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# Dye coloration of silica with completely incompatible organic dye using stably coexisting organic solvent

Ken-Ichi Kurumada [a,*], Yoshihiro Kamimura [a], Keiji Igarashi [a], Naoki Umeda [a], Hisashige Kambara [b], Tomohito Yuasa [b], Masahiko Hiro [b]

[a] *Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama 240 8501, Japan*
[b] *R&D Center, Hitachi Chemical Co. Ltd., Tsukuba 300 4247, Japan*

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## Abstract

We carried out dye coloration of sol–gel derived silica with near-infrared absorbing organic dye which is completely incompatible with silica sol. Since the direct dye coloration was impossible due to the incompatibility, the dye was introduced into the silica matrix being mediated by dye-dissolving amphiphilic solvents such as acetonitrile and ketones with various carbon numbers. The structural conditions for the uniform coloration were discussed based on optical microscopic observations and other auxiliary methods. The dye coloration was revealed to be possible when the dye-dissolving solvent remained in the form of small droplets, otherwise, the dye gets completely separated from the silica matrix in a dried powdery state. This result shows that the incompatible dye was immobilized in the silica matrix in a dissolved state inside the droplets. Optically transparent dye coloration which is more desirable from practical viewpoints was obtained when the dye-dissolving solvent has volatility in an appropriate region. Excessively high and low volatilities were found to lead to the segregation of powdery dry dye and larger droplets which made the sample look strongly opaque, respectively. In the case where the silica matrix was successfully colored retaining optical transparency, microscopic observation revealed that the size of the minute droplet structure was comparable to the wavelength of visible light being in the order of $10^2$ nm.

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*Keywords:* Dye coloration; Sol–gel derived silica matrix; Mediating solvent; Microdroplet structure; Optical transparency; Residual solvent

## 1. Introduction

Glass has been colored normally by dispersing atomized transient metals into glass matrix as seen in the manufacturing of stained glasses. Substitution of tetravalent Si ions by metal ions needs such a high processing temperature as 1300 °C, which severely restricts agents from dyeing glasses. For many applications, organic dye is more preferable because of the much greater variety in the wavelength of absorbance in IR, visible and UV regions. However, organic dyes are not easy to use in conventional glass coloration process because it requires quite high processing temperature. Sol–gel glass (silica) processing is, thus, quite promising to color glass or silica with organic dyes since it can circumvent a melting process at a very high temperature (~1000 °C). There have been a number of works of coloration of sol–gel derived silica using organic dye species [1–16]. In those works, inorganic dye was dissolved in the starting solution in which tetraethyl orthosilicate (TEOS) was simultaneously hydrolyzed. For direct dye coloration of silica, the organic dye species needs to be directly soluble in the sol–gel starting solution. This direct method for the incorporation of organic dye is quite simple and actually can be easily carried out. Łaczka et al. prepared optically filtrating glass by introducing an organic dye (2′,7′ dichlorofluorescein). Ohishi prepared colored silica film with epoxy-silano rhodamine B derivative. In their case, the chemically modified rhodamine B was covalently immobilized on the surface [3]. This method is indeed the most powerful one in that the

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* Corresponding author. Tel./fax: +81 453394307.
*E-mail address:* kurumada@ynu.ac.jp (K.-I. Kurumada).

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coloring agent is covalently stabilized on Si moiety, however, the epoxy-silano dye needs to be prepared in advance. From the practical viewpoint, a much more versatile dyeing method is more desirable. Costa et al. succeeded in entrapping benzoxazole dye in silica matrix by applying high pressure (4.5 GPa) [5]. As a result of that the dye was quite stably immobilized in the silica matrix and the coloration was resistant even to leaching. Some other works used adsorption of dye onto the silica surface, where the highly porous structure became significant to enhance the dyeing [12–17]. In these works, the affinity of the dye is quite essential. The high affinity of the dye readily leads to dissolution in the sol–gel starting solution/silica sol or adsorption.

