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Fading of Some Vinylsulfonyl Reactive Dyes on Cellulose under Various Conditions

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ABSTRACT

C.I. Reactive Red 22 and Black 5 and a monoazo violet dye (Violet) on cellulose showed reductive fading on exposure in deaerated water in the absence of substrate, although no fading of many other vinylsulfonyl reactive dyes was observed. These three dyes on dry cellulose underwent simultaneous oxidative and reductive fading. Whilst only oxidative fading for Red 22 and Violet on cellulose occurred on exposure in aerated water, and simultaneous oxidative and reductive fading for Black 5, the dyes on dry cellulose showed fading behavior intermediate between the fading in aerated and deaerated water. Not only the properties of the dye itself but also the conditions of exposure, especially the concentration of oxygen and the substrate on which dyes are adsorbed, determine whether reductive and/or oxidative fading occurs.

1 INTRODUCTION

Some vinylsulfonyl (VS) reactive dyes on cellulose have been shown to undergo oxidative fading on exposure in aerated water.[1-6] Their lightfastness is mainly dependent upon the ease with which they are

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oxidized. As reported in previous papers,[1-3] some VS dyes on cellulose showed no fading on exposure in deaerated water. However, as reported in this present paper, other VS dyes on cellulose were found to be faded slowly on exposure in deaerated water, even in the absence of substrate. Only C.I. Reactive Red 22 and Black 5 and a monoazo dye showed this fading behavior in the VS dyes examined in a series of studies.[1-6]

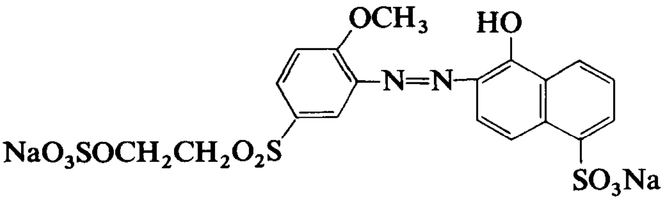
These dyes on cellulose were exposed under various conditions, i.e. dry, wet, aerobic and anaerobic; whether they underwent oxidative or reductive fading was examined by spectral analysis of the photodecomposition products on cellulose after exposure. Comparing the absorption spectra of the photodecomposition products on cellulose after exposure with those of the photoreduction products for the corresponding dyes,[4] it is confirmed that some VS dyes are photoreduced without addition of substrates such as DL-mandelic acid and L-lactic acid under some conditions.

2 EXPERIMENTAL

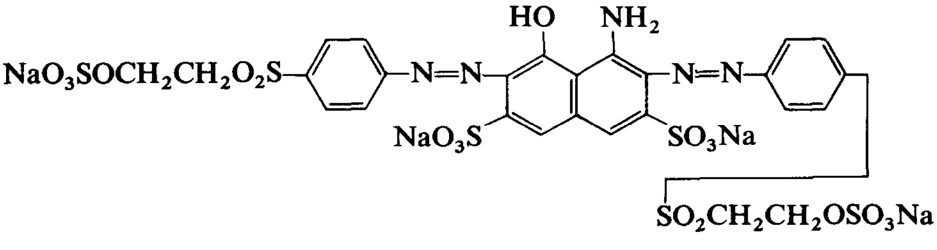
2.1 Dyes used

C.I. Reactive Red 22 and Black 5 (supplied by Sumitomo Chemical Co. Ltd, Osaka, Japan) and a monoazo violet dye (supplied by Hoechst Mitsubishi Kasei Co. Ltd, Tokyo, Japan) were used. Their chemical structure is shown below:

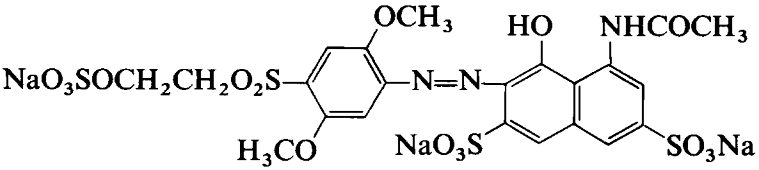
(1) C.I. Reactive Red 22 (C.I. 14824; Red 22)



(2) C.I. Reactive Black 5 (C.I. 20505; Black 5)



(3) A monoazo violet dye (Violet)



These VS dyes, cellophane films and the experimental methods were the same as previously described.[1-4]

2.2 Exposure of dyed cellophane

A sheet of dyed cellophane film set in a glass cell was exposed to a carbon-arc lamp in a glass vessel.[1,2] In the case of exposure of dry cellulose, silica gel was placed at the bottom of the glass vessel.[1] In the case of exposure of dyed cellophane at 100% RH, water was placed at the bottom of the glass vessel.[1] After a sheet of dyed cellophane was set in the glass cell, the glass vessel used for the exposure was maintained at 50°C for more than 24 h before exposure.

