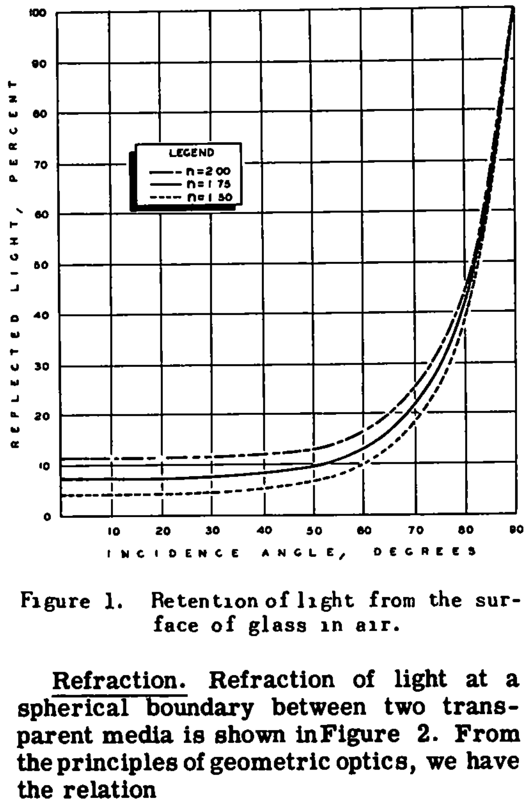

Figure 1. Retention of light from the surface of glass in air.

Refraction. Refraction of light at a spherical boundary between two transparent media is shown in Figure 2. From the principles of geometric optics, we have the relation

$$\frac{n_1}{p} + \frac{n_2}{q} = \frac{n_2-n_1}{R} \qquad (3)$$

where p is the distance of the light source from the vertex O, q is the image distance or focal length, n_1 is the refractive index of the first medium, n_2 the index of the second, and R is the radius of curvature of the boundary surface. This equation is an approximation which holds for rays near the axis and is sufficiently accurate for the present purpose. For the conditions under which glass beads are ordinarily viewed, the object distance p is so large in comparison to the radius R that

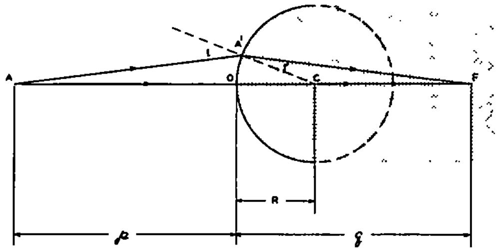

Figure 2. Refraction of light at a spherical boundary.

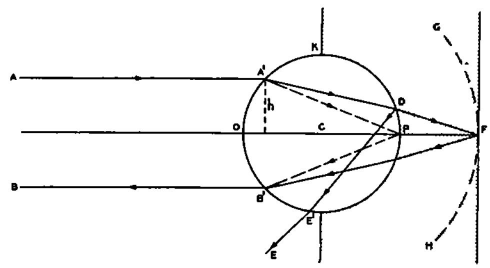

Figure 3. Refraction and reflection by a glass sphere in a third medium.

the incident light rays can be considered parallel and the first term of Equation 3 vanishes. Thus, for a glass of index 1.50 in air (n_{air} = 1.00), the focal surface is at a distance 3R from the vertex O, or a distance R behind an imaginary rear surface of a sphere, shown by the dashed line in the figure. Similarly, to focus parallel light on the rear surface (q = 2R) the glass must have a refractive index of 2.00.

Figure 3 is a sketch of a section through a glass sphere embedded to a depth of half its diameter in a third transparent medium, say an alkyd resin, of index n_3. Any parallel incident beam entering the sphere converges to a point on the axis of the beam at a distance PF behind the sphere. This distance is determined by the refractive indices of air, glass, and resin, n_1, n_2, and n_3 respectively. When n_2 and n_3 are equal, there is no change in direction of the rays at the glass-resin boundary and the distance PF can be determined by a single computation. If a spherically curved reflecting surface, GFH, concentric with the sphere, is now placed at F, the parallel rays of any beams which can enter the sphere will be refracted and reflected symmetrically with respect to the axis of the beam and again rendered parallel on emerging from the sphere to be returned in the direction of the source. It is also apparent from Figure 3 that if the rays of the incident beam are reflected from a point either ahead of or behind the focal surface, they will not emerge parallel. This is shown by tracing the ray along AA', which is refracted to the point D on the rear surface of a bead composed of an average glass of index around 1.5. If this ray were totally reflected at that point, it would emerge along E'E at a considerable angle to the direction of the incident ray. If, however, the index of the glass is increased to 2.0, the refracted ray A'D would be bent down to a focal point P on the rear surface, reflected to B' as shown by the dashed lines, and emerge parallel to its original direction. As a corrollary, it may be stated that spheroids or ellipsoids of the lower index glasses will give better reflex reflection than true spheres in traffic paint, provided their long axis is oriented in the general direction of the oncoming light source.

These principles are made use of in the construction of beaded sheets for reflectorized signs of various kinds. Long-range visibility is achieved by placing beads of a given refractive index on a transparent film of controlled thickness (approximately equal to R + PF in Figure 3), backed by a highly reflecting metallic foil. In this way the amount of light reflected is increased, and this returned light is conserved in a relatively narrow cone of high intensity. Such a reflecting surface is usually plane, however, so that it contains the focal point only at normal incidence and brightness falls off rapidly as the angle of incidence increases. Since the focal length of the bead is a function of its radius, it is obviously advantageous that the beads be as uniform in size as possible for this type of construction. With sufficiently high refractive index of the glass, the focal surface GFH is brought up to the rear surface of the bead, making a spacing coat unnecessary.