Incompatibility of the dye to silica matrix can be often a cause of difficulty when we need to color silica. Dong et al. used dioxane as an additive solvent for the dissolution of 2,2″-dimethyl-*p*-terphenyl dye [18]. Dioxane was necessary to incorporate the dye homogeneously into the silica matrix. Although they did not mention the role of residual dioxane which helps in the stabilization of the dye in the silica matrix, the residual solvent was obviously the requisite to mediate the dye coloration [18,19]. Rao and Rao dyed silica xerogel with rhodamine 6G using various additive solvents. They found that the UV–vis absorbance spectrum depends on the used additive solvent species [20]. This result shows that the additive solvent remained in the silica matrix even after the drying process and significantly affected the absorbance spectrum.

In some circumstances, the species need to be incorporated into silica matrix in a solvent-dissolved state to exhibit the intrinsic UV/vis/NIR/IR absorbance behavior. This method is expected to be useful when the dye is not compatible with silica matrix. In the present work, the authors needed to color silica matrix with a vivid green dye species (tetra(3-di(2-methylbutyl)aminophenyl)phenilenediaminodichloride) because of its conspicuous near-infrared absorbing ability. The chemical structure of the dye is shown in Fig. 1. This dye was required to be in a dissolved state to exhibit the desired infrared absorbing property. Nevertheless, it is completely incompatible with neat silica. To solve this technical problem, the dye was added to silica sol with a solvent species in which the dye can be readily dissolved. The technical clue for obtaining uniform coloration with the incompatible dye lies in the solidification process of silica during which the additive solvent for the coloration can or cannot remain. Here, the authors searched for proper coloring conditions with the help of those additive solvents by observing the micrometer-scale structure of the dyed sol–gel derived silica matrix. The state of the dye immobilization in the silica matrix was also discussed based on the elution behavior of the dye in the silica matrix into immersing solvent from the powdered sample. The presence or absence of residual carbon after the heat treatment of the sample also proveded an evince for the essential role of the mediating redisual solvent.

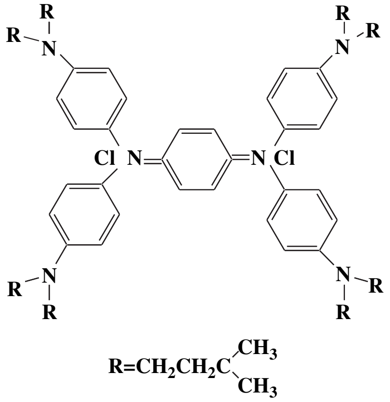

Fig. 1. Chemical structure of the dye used in the present work (tetra(3-di(2-methylbutyl)aminophenyl)phenilenediaminodichloride).

## 2. Experimental section

### 2.1. Materials

The dye used in the present work (tetra(3-di(2-methylbutyl) aminophenyl)phenilenediaminodichloride: to be abbreviated as TPPD dye in the following text) was gifted from Hitachi Chemical Co. Ltd. and was used as provided. It should be noted that this dye is soluble only in such organic solvents with intermediate polarity as ketones or acetonitrile. (Alcoholic solvents cannot be used because of the instability of TPPD dye in alcohols.) All other chemicals used in the present work (tetraethyl orthosilicate (TEOS), acetonitrile, ketones, hydrochloric acid) were of analytical grade and were provided from Wako Pure Chemical, Japan. The water used for the sample preparation was purified by ion exchange followed by distillation.

### 2.2. Sample preparation

The silica sol was prepared from 0.025 mol of tetraethyl orthosilicate (TEOS) hydrolyzed with 0.1 mol of water and 0.001 mol of hydrochloric acid. The hydrolysis was carried out at room temperature (approximately 298 K) for an hour with vigorous stirring by a magnetic stirrer. TPPD dye was added into the above silica sol after being dissolved in 2.5 g of the dye-dissolving solvents (acetonitrile/ketones) at the weight concentration of 0.5%. These solvents readily dissolve TPPD dye and exhibit vivid green color intrinsic in TPPD dye coloration. The TPPD dye solutions in these solvents were miscible with the silica sol. The sample was obtained by air-drying this mixture for solidification for a day.

### 2.3. Observation of the dyed state, etc.

The dyed state of the sample was observed using a magnifying glass and optical microscope (OLYMPUS BX41). The attention was mainly paid to the state of dispersion of TPPD dye and the dyed state.