On exposure in deaerated water, a glass plate was tightly fixed on the rear side of a sheet of the dyed sample to prevent the penetration of trace oxygen.[2]

When dyed cellophane was exposed in the dry state, the exposed sample was thoroughly washed in boiling water for *c.* 20 min after soaking in water overnight, and was then dried before measuring the absorption spectrum. No desorption of the unfaded dye on the cellulose occurred, as shown by the unchanged absorbance at λ_{max} before and after washing. By subtracting the corresponding spectrum of the original dye from the spectrum of the dyed film exposed under given conditions, the absorption spectrum of the photodecomposition products was obtained, by the same method previously used.[3,4]

3 RESULTS AND DISCUSSION

3.1 Fading of C.I. Reactive Red 22 on cellulose

3.1.1 Exposure in deaerated water

The fading behavior of Red 22 on cellulose on exposure under various conditions, estimated by the decrease in the absorption at λ_{max}, is shown in Fig. 1(a). Red 22 underwent considerable fading on exposure in deaerated water even in the absence of substrate, although the rate of fading was smaller than that on exposure in aerated water. The absorption spectra of

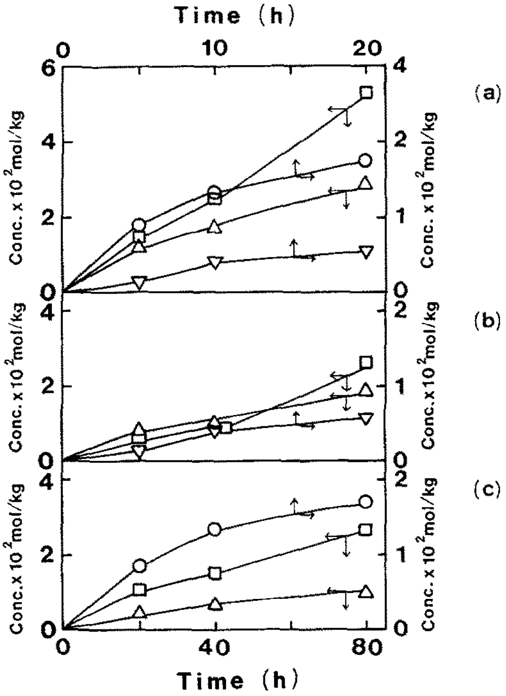


Fig. 1. (a) Decomposition, (b) formation of reduction product and (c) formation of oxidation product for C.I. Reactive Red 22 on exposure on dry cellulose (original conc. = 2·18 × 10^{-2} mol/kg) (△), on cellulose in air of 100% RH (original conc. = 2·14 × 10^{-2} mol/kg) (□), on cellulose on exposure in aerated water (original conc. = 2·37 × 10^{-2} mol/kg) (○) and in deaerated water in a nitrogen atmosphere (original conc. = 2·31 × 10^{-2} mol/kg) (▽).

the photodecomposition product on cellulose after the exposure, as shown in Fig. 2 (Spectra 1–3), were coincident with those of the reduction product,[4] implying that Red 22 on cellulose was photoreduced on exposure in deaerated water.

