

Adhesive Properties of Cured Epoxide Resin Containing the Intermolecular Compound of 2,4-Diamino-6-Vinyl-*s*-Triazine and Isocyanuric Acid

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Synopsis

The intermolecular compound of 2,4-diamino-6-vinyl-*s*-triazine and isocyanuric acid was synthesized, and the glass transition temperature and the adhesive properties of the cured epoxide resin containing the above compound were studied. Epoxide reacted with amino groups of 2,4-diamino-6-vinyl-*s*-triazine and isocyanuric acid at the curing conditions of 150 to 180°C for 60 min and formed the cured compounds. The infrared spectra showed that epoxide reacted with isocyanuric acid in the presence of imidazole compounds and converted to 2-oxazolidinone compound on the curing process. The glass transition temperatures of the cured compounds having isocyanurate and 2-oxazolidinone rings in their structures were higher than that of the epoxide resin cured with imidazole and rise as the curing temperature rises, but fall as 2-oxazolidinone ring content increases in their cured compounds. The tensile shear and peel strengths of the steel and steel bonded with the cured compounds and the cured epoxide resin were measured at 25 and 150°C. The adhesive strengths were improved due to isocyanurate and 2-oxazolidinone rings formed in their cured compounds.

INTRODUCTION

The mechanical properties of polymers are modified by interpenetrating polymer networks (IPN). The synthesis, morphology, and physical properties of IPN have been described by many authors.¹⁻⁵ The simultaneously cured compounds of epoxide resin and the intermolecular compound (VT · ICA) of 2,4-diamino-6-vinyl-*s*-triazine (VT) and isocyanuric acid (ICA) indicate the formation of IPN.⁶⁻⁸ Epoxide resin reacted with ICA and amino groups of VT at the curing condition of an elevated temperature and formed cured compounds. The thermal polymerization of VT is produced simultaneously. Therefore, VT may possess two functions as a monomer for IPN and a curing agent for epoxide resin, simultaneously.

Moreover, the simultaneously cured compounds of epoxide resin and VT ICA coated as solder resist inks on the printed circuit boards were substantially more effective in suppressing migration of silver of the circuits.⁹

In a previous paper,⁶ we reported on the chemical reactivity of epoxide resin and VT · ICA. It was estimated from the results of infrared spectra that epoxide reacted with isocyanuric acid to form an isocyanurate compound and then converted to a 2-oxazolidinone compound on the curing process. The above reaction was accelerated by the addition of imidazole compounds.

Kinjo et al.¹⁰ synthesized new thermosetting resins having isocyanurate and 2-oxazolidinone rings in their molecular structures by the reaction of poly-

functional isocyanate and epoxides in the presence of basic catalysts and studied the viscoelastic properties of the above resins. They reported that the viscoelastic behavior of the cured resins could be varied considerably by selecting an appropriate reactant species and changing the equivalent ratio of isocyanate and epoxide groups.

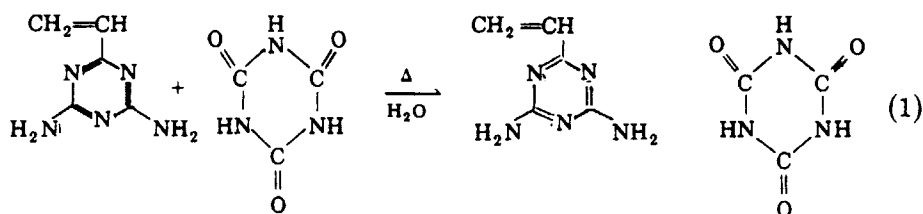
The cured epoxide resins having isocyanurate and 2-oxazolidinone rings in their molecular structures were obtained from the reaction of epoxide resin and isocyanuric acid in the presence of basic catalysts by Clarke¹¹ and us,¹² independently. The physical properties of the cured resin having isocyanurate and 2-oxazolidinone rings were superior to those of epoxide resins polymerized with imidazole compounds under the same curing conditions.

In this paper, we describe the adhesive properties of the cured epoxide resins containing VT · ICA as a possible compound which improves the adhesive strengths of epoxide resin by forming IPN and isocyanurate and 2-oxazolidinone rings in their cured networks.