Presence or absence of residual carbon after calcinating the sample at 800 °C can be used as a sign for the state of the sample after the completion of solidification, in particular, for whether the dye-dissolving solvent remains in an immobilized manner in the silica matrix or not. The presence or absence of the residual carbon is visibly indicated by the blackening of the sample after calcination.

The elution of TPPD dye from the sample was measured for a clue of the entrapped state of TPPD dye in the silica matrix. Sample (0.2 g) was fully ground for 30 min with an agate mortar with a diameter of 50 mm. The powered sample was immersed in acetonitrile at room temperature for a day to let the immobilized TPPD dye in the silica matrix to elute from the sample. After removing the solid sediment, UV—vis absorbance of the supernatant solution was measured from 500 nm to 1100 nm.

## 3. Results and discussion

As the preliminary experiment, we confirmed that TPPD dye is completely insoluble in the silica sol which consists of water, ethanol, tetraethyl orthosilicate and silanol. Therefore, direct dye coloration using TPPD dye in the sol—gel process was shown to be impossible and dye-dissolving solvent needs to be added for the dye coloration.

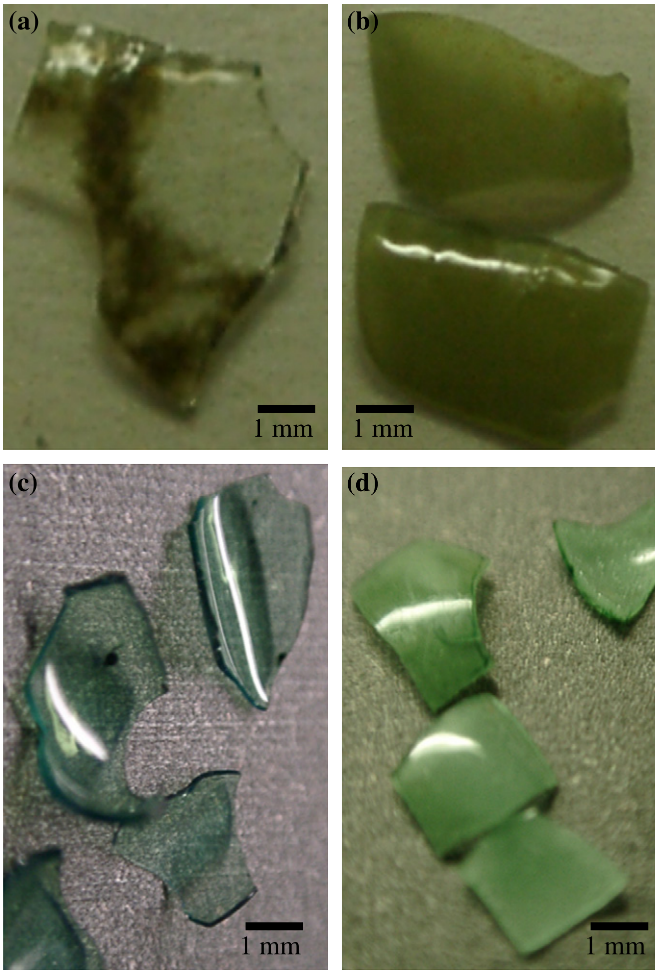

Fig. 2. Magnified view of dyed silica samples prepared using different dye-dissolving solvents. (a) Acetonitrile, (b) cyclopentanone, (c) 2-hexanone and (d) 2-heptanone.

Fig. 2 presents magnified photographs of the samples prepared using acetonitrile, cyclopentanone, 2-hexanone and 2-heptanone as the dye-dissolving solvents. When acetonitrile was used (Fig. 2(a)), the dye completely segregated from the silica matrix and did not exhibit vivid green color indicating that the dye was enclosed in the silica matrix in a dried powdery state. Contrastively, the silica matrix was uniformly dyed in vivid green when cyclopentanone or 2-hexanone was used as the dye-dissolving solvent, as seen in Fig. 2(b) and (c). The sample prepared using 2-pentanone was also well dyed exhibiting vivid green color, however, the silica matrix became quite opaque indicating that it has an inhomogeneous structure compared to those prepared with cyclopentanone or 2-hexanone. Table 1 presents the boiling points of the used solvent species in the present work. As a general trend, higher and lower volatilities of the dye-dissolving solvent lead to the segregation of the powdery dye and opacity, respectively. The use of dye-dissolving solvents of intermediate boiling points resulted in a more homogeneous dye coloration. This point is to be discussed in association with the results of the microscopic observations in the following as an important key factor for dye coloration by the present method.

