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Correlations between Refractive Index and Retroreflectance of Glass Beads for Use in Road-marking Applications under Wet Conditions

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Visibility of road-surface markings is one of the critical issues that should be secured for self-driving cars as well as human drivers. Glass beads are taking on the role of retroreflectors, and therefore are considered a necessity in modern pavements. In this context, retroreflectance is sensitively dependent not only on the refractive index of glass beads but also on that of the surrounding medium. This implies that the optimum refractive index of glass beads immersed in water, *i.e.* under wet conditions, is different from that of glass beads surrounded by air, *i.e.* under dry conditions. A refractive index of approximately 1.9, which is known to maximize retroreflectance under dry conditions, actually exhibits much poorer retro-reflectance under wet conditions. This suggests that glass beads with optimal refractive index for wet conditions need to be installed together with those for dry conditions. We propose a facile but practical model capable of calculating retroreflectance of glass beads surrounded by an arbitrary medium, here water in particular, and experimentally verify its capability of assessing the refractive index of commercial glass beads. Changes in retroreflectance according to the mixing ratio of glass beads with different refractive indices are also discussed, in an effort to propose the proper use of glass beads produced for dry and wet conditions.

Keywords : Glass beads, Road surface marking, Refractive index, Retroreflectance, Pavements
OCIS codes : (120.4800) Optical standards and testing; (120.5700) Reflection; (160.2750) Glass and other amorphous materials; (160.4670) Optical materials

I. INTRODUCTION

Visibility of road-surface markings becomes worse at night or in the rain, so nowadays glass beads acting as retroreflectors are installed together with road-marking paint, in an effort to enhance visibility in such situations [1]. For this purpose, it is of critical importance to choose glass beads of proper refractive index, and in this regard some previous studies have shown that the retroreflectance (R_A) of glass beads is strongly influenced by their refractive index (n), in addition to other concerns related to their installation on pavement [2, 3]. It is noteworthy that R_A induced by glass beads is known to be maximized at $n \approx 1.9$ under dry conditions, and at $n \geq 2.4$ for wet conditions [4]. Glass beads commercialized for use in road-surface markings have been produced from typical soda-lime silicate glass compositions, mainly for the sake of cost reduction, so that their n values are normally smaller than about 1.6 over the visible wavelengths; however, these days regulations associated with visibility issues have become more stringent, and thereby high-n glass beads are customized in terms of chemical composition to satisfy $n \approx 1.9$ for dry conditions and $n \approx 2.4$ for wet conditions. It is worth mentioning that, from the viewpoint of glass engineering, formation of transparent glass beads is exceptionally difficult when their n needs to be higher than about 1.8. The highest n available among commercial glass beads is approximately 2.4, to the best of authors' knowledge, but this refractive index is still lower than the optimal value for use under wet conditions. The dependence of retroreflectance on refractive index for glass beads immersed in water is delineated in detail in this paper. Since dry and wet conditions necessitate different

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optimal n values, we turn to arranging the mixing-ratio problem in their practical applications, *i.e.* maximizing retroreflectance [5]. Proper mixing of two different types of high-n glass beads should be harmonized in consideration of many factors; in this study, changes in retroreflectance are discussed in connection with the mixing ratio between two different glass-bead batches with refractive indices of 1.9 and 2.4.

Evaluation of refractive index for high-n glass beads that are nominally spherical needs to be performed within practical uncertainty tolerances. The Becke line method is adopted most widely for this purpose, and is listed as one of the industry standards [6]. It is noteworthy, however, that the Becke line method is not available for glass beads with $n > 1.8$, because standard refractive-index liquids to handle $n > 1.8$ contain toxic substances such as As and Br, and thus have been commercially banned. In addition, other methods cable of assessing the refractive index of a glass sphere require complicated laboratory setups, and lack statistical information about refractive index for a given glass-bead batch [7–13]. Based on the above reasoning, we have proposed a more facile but relatively accurate method for n assessment of glass beads based on comparison of calculated and measured R_A values [14]. Calculation of R_A is performed for a single perfect glass sphere upon which parallel optical rays are incident; here each optical ray is assumed to experience refraction when entering and escaping the glass sphere, as well as one-time internal specular reflection at the backside of the sphere, thus providing retroreflection. The Fresnel equations should apply at each interface, so one can calculate changes in retroreflectance from the glass sphere as a function of refractive index. Not only the seemingly oversimplified postulate associated with this calculation but also deviation of actual commercial glass beads from the perfect geometry assumed in the calculation would be alleviated by using an experimental reference standard. This reference is itself a batch of commercial glass beads, for which refractive index is precisely known, and which statistically represents all of the glass-bead batches in terms of shape, size, and irregularities [14].