If the beads functioned in the ideal manner just described, the resulting perfect reflex reflection would have little practical value, because all of the reflex-reflected light would be returned to the source without reaching the eye of the driver. Actually, however, the inherent aberrations in spherical lenses of this thickness and curvature are more than adequate to produce the necessary dispersion for useful reflex reflection. As mentioned previously, Equation 3 is only an approximation to the formula for refraction at a spherical surface. It holds only for rays near the axis. A more exact relation (6) is

$$\frac{n_1}{p}+\frac{n_2}{q}=\frac{n_2-n_1}{R}+\frac{h^2}{2}\left(\frac{n_2-n_1}{n_2^2}\right)\left[\frac{n_1^2}{R}-\frac{n_1(n_2+n_1)}{p}\right]\left(\frac{1}{R}-\frac{1}{p}\right)^2 \quad (4)$$

where the notation is the same as in Equation 3, and h (Fig. 3) is the distance of the parallel ray from the axis. Thus, to bring a ray which is incident at $h = R$ to a focus at the rear surface, n_2 is found from Equation 4 to be 1.75, and for one at $h = \frac{R}{2}$ the value of the refractive index to accomplish the same purpose is 1.96. When $h = 0$, the second term on the right of Equation 4 vanishes, and the relation reduces to Equation 3. From the foregoing it is evident that all parallel rays incident on the sphere cannot be brought to a focus at a single point. By taking the vertical coordinate of the centroid of the circular arc OA'K, which is equal to $\frac{2R}{\pi}$, as an average or resultant value of h, the corresponding average value of refractive index for optimum reflection is found to be about 1.90. Since external reflection increases rapidly as h approaches R, most of the light incident at the extremes of the diameter does not enter the sphere and the optimum index will be somewhat greater than 1.90.

Interrelation of Beads and Paint in Reflex Reflection

As shown earlier, the amount of light reflected from an interface of two transparent media is a function of their refractive indices. Referring again to Figure 3, assume a traffic paint has replaced the transparent resin which holds the bead. Since the finely divided pigment particles are enveloped by the vehicle, they do not come in direct contact with the bead, but are separated from it by a film of vehicle at least one molecule thick. Hence, when a beam of light strikes this interface, the portion reflected is determined by the refractive indices of glass and vehicle in accordance with Equation 1. The remainder is transmitted through the vehicle, with some loss by absorption, to the multitude of tiny pigment particles where some of it is absorbed, some transmitted and the balance diffusely reflected. The amount of light reflected from the pigment particles, again, is a function of their refractive index in relation to that of the vehicle, and the amount transmitted through them depends on their absorption characteristics.

From the above considerations, it is quite evident that beads and paint are intimately related in the reflective process. With a given bead, the amount of reflected light can be influenced considerably by the characteristics of vehicle and pigments in the paint in which it is placed. The converse is also true.

Compatibility of Beads and Paint. Another phase of the bead-paint relationship is mutual compatibility with respect to interfacial tensions, or wetting of the bead by the paint. It is important that the paint wet the bead sufficiently to form a bond that will resist dislodgement of the beads. Too great an attraction will cause the beads to "drown" too easily; too little will result in poor bond. The photographs of Figure 4 illustrate this point. In the first photograph, taken at an age of less than a week, the wetting is almost excessive. The paint has crawled up the sides of the spheres to an extent which limits initial reflex reflection at long range. The second photograph shows a small area of a reflectorized stripe at the age of 7½ months. Although the paint itself is still in good condition, the beads have almost entirely disappeared. The bead sockets and the few beads remaining in the paint seem to indicate a negative capillarity, with consequent poor retention. This is the other extreme.

The two aspects of interrelationship of beads and paint just discussed present a strong argument in favor of treating the reflectorized stripe as an entity rather than as a combination of independent materials. Any evaluation of beads or paint separately which does not take the above

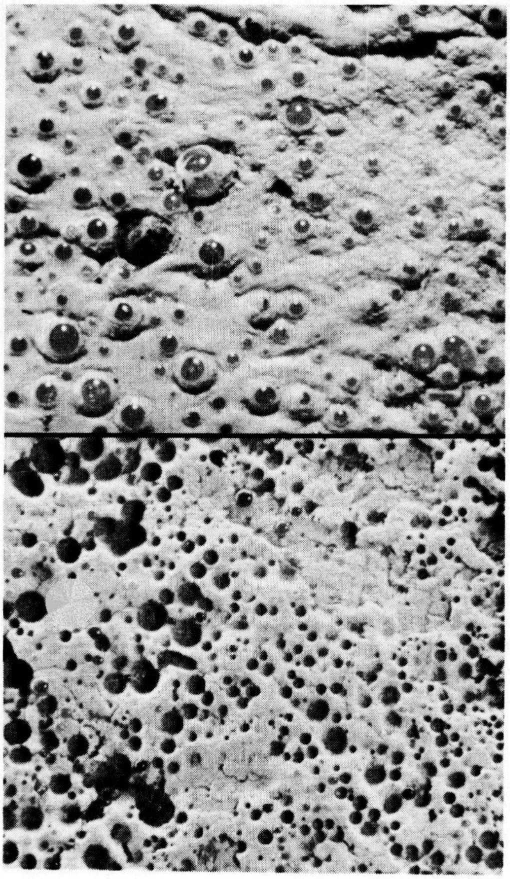

Figure 4. Wetting of beads by paint: Top, good wetting; bottom, poor wetting.

mutual effects into account is necessarily incomplete and may be misleading.