Fig. 3 presents optical micrographs of the samples prepared using ketones with various carbon numbers (C5, C6, C7, C9). When 2-pentanone was used the dye segregated from the silica matrix in the powdery state. The segregation was observed as a stain-like darker right-hand part in Fig. 3(a). The brown color of the micrograph shows that the dye is completely separated from the silica matrix in a dried powdery state. The homogenously colored state obtained when 2-hexanone was used as the dye-dissolving solvent was also seen in the optical micrograph, where the vivid green color was homogeneously distributed over the field of view of the optical microscope (Fig. 3(b)). When 2-heptanone or 2-nonanone was used, the sample was conspicuously opaque as shown above (Fig. 2(d)). The opacity could be characterized by the dots, as seen in Fig. 3(c) and (d). Because each of the dots was seen to contain the dye in the dissolved state exhibiting vivid green, the dye was considered to be mainly encapsulated in the droplets, the size of which is seen distributed in the range of 1—50 μm. Because these samples exhibit vivid green, the dye was considered to be contained in the droplets in a dissolved state in the added solvent. The opacity was due to the larger size of the inhomogeneous structure whose scale

Table 1
Boiling points of used dye-dissolving solvents and the states of the sample after the drying process for solidification

| Dye-dissolving solvent | Boiling point (°C) | State of dye after drying |
|---|---|---|
| Methyl ethyl ketone | 80 | Completely segregated |
| Acetonitrile | 82 | Completely segregated |
| 2-Pentanone | 105 | Completely segregated |
| 2-Hexanone | 127 | Uniformly colored |
| Cyclohexanone | 130 | Uniformly colored |
| 2-Heptanone | 144 | Uniformly colored, opaque |
| 2-Nonanone | 192 | Uniformly colored, opaque |

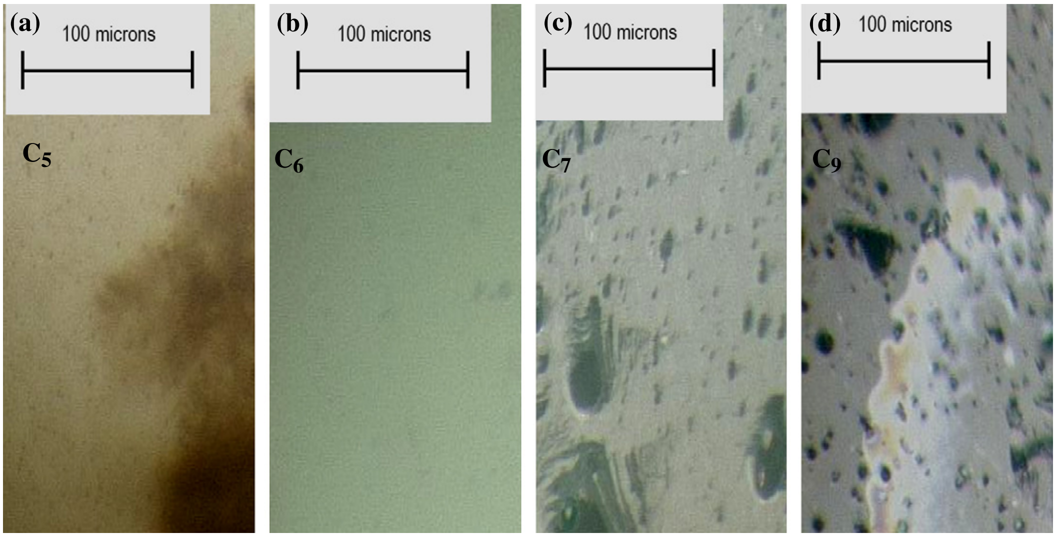

Fig. 3. Optical micrographs of dyed silica samples prepared using ketones of different carbon numbers. (a) 2-Pentanone, (b) 2-hexanone, (c) 2-heptanone and (d) 2-nonanone.

was far over the wavelength of visible light. Therefore, the opacity arose from the diffuse reflection caused by these droplets. Therefore, the extent of the volatility significantly affected the final dyed state in terms of the size of the droplets, although the fundamental structure of the dyed state is basically common.