The calculated R_A curves plotted against n of a glass bead feature an asymmetrical lineshape that peaks at ~1.9 under dry conditions, and therefore retroreflectance values can be identical even when two glass-bead batches possess very different refractive indices. This situation stimulates us to calculate R_A curves for glass beads immersed in various media of differing refractive indices. In this way, the retro-reflectance method for assessing the refractive index of glass beads can be more reliable.

II. MATERIALS AND METHODS

The commercially available glass-bead batches dealt in this paper are identical to those in the previous paper [14]. Summarized in Table 1 are the n values of the glass-bead batches, spanning approximately 1.5 to approximately 2.4, and thus covering the entire range of n for commercial glass beads. The Becke line method was applied to the prepared batches using standard refractive-index fluids (Refractive Index Liquids, Cargille Laboratories) when possible. In the case of high-n glass beads (for which refractive index cannot be assessed using the Becke line method due to the lack of proper reference refractive-index fluids), supplier-specified n values were adopted. Note that n for batch **F** was confirmed to be 1.88 using high-n standard refractive-index liquids purchased before the ban. Retroreflectance was measured using a commercially available instrument (Handheld Retroreflectometer 932; Roadvista). The instrument enables measurement of R_A of glass beads in accordance with the procedures described in industrial standards [6, 15, 16]. The irradiation angle and observation angle were fixed

TABLE 1. Refractive indices determined by the Becke line method and by the retroreflectance method proposed in this study using retroreflectance values measured under wet conditions

Glass-bead batch	n (Becke line method)	n (retroreflectance method)	Difference
A	1.70	1.67	0.03
B	1.93*	1.93 (set as reference)	
C	1.52	1.67	0.15
D	1.58	1.65	0.07
E	1.63	1.62	0.01
F	1.88	1.86	0.02
H**	1.9*	1.95	0.05
I**	2.4*	2.37	0.03
J**	1.9*	1.97	0.07
K	Unknown	1.88	Not available

* Not measured by Becke line method, but specified by supplier.

**Refractive index of these glass bead batches noted only to the first decimal place.

to 0° and 0.2° respectively, following the basic configuration of the instrument. Three liquid media (water, benzene and carbon disulfide) were utilized to provide different ambient refractive indices for the beads. After the glass beads were fully immersed, the liquid's surface was made still to obtain accurately measured R_A values. For each batch of glass beads, 27 specimens were sampled and their R_A values measured. After the maximum and minimum values were discarded, the remaining 25 values were averaged.

III. CALCULATION OF THE RETROREFLECTANCE OF A GLASS BEAD UNDER WET CONDITIONS

The calculation procedures for the numerical relations between n and R_A of glass beads are basically the same as those described in our previous study [14]. However, it is noteworthy that here the medium surrounding the glass bead is not air, so its refractive index should cause some conspicuous effects. If we assume that the glass bead is immersed in water, for example, as shown in Fig. 1, then we need to take into consideration an additional refraction of optical rays at each interface between air and water. Parallel optical rays emitted from the light source placed in the instrument strike the water at normal incidence, and then irradiate the surface of the glass bead at Interface **1**. After being refracted at Interface **1**, an optical ray undergoes internal specular reflection at Interface **2** and subsequently escapes the glass bead after experiencing refraction at Interface **3**. Eventually, this optical ray encounters the air/water interface again, and refraction occurs. The retro-reflection angle (θ) can be expressed in terms of incidence angle (a), refraction angle (b), and another refraction angle at the interface between air and the surrounding medium [14, 17].