Glass Bead Gradations

Most users have assumed thus far that the glass beads should be uniformly graded from coarse to fine, the theory being that the smaller beads would be successively exposed for effective reflection as the paint wore down. Although the theory is logical and plausible, there are no published data to show exactly the relation between gradation and continuing optimum reflectivity. There are certain well-established facts, however, based on experience and simple geometry, which definitely indicate the desirability of using beads of smaller maximum size.

Other things equal, the projected reflecting area per pound of beads is greatly increased as the average diameter of the beads is decreased. This is true because the volume and cross-sectional area are proportional to the cube and square of the radius respectively. If the radius is halved, it takes eight times as many beads for equivalent volume. The total cross-sectional area of these eight beads is twice that of the larger bead. Similarly, if the average radius is reduced to one third, the surface area is tripled for the same weight of beads. Since beads are sold by weight, which is proportional to volume, it is obvious that a dollar will buy more reflection in the smaller beads.

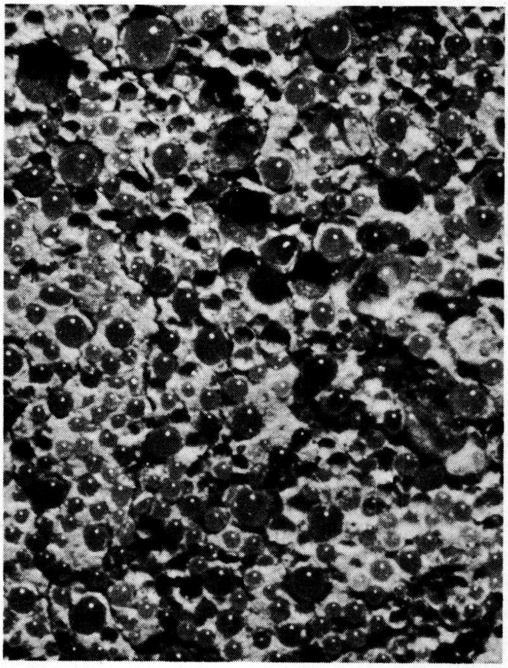

Figure 5. Effect of size on bead retention.

Fortunately, the smaller beads not only are more economical but also have several other distinct advantages over the larger ones. Pound for pound, small beads, because of their greater surface to mass ratio, maintain useful reflection longer, thus adding materially to the life of the stripe. Not only is this true theoretically, but it has also been amply substantiated by experience. Figure 5 is a photograph of a month-old stripe containing premixed beads overlaid with larger ones. For every large bead lost, represented by the empty sockets in the picture, four smaller ones of half the diameter would have to be dislodged to bring about an equivalent loss in reflection. The figure shows that the smaller sizes are not lost in anywhere near that proportion. Furthermore, better distribution, with accompanying uniformity of light return, is possible with the smaller beads. Other advantages of the smaller beads are that they: (1) can be premixed with the paint; (2) reduce drying time; (3) reduce the effect of relative humidity on drying time; and (4) lower the loss by rebound when bead-paint mixtures are sprayed on the pavement. One more significant fact on bead size remains to be mentioned, however. Apparently owing to the method of manufacture, the percentage of irregular and fragmentary particles is noticeably lower in beads of smaller size.

Effect of Imperfections on Reflection

The most common imperfections occurring in glass beads, and the ones generally taken into account in evaluating the beads, are: (1) irregularly shaped particles and (2) gas inclusions. The presence of extraneous material and other imperfections of relatively rare occurrence need not be considered here.

Particle Shape. The test for roundness has received a great deal of attention, and apparatus for measuring this property has reached an advanced stage of development. As far as is known now, however, no one has determined the significance of this property quantitatively. Fragments, of course, are practically useless as far as reflex reflection is concerned, and a large percentage of them cuts down efficiency. Nonspherical shapes, such as spheroids, ellipsoids, etc., are probably not too detrimental. As mentioned previously, when these particles are oriented with their long axis is the direction of light incidence, they give a more efficient light return than round ones for the lower index glasses. If the nonround particles are randomly oriented in the paint, the number of particles with their long axis in line with the direction of light should compensate approximately for those not so oriented in the efficiency of light return. The influence of particle shape can be determined experimentally, and such tests should be performed soon.

Gas Inclusions. Gas inclusions are a serious defect in glass beads because they interfere with reflex reflection and weaken the bead structurally. Experiments in the Michigan State Highway Research Laboratory show that losses in specific intensity of 20 to 40 percent can result from excessive gas inclusions in commercially produced beads. The tests were performed by measuring the brightness of two sets of panels coated respectively with beads which had been separated at a predetermined specific gravity into two fractions by a sink-float method. Work is now under way to find a satisfactory method of measuring gas content. The problem is complicated by the fact that optical characteristics are influenced strongly by the size and number of the bubbles, as well as the total volume of gas present.

Tests such as these, and others currently being developed for clarity of glass beads, are probably helpful mostly from the standpoint of providing a general background of knowledge for development of the product and interpretation of test results. In the final analysis, photometric tests give a practical and realistic picture of prospective performance unobtainable in any other way. In these tests, the effects of refractive index, roundness, gas inclusions, and imperfections of all kinds are lumped into one resultant figure representing optical performance. For specification purposes, measurement of the contributing properties is probably unnecessary.

PRINCIPLES OF APPLICATION

Application of transparent spheres for the purpose of reflectorizing pavement marking stripes can be said to involve two techniques. In the first of these, the beads are dropped directly on the wet paint; in the second, beads are mixed in the paint and the combination sprayed through the gun. In some instances, both methods are employed simultaneously (overlay).