The photoreduction of dyes exposed in a deaerated aqueous or alcoholic solution has been observed for some thiazine and xanthene dyes, i.e. fluorescein,[7] eosin,[8,9] methylene blue,[10] thiopyronine,[11] acridine orange[12] and thionine.[13–16] As a primary process for the oxidative and reductive photobleaching of xanthene and thiazine dyes in aqueous and ethanol solutions, Koizumi and co-workers[17,18] reported the interaction of triplet dye and oxidizing or reducing agent (the D–O and D–R mechanism) at lower concentrations of dyes, and a photoreaction starting from the interaction between triplet and the ground state of dye (the D–D mechanism) at higher concentrations of dyes. In the D–D mechanism,[18] partly the dye in the ground state is generated and partly semi-oxidized, and semi-reduced dyes are produced, the latter being confirmed by the appearance of new

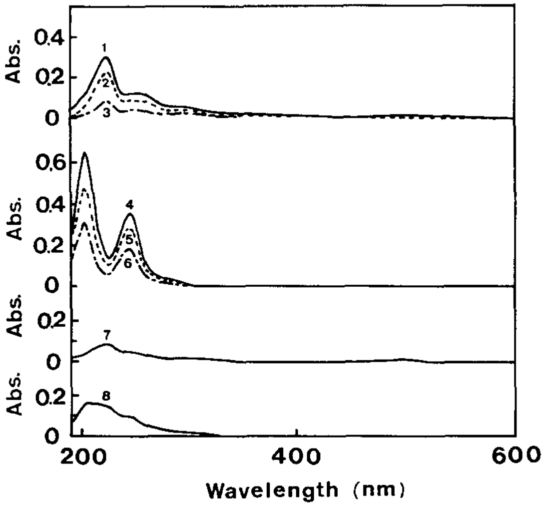


Fig. 2. Absorption spectra of the photodecomposition products for Red 22 on cellulose after exposure. 1–3, Red 22 (original dye conc. = $2{\cdot}31 \times 10^{-2}$ mol/kg) in deaerated water in a nitrogen atmosphere for 20, 10 and 5 h; 4–6, Red 22 (original dye conc. = $2{\cdot}37 \times 10^{-2}$ mol/kg) after exposure in aerated water for 20, 10 and 5 h; 7, Red 22 in dry air (original dye conc. = $2{\cdot}18 \times 10^{-2}$ mol/kg) after exposure for 80 h; 8, Red 22 (original dye conc. = $2{\cdot}14 \times 10^{-2}$ mol/kg) at 100% RH after exposure for 80 h.

absorption for the corresponding species. (In the present study, simultaneous oxidative and reductive fading was observed in many cases. However, the molar ratios of the oxidative and reductive products formed varied with time of exposure and were not equal to unity in most cases. No D–D mechanism, therefore, seems to hold in all cases and there is no discussion of this mechanism in this study.)

In the present case, only the formation of the photoreduction product for Red 22 was observed as a result of equimolar decomposition of the original dye (Fig. 1). In such a photoreaction system, there must be a substrate which reduces the dyes on cellulose. We could not assign any source of such a substrate in this present study, although Rusznák and co-workers[19,20] have reported the generation of polymer radical in the photofading of dyes, i.e. the polymer can act as reducing agent.

3.1.2 Exposure under aerobic conditions

As has been reported in studies on the photobleaching of thiazine and xanthene dyes,[17,18] and in our previous papers,[2–4] oxygen strongly suppresses the photoreduction. In this present study, oxygen had a complex effect on the fading of Red 22.

The absorption spectra of the photodecomposition products for Red 22 on cellulose after exposure in aerated water had double peaks in the UV region[4]

(Fig. 2, Spectra 4–6). On exposure in aerated water, oxygen not only completely inhibited the photoreduction but also caused oxidative fading. The amounts of decomposition estimated by the absorbance at λ_{max} coincided with those of the formation of oxidation product—Fig. 1(a) and (c). It is concluded that Red 22 on cellulose undergoes only oxidative fading on exposure in aerated water.

On exposure of this dye on dry cellulose, on the other hand, the absorption spectra of the photodecomposition product showed that reductive fading occurred (Fig. 2, Spectrum 7). However, the amounts of photoreduction products formed were smaller than those of a photodecomposition—Fig. 1(a) and (b). Since the photo-oxidation products for some VS dyes on cellulose were further decomposed on subsequent exposure,[3,4] the difference between the above amounts may correspond to the degree of oxidative fading, i.e. simultaneous oxidative and reductive fading occurs.

This behavior was also observed in the fading on cellulose at 100% RH. The absorption spectra of the photodecomposition products on cellulose after exposure at 100% RH showed the coexistence of oxidative and reductive fading (Fig. 2, Spectrum 8). The amounts of both the products were calculated by the same method as reported previously.[4] Since Red 22 has a high tendency to be reduced as well as oxidized, this dye may show both types of fading, unless oxygen completely inhibits the reductive fading.