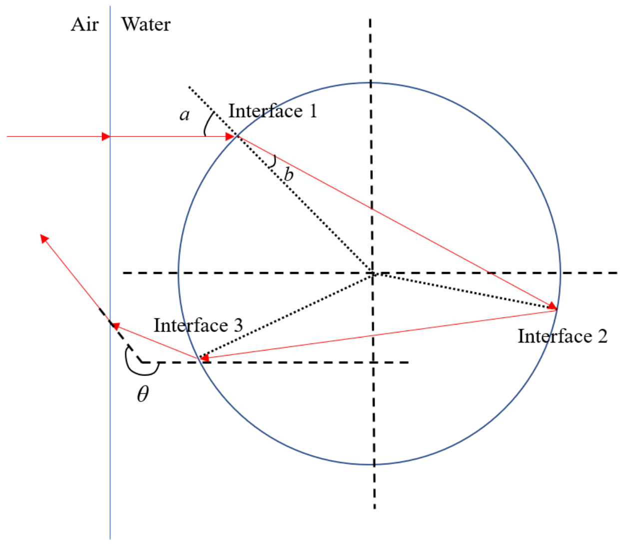

FIG. 1. Schematic drawing of a single glass bead immersed in water. The optical ray indicates the situation for our calculation, *i.e.* retroreflection made via one internal specular reflection at the backside of the glass sphere.

As displayed in Fig. 2, when n of the glass bead is less than 2.6, the angle θ starts to decrease, then shows a minimum in the middle, and finally increases with increasing incidence angle. On the other hand, when n is greater than or equal to 2.6, θ monotonically increases with increasing a across the entire range. It is noteworthy that this behavior appears at a lower refractive index (close to 1.9) under dry conditions [14], which qualitatively shows that the number of optical rays evenly irradiating the glass bead surface and satisfying the retroreflection condition ($\theta \approx 180°$) sensitively depends on n of the glass beads as well as of the surrounding medium. We employ the Fresnel equations to calculate transmittance and reflectance of each optical ray at the interfaces formed between air and water and between water and glass bead (see Fig. 1 again). The relative intensity (I_r) can be calculated as a function of θ [14]. Figure 3 reveals that the calculated I_r values satisfying the

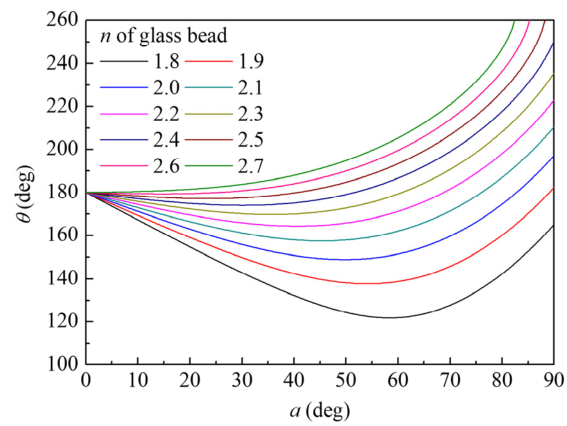

FIG. 2. Relation between angles a and θ, plotted for different values of refractive index of a glass sphere, under wet conditions.

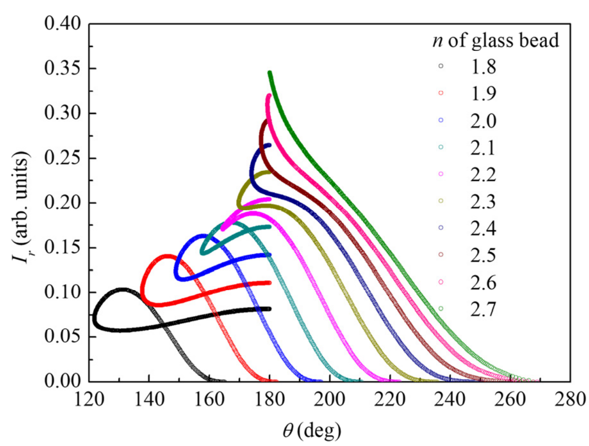

FIG. 3. Relation between θ and I_r, for various n values of a glass sphere, under wet conditions.