Bead dispensers designed for use in dropping beads on the fresh paint are positioned low on the paint truck as close as possible to the stripe, in order to minimize effects of air movement and mechanical vibration. They are located approximately 1 ft. behind the spray guns,

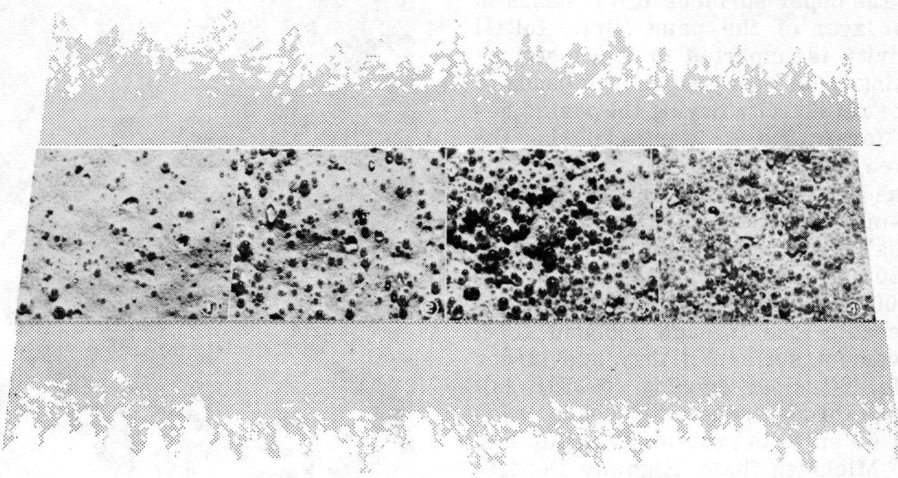

Figure 6. Nonuniform bead distribution across a traffic stripe.

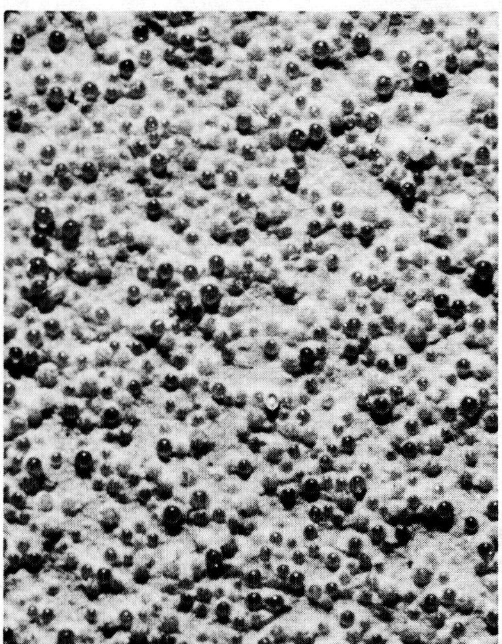

Figure 7. Ideal bead application on laboratory prepared panel.

so that the paint has had contact with the pavement a little more than a tenth of a second before it is covered with beads.

Although beads applied by dropping impart the highest initial reflectivity, the technique is open to several objections. It is very difficult to assure uniform dispersal of beads across the width of the paint stripe (see Fig. 6). A large percentage of beads is lost as a result of winds, inaccurate orientation of the dispenser, or other mechanical variables not necessarily under the control of the operator. Also, the beads may tend to pick up moisture from the air and clump together.

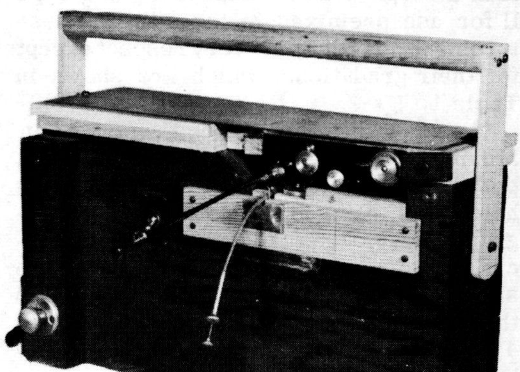

Figure 8. Stereophotomacrographic camera.

For these and other reasons, interest has developed in spraying paint containing premixed beads, depending on traffic to expose the upper surfaces of the beads in the top layer of the paint film. Initial reflectivity is imparted to these stripes by coating them with just enough beads to promote reflectivity during the period required for traffic to start exposing the premixed beads.

It has been found that beads mixed in traffic-marking paint and subjected to the usual pressures of spray application (40 to 80 psi. or higher on the paint, and 60 to 100 psi. for atomization) will undergo considerable loss through rebound from the pavement surface if they are larger than No. 60 sieve opening (0.0098 in). Bead loss through rebound of beads passing No. 60 sieve is practically negligible.

The Michigan State Highway Department, until recently, has recognized two types of beads for use in reflectorizing pavement marking stripes. These are Type I for application on the wet paint film through a bead dispenser, and Type II for use premixed in the paint. These types are identical in every respect except for their gradations, which are shown in Table 1.

Actually, it has been found expedient in Michigan to use Type II beads exclusively, both in and on the paint, and specifications have been revised accordingly. Photographs have been taken at large magnifications to show that the majority of the small beads do not sink completely into the paint and become covered, provided 4 lb. of beads per gallon have already been mixed in the paint.