Whether oxidative or reductive fading occurs under various conditions is summarized in Table 1. The rates of fading were in the following order:

$$\text{in aerated water} > \text{in deaerated water} > \text{at 100\% RH} > \text{in dry air} \quad (1)$$

Humidity had only an acceleration effect on the rate of fading and little effect on the fading behavior. As shown in Table 1, Red 22 on cellulose exposed in dry air and at 100% RH showed intermediate fading behavior between that in deaerated and aerated water, although the rates of fading on dry cellulose were lower than those under wet conditions.

3.2 Fading of Violet

The absorption spectra of Violet on cellulose after exposure in deaerated water were similar to those after exposure in anaerobic aqueous DL-mandelate solution (Fig. 1 in Ref. 3). The spectra of the photodecomposition products for Violet on cellulose on exposure in deaerated water, in dry air and at 100% RH (Fig. 3, Spectra 1–4) showed the formation of reduction products, the spectra of which have been reported previously.[3] The amounts of the photoreduction products for Violet on cellulose after exposure in deaerated water coincided with those of the corresponding fading within experimental errors (Fig. 4(a) and (b)).

TABLE 1
Fading Behavior of VS Dyes under Various Conditions

Exposure of VS dyes on cellulose	*Red 22*	*Violet*	*Black 5*
In deaerated water	Reduction	Reduction	Reduction and intermediates[b]
In dry air	Reduction (+oxidation)[a]	Reduction (+oxidation)[a]	Reduction and intermediates[b] (+oxidation)[c]
In air of RH 100%	Reduction and oxidation	Reduction (+oxidation)[a]	Reduction and intermediates[b] (+oxidation)[c]
In aerated water	Oxidation	Oxidation	Oxidation, reduction and intermediates[b]

[a] From the differences between the amounts of photodecomposition and of reduction products formed, the coexistence of oxidative fading was presumed.
[b] The formation of monoazo intermediates.[4]
[c] See text.

No spectrum for the decomposition products was apparent after exposure in aerated water for less than 40 h, as reported in a previous paper.[3] The amounts of the photodecomposition products after exposure in aerated water may correspond to those of the photo-oxidation products, i.e. only oxidative fading occurs.

On exposure of Violet on cellulose in dry air and at 100% RH, on the other hand, the amounts of reduction products were smaller than the amounts of fading—Fig. 4(a) and (b). Since the oxidation products for Violet on cellulose were further decomposed during further exposure,[3] the

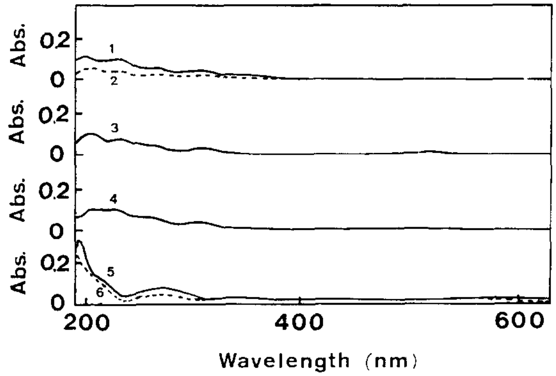


Fig. 3. Absorption spectra of the photodecomposition products for Violet and Black 5 on cellulose after exposure. 1–2, Violet (original dye conc. = $1{\cdot}38 \times 10^{-2}$ mol/kg) in deaerated water for 40 and 20 h; 3, Violet (original dye conc. = $1{\cdot}47 \times 10^{-2}$ mol/kg) in dry air for 80 h; 4, Violet (original dye conc. = $1{\cdot}46 \times 10^{-2}$ mol/kg) at 100% RH for 80 h; 5–6, Black 5 (original dye conc. = $5{\cdot}77 \times 10^{-3}$ mol/kg) in aerated water for 40 and 10 h.