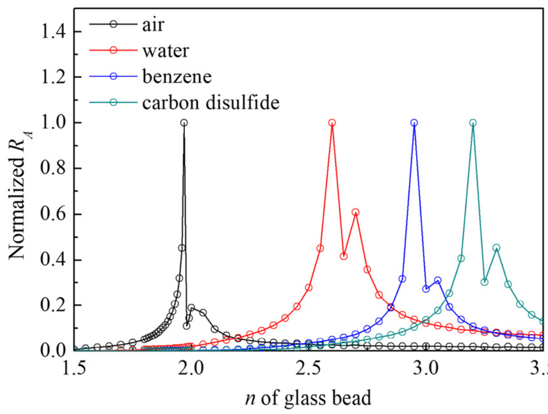

FIG. 4. Normalized R_A values plotted as a function of n for a glass sphere immersed in different liquids. Note that the refractive index of water, benzene and carbon disulfide is set to 1.33, 1.50 and 1.63 respectively.

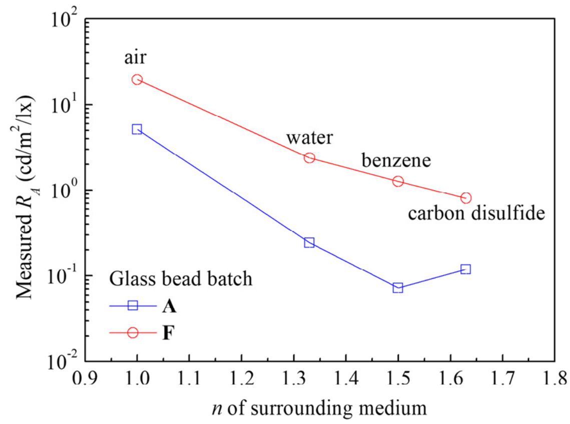

FIG. 5. Measured retroreflectance of batches **A** and **F** immersed in different media.

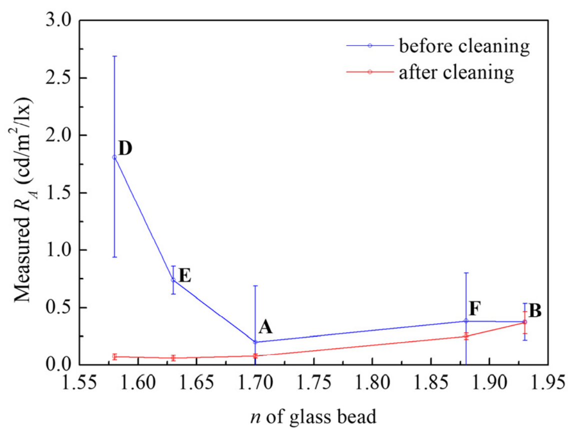

FIG. 6. Measured retroreflectance of glass-bead batches before and after cleaning. Refer to Table 1 for the letters identifying the batches.

retroreflection condition ($\theta \approx 180°$) are sensitive to n of the glass bead. To visualize this behavior more clearly, we sum the relative intensities of the rays falling within θ ranging from $179.8 \pm 0.05°$ to $180.2 \pm 0.05°$, which coincides with the observation angle of the instrument used in this study. Figure 4 presents R_A values plotted as a function of n of the glass bead immersed in different media; air, water, benzene and carbon disulfide. It is noticed that the refractive index for the maximum in R_A becomes higher with increasing n of the surrounding medium.

IV. ASSESSING REFRACTIVE INDEX OF GLASS BEADS USING RETROREFLECTANCE

To experimentally verify the effects of varying the refractive index of the surrounding medium, as shown in Fig. 5, we measured R_A values for glass-bead batches **A** and **F**. One can see that the measured R_A varies conspicuously with varying refractive index of the surrounding medium. On the other hand, we find that the measured R_A under wet conditions is sensitive to surface cleaning of the glass beads: Before an appropriate cleaning process is applied, glass beads (low-n beads in particular) tend to show quite a large deviation, as presented in Fig. 6. However, after cleaning, the measured R_A values exhibit the normal behavior that we expect. In this study, in an effort to enhance the contact between water and glass beads, each batch was ultrasonicated in acetone and ethanol for 30 minutes each, and then dried at 80°C. Afterward each batch was soaked in distilled water for 1 day before retro-reflectance measurement. This cleaning process is focused on removal of (mainly oily) contaminants and tiny pores from the surface of every glass bead to enable direct contact between water and glass, which then enhances the reliability of the retroreflection method performed under wet conditions.