Fig. 4 presents magnified views up to the limit of the optical microscope. As seen in Fig. 4(a), there are innumerable dot-like structures even in the uniformly dyed sample. The authors consider that the dye was contained in these small droplets in a dissolved state in 2-hexanone. It should be noted that the size of these droplets is obviously less than 1 μm as compared with the scale shown below in the figure. (Probably, the actual average size is much smaller than it is seen in the micrograph because of scattering effect of the visible light which stands out in the submicron size of the scattering objects.) When 2-heptanone was used as the dye-dissolving solvent (Fig. 4(b)), the droplet structure was much larger than in the case of using 2-hexane, as seen in Fig. 4(a). In contrast to those in Fig. 4(a), the droplets were sufficiently large to be clearly captured in the outline by the optical microscope. Therefore, the uniformly dyed state occurs as a result of the formation of fine droplets which contain the dye in the dissolved state. For the optical transparency of the dyed silica matrix, those droplets need to be at least comparable to the wavelength of visible light or smaller than that.

Fig. 5 presents absorbance spectra of elution into acetonitrile from the samples prepared using 2-hexanone and 2-heptanone. Both in the case of 2-hexanone and 2-heptanone, powdering the sample leads to obvious increase in the elution. In the bulk samples, the dye was well encapsulated to be prevented from eluting out of the samples. The more elution from the powered sample prepared using 2-heptanone indicates that the elution occurred more easily from the larger droplets as seen in Fig. 3(c) or (d). In particular, near-infrared absorbance

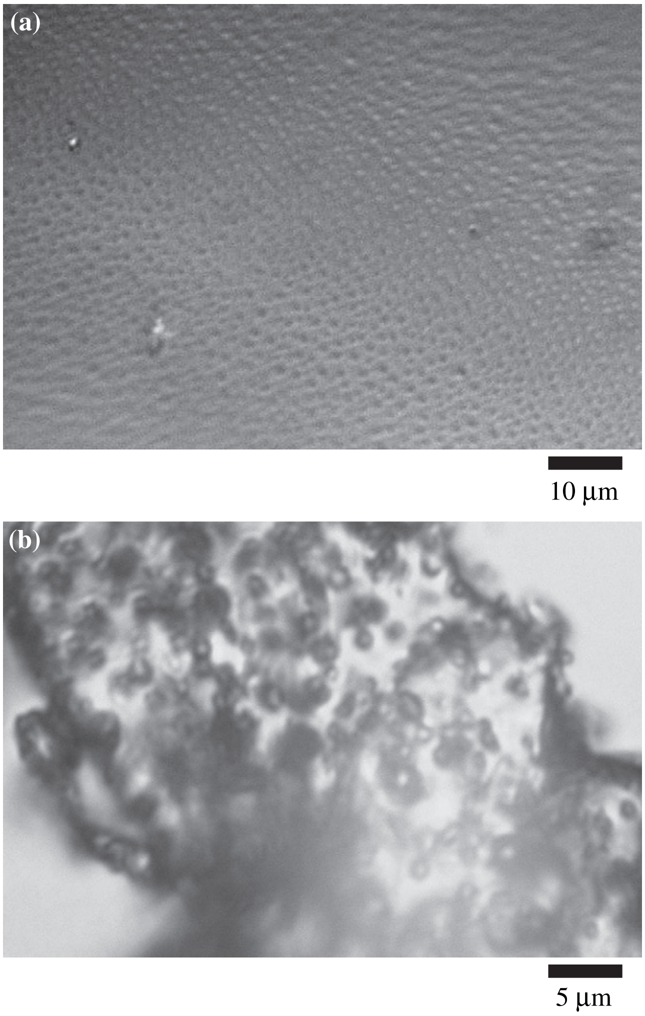

Fig. 4. Optical micrographs of dyed silica samples prepared using ketones of (a) 2-hexanone and (b) 2-heptanone observed at the maximum magnification by optical microscopy. These views were taken at the magnification up to the limit of optical microscopy.