EXPERIMENTAL

Material

Synthesis of VT · ICA. VT · ICA was synthesized from VT and ICA by the method which has been reported in a previous paper.⁶ An infrared spectrum of VT · ICA showed a different result from that of a blend of VT and ICA. The structural formula of VT · ICA is as follows:



Diglycidyl ether of bisphenol A was used as epoxide resin. The epoxide resin used here is manufactured by Yuka Shell Epoxy Co., Ltd., under the trade name of Epikote #828. The equivalent weight of Epikote #828 was 187, and the viscosity was 12,500 cP at 25°C.

As the curing agent for epoxide resin, 2,4-diamino-6-[2(2-methyl-1-imidazolyl)ethyl]-s-triazine (2MA). 2MA is a popular curing agent for epoxide resins. The compounds of epoxide resin and VT · ICA were prepared by mixing 100 g of Epikote #828, 20 g of VT · ICA, and 2 g of 2MA before curing. Because of 100 g of Epikote #828 and 20 g of VT is the stoichiometry,⁷ 20 g of VT · ICA is less than the stoichiometry. VT · ICA is a stable compound in the blends with liquefied epoxide resins. Raising the temperature, VT · ICA reacts quickly with epoxide. The reaction of VT · ICA and epoxide

proceeds more rapidly than that of VT and epoxide.⁶ The curing conditions of 150, 160, 170, or 180°C for 60 min were employed sequentially.

Apparatus and Procedure

Adhesive strengths were measured with Autograph DDS-2000 (made by Shimadzu Co., Ltd., Kyoto). Two types of testing methods, namely, tensile shear and peel strengths, were employed for the cured epoxide resins with and without VT · ICA, respectively. The tensile shear strength was measured by the single-lap tensile shear method. The peel strength was measured by the pulling-off adhesive strength of T style. Crosshead speeds were employed 5 mm/min for the tensile shear and 200 mm/min for the peel strengths and temperatures were 25 and 150°C. The adherend used was the steel plate based on JIS G 8141 SPCC. The sizes of specimens were as follows: 100 mm (length) × 25 mm (width) × 1.6 mm (thickness) for the tensile shear strength; 200 mm (length) × 25 mm (width) × 0.8 mm (thickness) for the peel strength. The adherend specimens were polished with the emery paper of grade 240 mesh, and then washed with trichloroethylene successively before bondings with the compounds.

The bonding areas were as follows: 10 mm (length) × 25 mm (width) × 0.15 mm (thickness) for the tensile shear strength; 200 mm (length) × 25 mm (width) × 0.2 mm (thickness) for the peel strength.

From the five measurements, the middle three values were averaged to obtain the mean values of adhesive strengths. In any case, the difference of maximum and minimum values was less than 10% of the mean values.

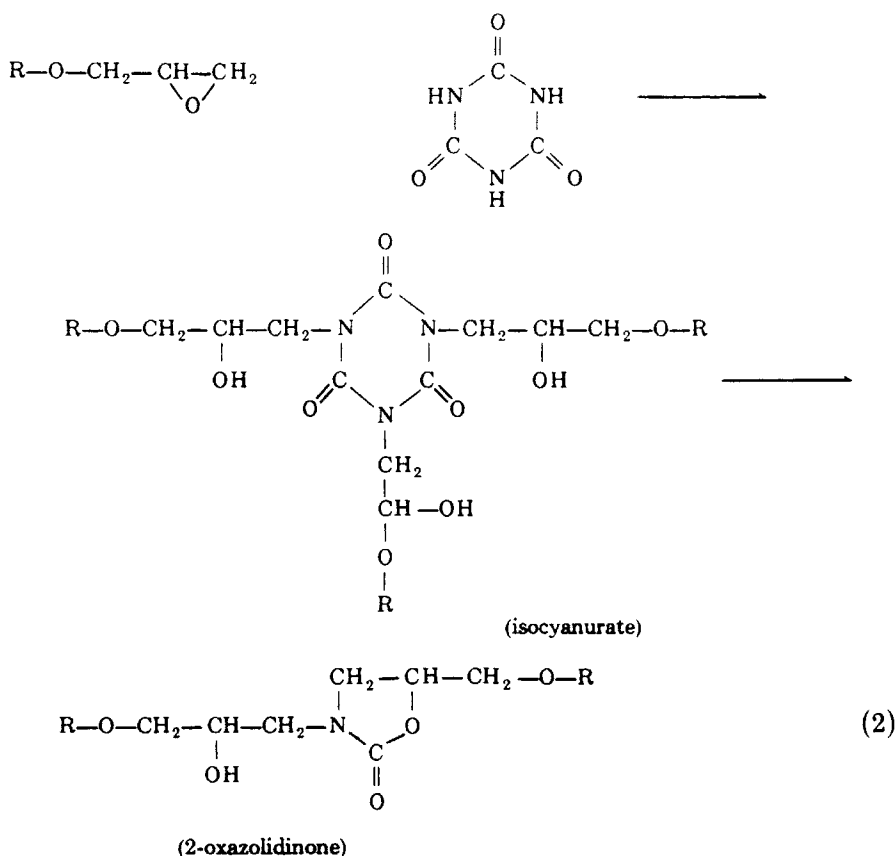
Logarithmic decrement of the cured compounds was measured by a torsional braid analysis (TBA) using a fully automated torsional pendulum type viscoelastic tester RD-1100AD (made by Rhesca Co., Ltd., Tokyo). Specimens were made by permeating the compound into glass brads having a diameter of 1 mm and then curing at the condition of 150, 160, 170, or 180°C for 60 min. The temperature dependence of logarithmic decrement was measured at the heating rate of 3°C/min in a vacuum oven in the temperature range from 25 to 300°C. The infrared spectra of the cured compounds were obtained with KBr pellets by using a Hitachi 260-10 infrared spectrometer.