Figure 7 shows the calculated R_A values plotted together with the measured R_A values for properly treated glass beads under wet conditions. Batch **B** is designated as a reference, because it is supposed to represent all of the glass-bead batches in terms of morphology and roundness as well as having a sufficiently large R_A value. Whereas the R_A curve calculated for a glass bead under dry conditions undergoes a rather complicated change in lineshape over n range of 1.5 to 2.4 (as shown in Fig. 4), the corresponding R_A curve for wet conditions exhibits a monotonic increase. Taking a look at Fig. 7, one can notice that the measured R_A values of the prepared glass-bead batches are close to the calculated R_A values, except for batch **C**. The refractive-index values for batches **H**, **I** and **J** are available only up to the first decimal place, so the corresponding mismatches would be more significant than for the other batches. Notably, batch **G** exhibits an exceptionally large deviation under dry conditions [14], and also under wet conditions. Batch **G** consists of glass beads with remarkably poor surface quality and internal defects as well as bad roundness.

This implies that glass beads ought to possess reasonably good morphology and roundness for the retroreflectance method to be applied.

Now we explicate how to assess n of glass beads based on measured R_A and calculated values: Using the retroreflectance method performed under wet conditions, n of each specimen is derived and compared to that either obtained using the Becke line method or specified by supplier (see Table 1). As mentioned above, the calculated R_A curve monotonically increases with increasing refractive index up to approximately 2.6, and this makes it possible to prevent the confusion encountered in the case of dry conditions, *i.e.* the observation of identical R_A at different n values. Nevertheless, glass beads (low-n glass beads in particular) exhibit relatively lower R_A values under wet conditions, and therefore tend to be more affected by extrinsic factors such as morphology, defects and roundness. Small pores or oily contaminants on the surfaces of the glass beads would also increase the deviations, if not fully removed. In this regard, it is understandable that batch **C**, for which n is lowest among the tested batches, presents a very large deviation (see Fig. 7 again), and the Becke line method is more advantageous for glass beads with $n < 1.80$, for which standard refractive index fluids are commercially available. For glass beads with $n > 1.80$ in particular, n can be more accurately evaluated via combining R_A values obtained for dry and wet conditions. For example, in the case of batch **I** ($n \approx 2.4$) under dry conditions, its n may be assigned to be either higher than 2.4 or less than 1.6 [14]; however, its n can be simply assigned to be about 2.4 rather than about 1.6 under wet conditions, because its measured R_A is much higher than for the other glass beads. In the case of batch **K**, for which n is unknown, its n is consistently assigned to be close to 1.88 for both dry and wet conditions. Based on these results, it can be justified that the present method can acquire extra reliability when performed with high-n glass beads under both dry and wet conditions.

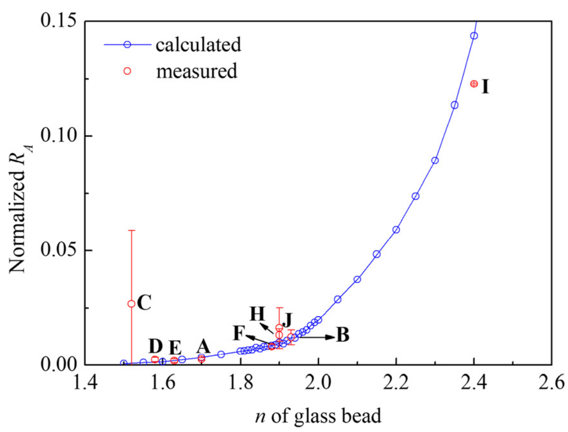

FIG. 7. Comparison between the calculated and measured R_A values for wet conditions. Observation angle is fixed to 0.2 ± 0.05° in this plot. Note that glass-bead batch **K** is not included, because its refractive index is unknown.