Figure 7 illustrates an ideal application of this kind. Figure 8 shows the apparatus used in making these photographs. Further, laboratory studies have shown that beaded panels prepared with white paint

TABLE 1

GLASS BEAD GRADATIONS

Sieve No.	Sieve Opening *inches*	Amount Passing Type I %	Amount Passing Type II %
30	0.0232	100	
40	0.0165	30 - 70	
50	0.0117	10 - 35	100
60	0.0098		95 - 100
100	0.0059	0 - 5	45 - 75
200	0.0029	0	0 - 2

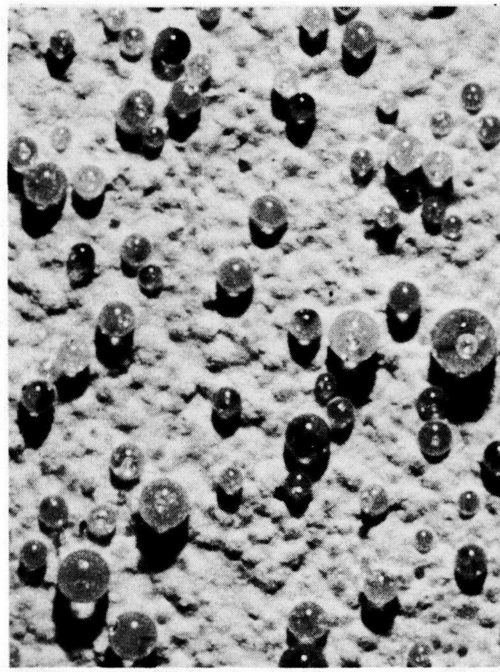

Figure 9. Application of large beads by overlay on laboratory panel.

containing 4 lb. per gal. of Type II beads and supporting 2 lb. per gal. of the same type will reflect fully as much of the incident light as is reflected by corresponding panels with 4 lb. per gallon of Type II beads in the paint and 2 lb. per gallon of Type I beads on the paint. The latter application is shown in Figure 9. From an economical standpoint, it would therefore appear advantageous to use the Type II beads exclusively.

In addition to the questions of optimum size and other operational factors, the depth of embedment of the glass bead in the paint film and rate of application of the beads are also important in relation to the efficiency of light return.

Effect of Depth of Embedment on Reflex Reflection

Figure 10 (a) shows a perspective sketch of a glass bead in a pavement stripe receiving and reflecting light from the headlamps of a car somewhere to the left, and Figure 10 (b) a vertical section through the center of the same bead in the line of light propagation between source and re-

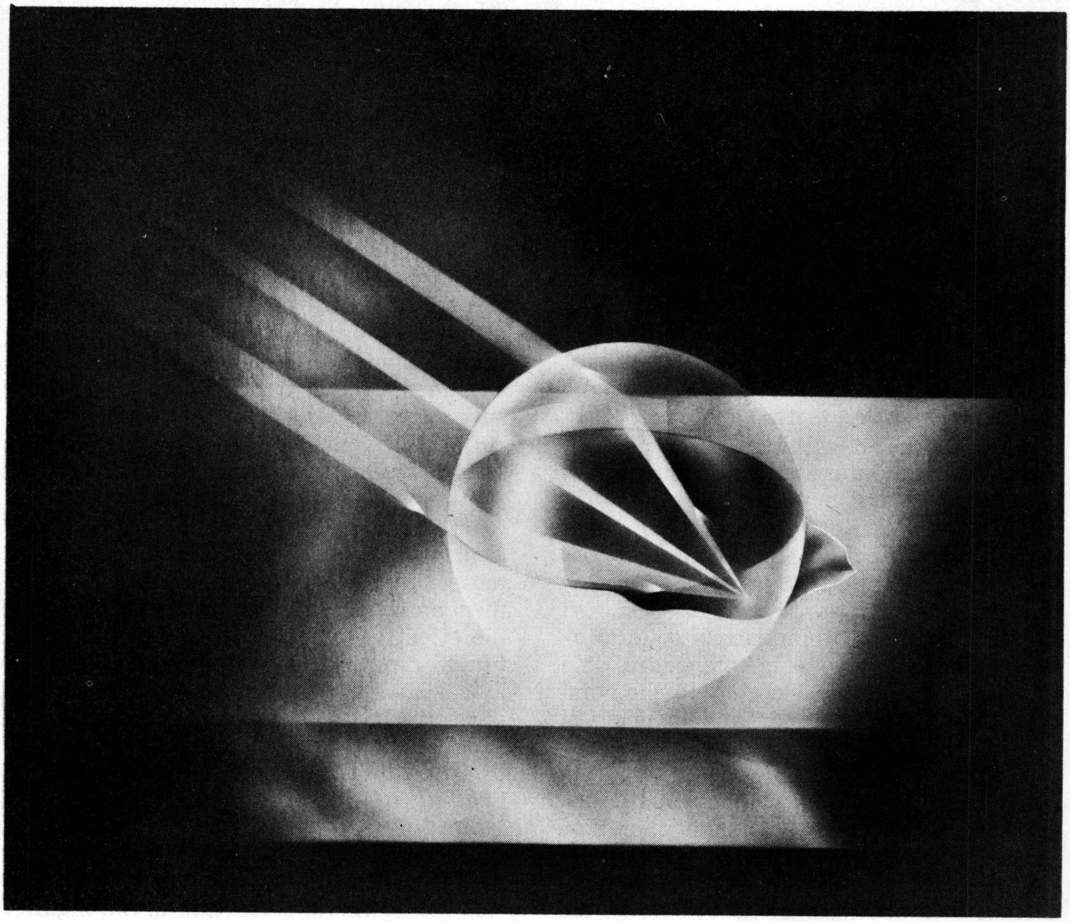

Figure 10 (a). Reflex reflection by a glass bead in traffic paint: Perspective sketch of bead in paint.

flector. The bead is shown embedded to a depth of 50 percent of its diameter and is presumed to have a refractive index of 2.0, which brings paraxial rays to a focus at the rear surface.

An incident ray along AA', the lowest level at which light may enter, will leave the bead along B'B, approximately parallel to AA'. Refraction occurs at the points A' and B', and internal reflection at the focal point P. Similarly, a ray incident along BB' will emerge along A'A.