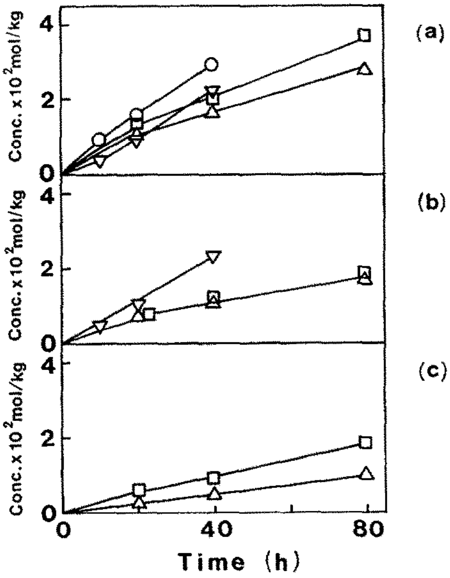


Fig. 4. (a) Decomposition, (b) formation of reduction product and (c) formation of oxidation product for Violet on exposure on dry cellulose (original conc. = $1{\cdot}47 \times 10^{-2}$ mol/kg) (△), on cellulose in air of 100% RH (original conc. = $1{\cdot}46 \times 10^{-2}$ mol/kg) (□), on cellulose on exposure in aerated water (original conc. = $1{\cdot}40 \times 10^{-2}$ mol/kg) (○) and in deaerated water in a nitrogen atmosphere (original conc. = $1{\cdot}38 \times 10^{-2}$ mol/kg) (▽).

differences between the amounts of fading and of the reduction products may correspond to the amount of oxidative fading which occurs—Fig. 4(c). Thus Violet on cellulose showed the same fading behavior as that of Red 22, except for the humidity effect (see below).

Fading behavior for Violet under various conditions is summarized in Table 1. The order of the rates of fading for Violet on cellulose on exposure under various conditions, as shown in Fig. 3, was very similar to that for Red 22, i.e.

$$\text{in aerated water} > \text{in deaerated water} = \text{at 100\% RH} > \text{in dry air} \quad (2)$$

Humidity had an acceleration effect on the rates of oxidative fading, and no effect on the reductive fading for Violet on dry cellulose (Fig. 4).

3.3 Fading of Black 5

3.3.1 Exposure under wet conditions

In a previous paper,[4] the absorption spectra of the photodecomposition products for Black 5 on cellulose in the presence of substrate under anaerobic and aerobic conditions were analysed. Black 5 contains two azo groups showing different photoreaction behavior. Since not all of the two reactive groups are bound with cellulose and since the photodecomposition process is complex, a quantitative treatment of the photodecomposition products is inevitably restricted. Thus precise estimation of the oxidation products was impossible.

According to the estimation method used for the photodecomposition products for Black 5,[4] the amounts of each species formed on exposure under various conditions can be calculated, although errors in the estimation may be large due to the small degree of fading. The results are shown in Fig. 5 and summarized in Table 1.

Taking into consideration the absorption spectra of the decomposition products for Black 5 (Fig. 4 in Ref. 4) reported previously, monoazo intermediates and the reduction product were formed on exposure in all cases, and simultaneous oxidative and reductive fading was presumed to occur on exposure in aerated water (Fig. 3, Spectra 5 and 6).

On exposure of Black 5 on cellulose in deaerated water, only reductive fading occurred with formation of a small amount of monoazo intermediates—Fig. 5(b).

In the initial period of exposure in aerated water, little formation of a reduction product was recognized irrespective of the fading of Black 5 (Fig. 5). Only oxidative fading occurred in the initial period. After exposure for 20 h, the formation of reduction products was observed, whilst the rate of the simultaneously occurring oxidative fading decreased with time of exposure, the differences between the amount of fading and of the formation of the

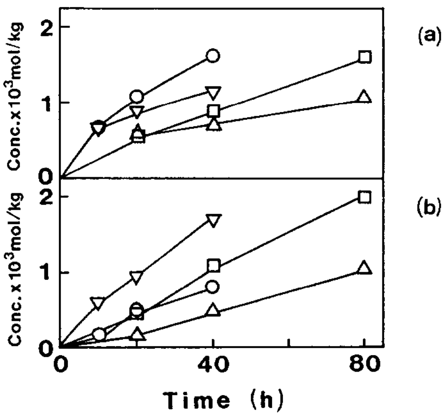


Fig. 5. (a) Decomposition and (b) formation of reduction product for C.I. Reactive Black 5 on exposure on dry cellulose (original conc. = 5·70 × 10^{-3} mol/kg) (△), on cellulose in air of 100% RH (original conc. = 5·64 × 10^{-3} mol/kg) (□), on cellulose on exposure in aerated water (original conc. = 5·77 × 10^{-3} mol/kg) (○) and in deaerated water in a nitrogen atmosphere (original conc. = 5·92 × 10^{-3} mol/kg) (▽).

reduction product decreasing with time. As a result, the rate of fading on exposure in aerated water decreased gradually.