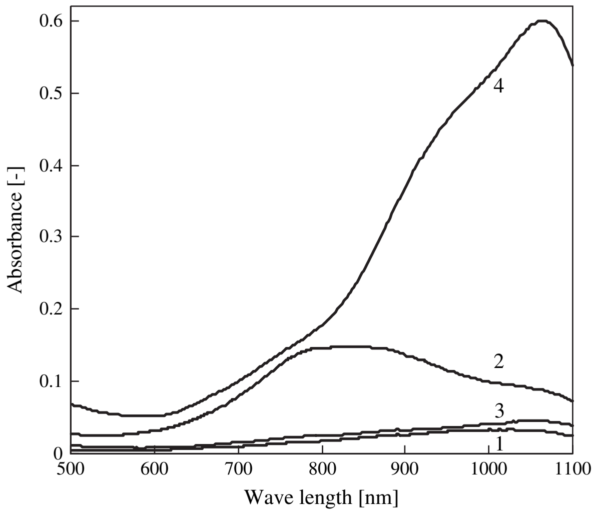

Fig. 5. UV–vis absorbance spectra of acetonitrile solution of eluted TPPD dye from (1) bulk sample prepared using 2-hexanone, (2) powdered sample prepared using 2-hexanone, (3) bulk sample prepared using 2-heptanone and (4) powdered sample prepared using 2-heptanone.

stood out due to the elution of the dye which had been encapsulated with the dye-dissolving solvent in the droplets (curve 4). Therefore, from the practical viewpoint, the formation of the smaller droplets is advantageous for preventing the loss of the dye.

Table 2 presents the absence or presence of residual carbon after calcinating the sample at 800 °C for 2 h. The segregation of the dried powdery dye coincided with the absence of residual carbon after calcination. On the other hand, the samples had residual carbon when they were well dyed in vivid green color. Thus, the presence of the residual carbon after calcination shows that a moiety of the dye-dissolving solvent was retained in the solidified matrix in the form of droplets. The results in Table 2 indicate that there needs to be the residual solvent for the coloration by the dye species when the dye is incompatible with the silica matrix itself.

In summary, the role of the dye-dissolving solvent was not limited to the dissolution of the dye which is incompatible with the starting silica sol. The dye-dissolving solvent needs to remain in the silica matrix even after solidification. The solvent was shown to be necessary for exhibiting vivid dye coloration by being encapsulated in the silica matrix with the dye dissolved in itself. Optically transparent dye coloration was possible in the case where the capsules (droplets) of the solvent are small enough not to strongly interact with visible light whose wavelength is in the order of $10^2$ nm. Lower volatility of the solvent tended to result in the formation of larger droplets giving the dyed silica matrix outstanding opacity due to the diffuse reflection. This is probably because the larger droplets were immobilized during the solidification process of the silica matrix due to the slower vaporization. For obtaining the optically transparent dye-colored state, the dye-dissolving solvent needs to have an intermediate volatility to give a rise to the appropriate average size of the droplets.

Table 2
Presence or absence of residual carbon after calcinating the sample for 2 h at 800 °C

| Dye-dissolving solvent | Presence or absence of residual carbon |
|---|---|
| Methyl ethyl ketone | Absent |
| Acetonitrile | Absent |
| 2-Pentanone | Absent |
| 2-Hexanone | Present |
| Cyclohexanone | Present |
| 2-Heptanone | Present |
| 2-Nonanone | Present |

## 4. Conclusion

Sol–gel derived silica matrix could be colored with completely incompatible dye with the mediation of the dye-dissolving solvent. Based on the results of microscopic observations, the necessary structural conditions for the uniform dye coloration were discussed. Dye coloration was found to be possible when the solvent remained in the silica matrix in the form of small droplets. It was revealed that the dye-dissolving solvent needs to have a proper volatility to remain in the silica matrix even after solidification. When the average size of the droplets was comparable to or smaller than the scale of the wavelength of visible light ($\sim 10^2$ nm), the silica matrix was uniformly dyed keeping its optical transparency. Other auxiliary experiments were quite consistent with the results of the microscopic observations. When carbon moiety remained after calcinating the sample for 2 h at 800 °C, vivid dye coloration was found to be induced by the formation of those microdroplets.

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