RESULTS AND DISCUSSION

Glass Transition Temperature

Infrared spectra of the cured compounds obtained at various curing conditions are shown in Figure 1. Absorptions due to the stretching vibrations of carbonyl groups of isocyanurate and 2-oxazolidinone rings could be observed at 1690 and 1740 cm^{-1} , respectively. On the other hand, absorptions due to the stretching vibration of carbonyl groups of ICA are observed at 1725, 1750, and 1775 cm^{-1} . But the above absorptions could not be observed in the cured compounds. In a previous paper,¹³ we reported that epoxide reacts with ICA in the presence of imidazole compounds to form an isocyanurate compound and then converted to an 2-oxazolidinone compound on the curing process. This reaction is also produced by the reaction between ICA of VT · ICA and epoxide resin in the presence of imidazole compounds.⁶ The reaction can be

written as follows:



Moreover, it was reported that the ratio isocyanurate and 2-oxazolidinone rings in their cured structures depends on the curing conditions for the compounds rather than the equivalent ratio of ICA and epoxide resin. In Figure 1, absorptions due to the stretching vibration of carbonyl group of an 2-oxazolidinone ring increases as the curing temperature rises. Conversely, absorptions due to the stretching vibration of carbonyl group of an isocyanurate ring decreases and could not be readily observed in Figure 1(D). The absorption at 910 cm^{-1} due to epoxide is clearly observed in Figure 1(A), but could not be observed in Figures 1(C) and 1(D). Epoxide reacts with ICA and amino groups of VT, and further is polymerized by 2MA in the curing process. Moreover, the absorption at 1640 cm^{-1} due to the bending vibration of amino groups is slightly observed in Figure 2(A), but could not be observed in Figure 1(B).

From these results, it is concluded that most of the epoxides proved to react by the heating at 170°C for 60 min. It is considered that some of the epoxide reacts with ICA in the first period of the curing process and unreacted epoxides react with amino groups of VT in the next period of the curing process. The conversion from an isocyanurate ring to an 2-oxazolidinone ring takes place in the early period of the curing process. VT is polymerized in the

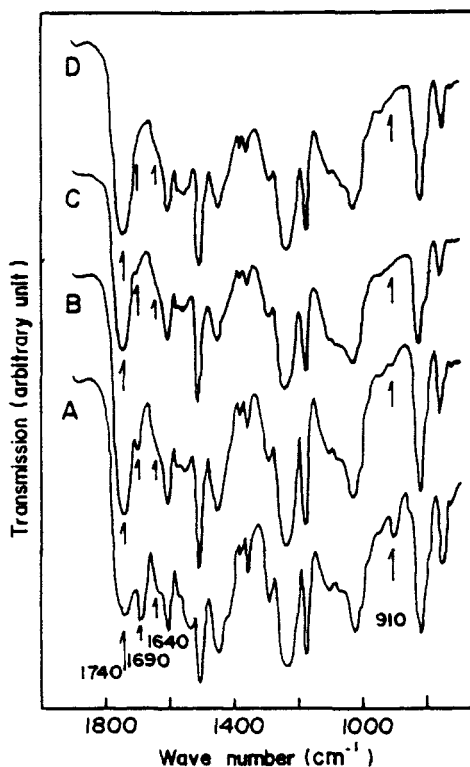


Fig. 1. Infrared spectra of the cured compounds at various curing conditions. Curing conditions: (A) 150°C/60 min, (B) 160°C/60 min; (C) 170°C/60 min; (D) 180°C/60 min.

above curing process simultaneously. It is assumed that polymer networks of VT and those of the cured epoxide resin containing isocyanurate and 2-oxazolidinone rings have formed IPN in their molecular structures.