A parallel ray NN', normal to the front surface of the bead, will enter without change in direction, pass through the center O, and be reflected at point P to retrace its path in the opposite direction. Since the internal path of the rays is symmetrical with respect to the axis of the beam, the chord A'B' at right angles to the axis represents the limits of aperture in a vertical plane, hereinafter referred to as vertical aperture, through which light may be received for reflex reflection. It is evident from the figure that any parallel ray XX' entering the sphere above B' will be doubly reflected within the sphere below the paint line and sent off in an ineffective direction.

The effective vertical aperture A'B' is $2r \sin\alpha$, where r is the radius of the sphere and α the angle the incident beam makes with the horizontal. The angle α changes continuously with distance between bead and source, becoming larger as the separation distance decreases, so that the aperture widens progressively as the bead is approached. It is obvious, therefore, that the efficiency of light return becomes very small under the

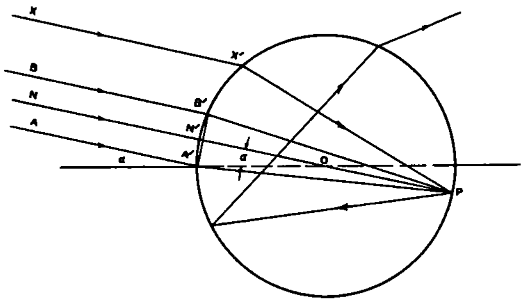

Figure 10 (b) Optical diagram for a median vertical section in the line of light propagation.

conditions of illumination ordinarily encountered in driving, when the beads are embedded to a depth of half their diameters. Where beads are embedded less than 50 percent, the vertical aperture for reflex reflection is correspondingly greater, but this advantage is offset to some extent by the likelihood of poor bead retention. At the small angles of illumination usually involved, beads have to be embedded only slightly over 50 percent (up to the point N' in the figure, an increase in depth of approximately r sin α) to lose the property of reflex reflection altogether. This fact should be of significance when interpreting the efficiency of beads premixed in paint. Stripes of this kind may be expected to show up clearly at short viewing distances at earlier ages than would be the case at greater viewing distances.

Rate of Application

On the basis of an assumed headlamp-to-pavement distance of 32 in., a ray of light from a headlamp will impinge upon a glass bead 500 ft. in front of a vehicle at an angle of 0 deg. 18.5 min. with the horizontal. At 50 ft. this angle is 3 deg. 3.4 min.

Michigan State Highway Department specifications for Type I beads (for application on the paint) require that a maximum of 70 percent pass the No. 40 sieve. This means that at least 30 percent of the beads will be 0.0165 in. in diameter, or larger. When illuminated from a distance of 500 ft., two such beads of the same size embedded one behind the other to half their depth in a traffic stripe would have to be spaced at least 1.55 in. apart, center to center, in order to prevent the near bead from partially obscuring the far bead. This spacing is less for smaller beads and for shorter distances, dropping to 0.06 in. for a Type II bead (premix type) passing the No. 100 sieve and illuminated at 50 ft.

Analysis of Figure 11 discloses that if two beads of the same diameter are lined up at the critical separation distance (x + r), the zone of the incident beam which can be completely reflex-reflected from the second bead will just clear the first bead. When this distance is shortened by an amount equal to the radius of the sphere, only a few thousandths of an inch, reflex reflection from the median vertical aperture of the second bead is entirely cut off. As the beads are placed nearer and nearer together, the zone of possible reflex reflection in the second bead is obscured more and more, first at a rapid rate and then more slowly, so that the eclipse of the effective zone is very nearly complete for all practical purposes when the beads are at about half the original critical distance from each other. Some critical separation distances under various conditions of illumination distance and bead size are given in Table 2. Probably some laboratory research could profitably be done in pursuing this subject a little further to determine actual rates of application for optimum reflection in the significant range of viewing distances. It is quite possible that some bead economy could be achieved as a result of such tests. Long-range visibility is probably the controlling factor, since the wider aperture of reflex reflection and greater intensity of illumination at the shorter distances compensate to some extent for sparser distribution of the beads.

TABLE 2

CRITICAL SEPARATION DISTANCE BETWEEN BEADS ARRANGED IN LINE OF SIGHT

Diameter of Beads	Corresponding Sieve	Critical Separation Distance	
		At 500 ft.	At 50 ft.
in.	No.	in.	in.
0 0165	40	1.55	0.16
0.0117	50	1.10	0.12
0.0059	100	0.55	0.06

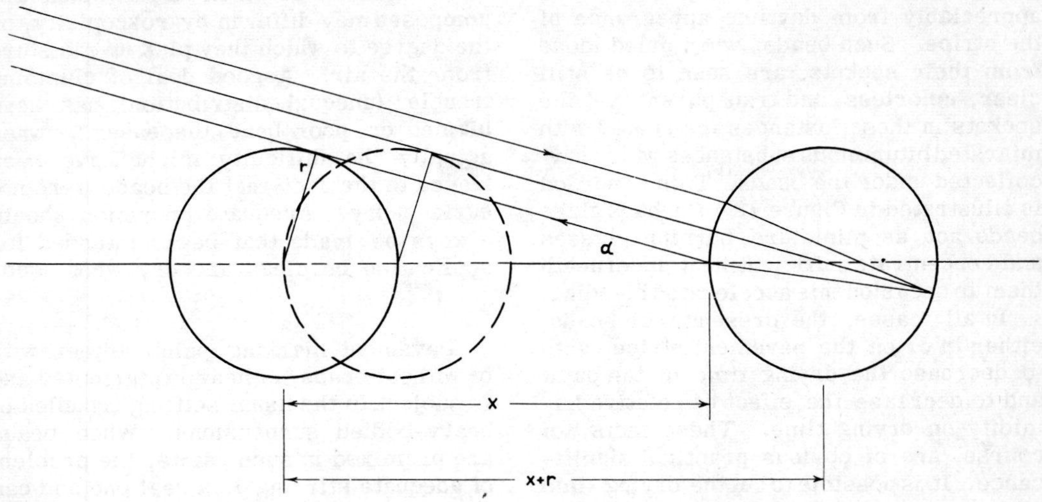

Figure 11. Bead interference in reflex reflection.