V. MIXING-RATIO DEPENDENCE OF RETROREFLECTANCE

As described above, the maximum retroreflectance values for dry and wet conditions differ from each other. This necessitates the use of mixtures of dry- and wet-type glass beads in actual applications, and so it is important to find a good mixing ratio between two glass bead batches to enhance the visibility of road markings under any conditions. For this purpose, we measured R_A for mixtures of batches **H** (denoted as dry-type bead) and **I** (wet-type bead) with n values of about 1.9 and about 2.4, respectively, under dry and wet conditions. If mixing two batches alters the effective refractive index according to the mixing ratio, then the measured R_A would follow the calculated R_A curve. However, as shown in Fig. 8, upon increase of volume fraction of batch **I**, the measured R_A decreases monotonically under dry conditions, whereas it increases under wet conditions. These results coincide well with the

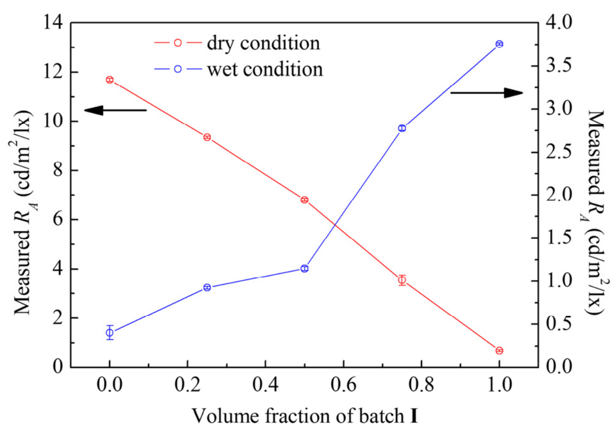

FIG. 8. Measured retroreflectance as a function of mixing ratio between batches **H** and **I** for dry and wet conditions.

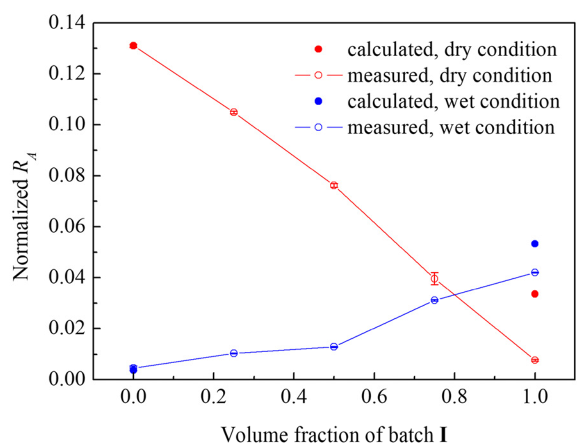

FIG. 9. Comparison of measured R_A of the mixtures and the calculated R_A for glass beads with n = 1.9 or 2.4. The values are normalized with respect to the calculated R_A for beads with n = 1.9 under dry conditions.

R_A curves calculated in this study: Presented in Fig. 9 are R_A values normalized with respect to the calculated R_A for the $n = 1.9$ beads under dry conditions, so that data points for the calculated and measured R_A under the dry condition are superimposed. It is justified once again that the overall behaviors experimentally observed for the two different conditions coincide reasonably well with those behaviors from our calculations.

To fix the mixing ratio properly for practical applications, other factors need to be taken into account: First, needless to say, a higher fraction of the wet-type batch is more effective in a region with high rainfall, which implies that the mixing ratio needs to be carefully engineered in deference to the average weather of the region under consideration. Second, traffic volume and environments around the pavement need to be further considered. This means resources (visibility of road-surface markings in this case) should be prioritized to obtain a larger profit in connection with traffic accidents. Third, the actual R_A value does not need to be very high, because the effects concerning visibility of road lines cease at a certain value of R_A [18]. As such, it would be economically inefficient to increase the fraction of the wet-type beads, because these cost a lot more than the dry-type beads. The factors outlined above need to be taken into consideration when optimizing the mixing ratio, and our results presented in this paper should be useful to that end.

VI. SUMMARY

In an effort to augment the utility of the retroreflectance method in assessing the refractive index of high-n glass beads, R_A is calculated as a function of n of glass beads under wet conditions using the Fresnel equations. Our experimental results confirm that R_A values measured under wet conditions coincide well with R_A values calculated under the same conditions. This implies that the refractive index of glass beads can be precisely evaluated using the present method via combining R_A values obtained under dry and wet conditions. In addition, we also verify that the actual retroreflectance can be engineered by mixing two glass-bead batches with different refractive indices, and our experimental results should be beneficial for that endeavor.

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