3.3.2 Exposure under dry conditions

The absorption spectra of the decomposition products after exposure in dry air were the same as those obtained on exposure under anaerobic conditions.[4] The rates of fading on dry cellulose were smaller than those on exposure under wet conditions. In cases of exposure under dry conditions, the initial rates of fading were larger than those of the subsequent fading, whilst the initial rates of fading for the formation of reduction products were smaller than those of the subsequent fading. The ratio of the amounts of reduction products formed to the overall amount of fading decreased gradually. Thus reductive fading was initially suppressed, or preferential oxidative fading occurred in the initial stages followed by preferential reductive fading in the later stages. Although the formation of oxidation products was not shown by the absorption spectrum, the rates of fading and of the formation of the reduction products do indicate such a fading behavior.

On exposure at 100% RH, similar results to those in dry air were obtained (Fig. 5), but humidity accelerated the photoreduction in contrast to the case of Violet (cf. Fig. 4).

The order of the rates of fading for Black 5 on cellulose under various conditions was the same as that for Violet, although the fading behavior in deaerated water and the effect of humidity on the fading were a little different from the cases of Violet.

3.4 Comparison of fading behavior

As noted above, oxygen strongly suppressed the photoreduction, especially in the initial period of exposure, and the degree of suppression varied with the dyes. Thus oxygen in aerated water inhibited the photoreduction of Red 22 and Violet on cellulose and suppressed that of Black 5, i.e. photo-oxidation occurred on exposure in aerated water either totally or predominantly. The amounts of the formation of the oxidation products for Red 22 and Violet corresponded to the amounts of fading in aerated water. However, as a result of the lower concentration of oxygen in the cellulose in dry air and at 100% RH, simultaneous oxidative and reductive fading was observed, oxygen partially inhibiting the photoreduction.

Whether reductive fading occurs or not may depend upon the interaction between dye in the triplet state and a part of the cellulose molecule, and also upon the ease with which the dye is reduced and the reduction potential of the azo group in the triplet state. The oxidation potential of a dye whose azo group is semi-reduced, as well as the concentration of oxygen, may determine the degree of inhibition of reductive fading by oxygen. It may be concluded that the abstraction of hydrogen from the substrate is dependent on the chemical structure of the dyes.

Dyes undergoing reductive fading at a faster rate in deaerated water in the absence of substrate seem to have a higher tendency to be photoreduced on exposure in anaerobic DL-mandelate solution, with a few exceptions.[2–4] Many monochlorotriazinyl reactive dyes may have a high tendency to be photoreduced.[21] Thus the properties of the dye itself as well as the atmospheric conditions of the exposure, particularly with respect to the concentration of oxygen, may determine whether dyes on cellulose undergo reductive fading on exposure under given conditions.[18]

4 SUMMARY

C.I. Reactive Red 22, Black 5 and a monoazo violet dye on cellulose underwent reductive fading on exposure in deaerated water, although many other VS dyes showed no fading. Three dyes on cellulose in dry air and at 100% RH showed simultaneous oxidative and reductive fading. On exposure in aerated water, Red 22 and Violet underwent only oxidative fading as usual, whilst Black 5 showed simultaneous oxidative and reductive fading. Thus the atmospheric conditions of exposure, and especially the concentration of oxygen, determine whether oxidative or reductive fading occurs, although the possibility of reductive fading may also depend upon the properties of dyes.

VS dyes on dry cellulose, irrespective of humidity, showed intermediate fading behavior between those in deaerated and aerated water. In view of the conclusions of Rusznák *et al.*[19,20] on the formation of polymer radicals on exposure of dyed cellulose, some types of dye, e.g. those whose coupling component is a derivative of H-acid, may have the property to oxidize cellulose.

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