Miscellaneous Practical Considerations

It is generally conceded that the use of glass beads for purposes of reflectorization has the further advantage of materially lengthening stripe life. A rational explanation of this would be to consider the beads as bearing the brunt of the traffic loads, thus protecting the paint film which remains between the beads from such abrasion, so long as the beads remain in place. Beads which break loose, however, would have exactly the reverse effect, contributing by grinding or shearing action to the breakdown of the stripe, and the situation would be worse than one in which no beads were present. It becomes a matter of concern, therefore, to provide adequate cementing of beads in place, both from the reflectorization and abrasion standpoints. Cementing of beads in place is a function not only of degree of penetration (anchorage, or tooth), but also of the wetting properties of the paint for the glass surfaces of the beads. As mentioned earlier, paint-bead combinations exhibiting adverse wetting of the beads by the paint cannot be expected to exhibit satisfactory bead retention.

It has been shown rather conclusively that beaded-reflectorized pavement-marking stripes give longer service life when applied on bituminous pavements than when applied on concrete, due, probably to the resilience of the former. The added stripe life is not without its drawbacks, however, one of which is bleeding of the bituminous material through the paint film. Such bleeding appears to be accentuated by the presence of beads. It is as though the beads constitute individual foci for the development of bleeding, for wherever bleeding occurs, it appears to occur first under the beads. In fact, the beads frequently become "discolored", turning

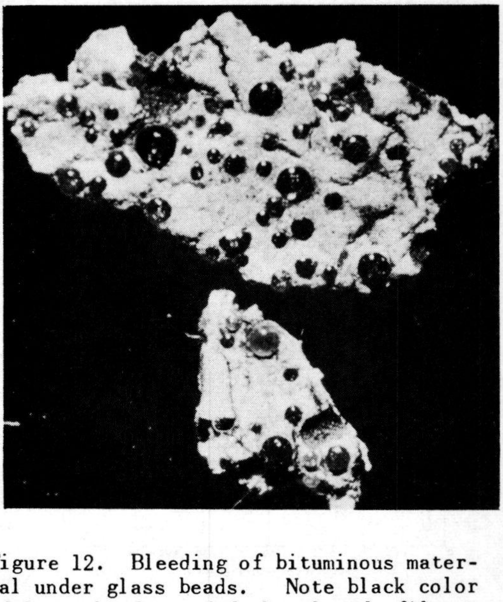

Figure 12. Bleeding of bituminous material under glass beads. Note black color of large beads, and dark-colored film at bottom of empty bead sockets.

quite dark, sometimes black, and detract appreciably from daytime appearance of the stripe. Such beads, when pried loose from their sockets, are seen to be still clear, colorless, and transparent, yet the sockets in these instances are coated with migrated bituminous substances which have collected under the beads. This condition is illustrated in Figure 12. Perhaps glass beads act as miniature burning glasses and concentrate sufficient heat underneath them to occasion this accelerated bleeding.

In all cases, the presence of beads, either in or on the pavement stripe, acts to decrease the drying time of the paint and to decrease the effect of relative humidity on drying time. These facts, of course, are of obvious practical significance. It is possible to cut the drying time of a pavement-marking paint in half by the use of beads alone. Some data on this effect are shown in the graphs of Figure 13.

After a generation of experience with pavement-marking stripes, the critical need still persists for an effective seal to prevent bituminous materials from bleeding through superimposed paint films. The use of glass beads has made this need more acute than ever.

The glasses of which various beads are composed may differ in hygroscopicity, or the degree to which they pick up moisture from the air. A good deal of clumping trouble (unequal distribution) has been blamed on poor bead dispensers, when actually the difficulty might have been traced to the fact that the beads were not surface-dry. Adequate provision should always be made that beads intended for application be clean and dry when used.

Pavement-marking paint, either with or without beads, is heavily pigmented and is subject to the usual settling troubles of heavy-bodied suspensions. When beads are premixed in such paints, the problem of adequate stirring is a real one and can become a source of delays in the striping program. If these paints are allowed to settle undisturbed for weeks at a time, it may become practically impossible to restore them to their original uniform consistency by conventional means. If, however, drums are rolled or up-ended at frequent intervals, such troubles have a way of disappearing, and stirring usually proceeds without complication.

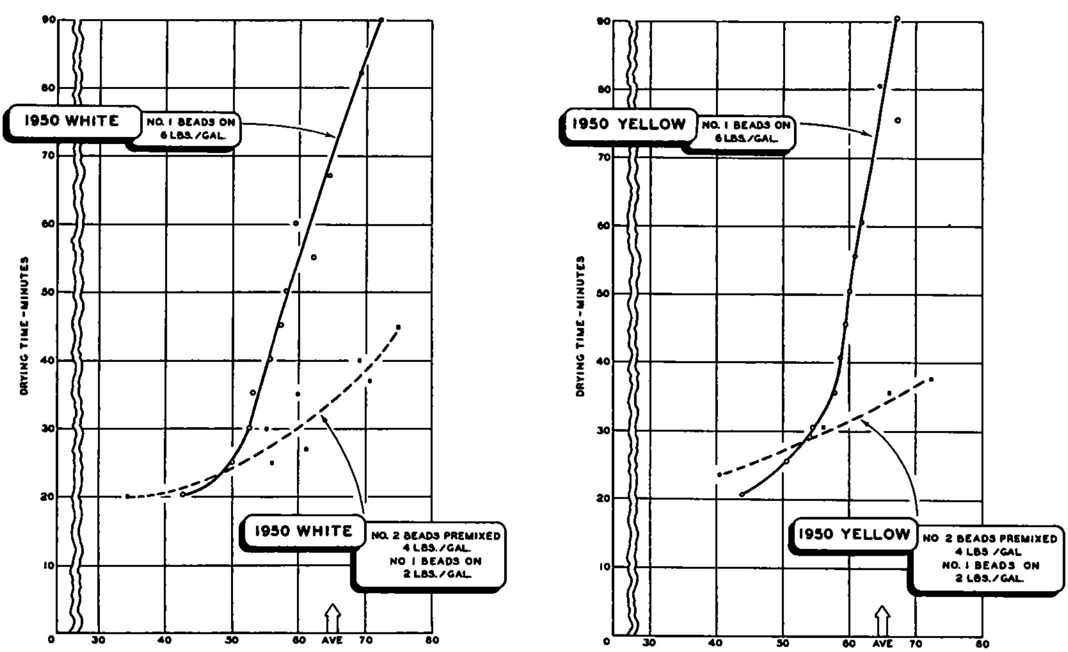

Figure 13. Effect of premixed glass beads on relationship between drying time and relative humidity.

RECAPITULATION

In retrospect, the more significant facts and ideas of the foregoing discussion to be remembered in relation to the use and performance of glass beads in traffic paint are given below. Some of these are stated specifically for the first time in the summary but may be inferred directly from previous statements in the text.

First, all of the properties of glass which significantly affect bead reflectorization are directly related to composition. There is considerable latitude in the selection of desired attributes by proper compounding and processing. The most important factor limiting the range of composition is devitrification, or crystalization, on cooling. The high-silica glasses are, in general, stronger and more durable than the others, but do not have a sufficiently high refractive index for maximum efficiency of reflectorization. It should be possible to produce commercially a glass of satisfactory durability and considerably higher index without undue increase in cost. As a matter of fact, several such products have already appeared on the market.

Second, chemical durability and serviceability are not synonymous terms in defining the qualities of glass beads. Many glasses of relatively poor durability give excellent service. Loss of weight by solution or dulling of surface luster are not infallible criteria of optical performance. Formation of film on some glasses gives noticeable improvement in transmittance and reduction of external reflection, a fact made use of in the present practice of lens coating. Therefore, laboratory results based on loss of luster or weight in extraction or weathering tests may wrongly condemn a perfectly satisfactory glass. Moreover, bead durability should be tied in with the life expectancy of the binder or stripe as a whole. At best, the life of a pavement stripe is relaitvely short. Chemical durability in a bead, then, is not as significant as serviceability, and optical tests are the most reliable method of evaluating serviceability.

Third, color of the beads is important mostly from the standpoint of possible objectionable modification of the color of the painted stripe. However, a noticeable color of the beads in bulk may be totally imperceptible when they are applied to the paint, and a color specification which is unnecessarily restrictive may hamper the development of glasses superior in other respects.

Fourth, the amount and distribution of reflected light is largely determined by the refractive index of the glass composing the beads and its relation to the index of vehicle and pigments in the paint. The pattern of the returned light (divergance-angle characteristis) depends on the index of the glass. Maximum efficiency in the conservation of reflected light is achieved when this index is about 1.90, which brings parallel rays to an approximate focus at the rear surface of the bead. The amount of light specularly reflected from the boundary between paint and bead is a function of the difference in their refractive indices. More particularly, it depends on the difference in index of bead and paint vehicle, since the vehicle completely envelopes the pigment particles and light reaching the latter is diffusely reflected.

Fifth, the depth and firmness of embedment of beads in paint depends on compatibility with respect to the ability of the paint to wet the bead surfaces. Thus, paint and beads, are intimately related in service performance. and the reflectorized stripe should be evaluated as an entity rather than as a combination of independent materials.

Sixth, optimum gradations of beads for maximum usefulness have not been completely determined experimentally. However, experience and the geometry of surface to mass ratios definitely indicate the desirability of using beads of smaller maximum size. The principal advantages of using smaller beads are: (1) pound for pound, they present more reflective surface and are retained better; (2) they can be premixed with the paint; (3) they reduce both drying time of the paint and the effect of relative humidity on drying time; (4) they contain a smaller percentage of imperfect particles; and (5)they suffer smaller rebound losses in spray application.

Seventh, the two kinds of imperfections receiving most attention at present are nonroundness and gas inclusions. A large percentage of fragments is detrimental, but it is doubtful whether other nonrounds, such as spheroids, ellipsoids, etc., significantly affect optical performance. Gas inclusions are definitely harmful, because they interfere with reflex reflection and weaken the bead structurally.

Eighth, depth of embedment is an important factor in reflex reflection of pavement marking beads, because at the very small angles of incidence involved, the effective reflex-reflecting zone of the bead is extremely narrow. When the bead is embedded to a depth of half its diameter, the height of the vertical aperture through which light may be received for reflex reflection is approximately the product of the diameter and the sine of the incidence angle, or only a few thousandths of the bead radius. With only a slight increase in depth of embedment (half of the above vertical aperture), reflex reflection is lost altogether. Decreasing the depth of embedment extends the effective zone vertically, but this advantage is off-set to some extent by the likelihood of poor bead retention.

Ninth, from an analysis of bead interference in relation to critical separation distances, it appears that some bead economy may be achieved by further experimental study of the problem of application rates.

Finally, experience so far indicates that the use of beads lengthens the life of the painted stripe, and that beaded stripes last longer on bituminous pavements than on concrete.

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