Figure 2 shows the temperature dependence of logarithmic decrement measured with TBA for the compounds cured at various curing conditions and the epoxide resin polymerized with 2MA. It is supposed that the main peak observed in the temperature range from 110 to 144°C correspond to the glass transition temperatures of the cured compounds and the cured epoxide resin and the secondary peak observed as shoulder at 55–76°C correspond to the very beginning products of the reaction of epoxide with ICA. The glass transition temperatures of the cured compounds were superior to that of the cured epoxide resin polymerized with 2MA. In the cured compounds, the glass transition temperatures rise as the curing temperature rises, taking a maximum value at the curing condition of 170°C for 60 min, and then slightly fall at the curing condition of 180°C for 60 min.

On the other hand, the secondary peak shifts toward the higher temperature side as the curing temperature rises. It is estimated that the changes of the glass transition temperature and secondary peak due to the curing condition correspond to the chemical structures of their cured compounds.

An isocyanurate ring has three bonding "hands," while a 2-oxazolidinone ring has two bonding "hands." Generally speaking, the crosslinking density of the cured compounds is reduced by the increasing of a 2-oxazolidinone ring

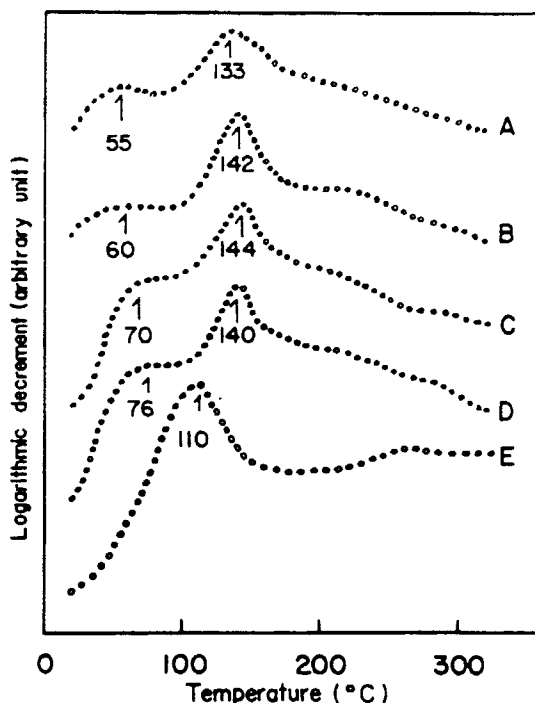


Fig. 2. Logarithmic decrement of the cured compounds and the cured epoxide resin at various curing conditions. Curing conditions for the cured compounds: (A) 150°C/60 min; (B) 160°C/60 min; (C) 170°C/60 min; (D) 180°C/60 min. Curing conditions for the cured epoxide resin: (E) 100°C/4 h + 180°C/2 h - 250°C/1 h.

in their molecular structures. However, the glass transition temperatures of the cured compounds rose in the case that an 2-oxazolidinone ring content slightly increased in their structures. The reducing of the glass transition temperatures of the compound cured at 180°C for 60 min is due to increased amount of an 2-oxazolidinone ring content.

Relationships between Curing Temperature and Adhesive Strengths

The tensile shear and peel strengths of the steel/steel bonded with the cured compounds and epoxide resin polymerized with 2MA were measured at 25 and 150°C. Plots of tensile shear strength and peel strength against curing temperatures are shown in Figures 3 and 4, respectively. As shown in Figure 3, tensile shear strength measured at 25°C takes a minimum value at the curing condition of 160°C for 60 min and then slowly increases as the curing temperature rises. However, tensile shear strength measured at 150°C take a maximum value at the curing condition of 170°C for 60 min. On the other hand, tensile shear strength of epoxide resin polymerized with 2MA simply increases as the curing temperature rises. But the measured values were lower than those of cured compounds. Tensile shear strength often depends on the cohesive energy density and the crosslinking density of the cured compounds. Generally speaking, it is considered that the cohesive energy density of the cured compounds decreases at temperatures below the glass transition temper-

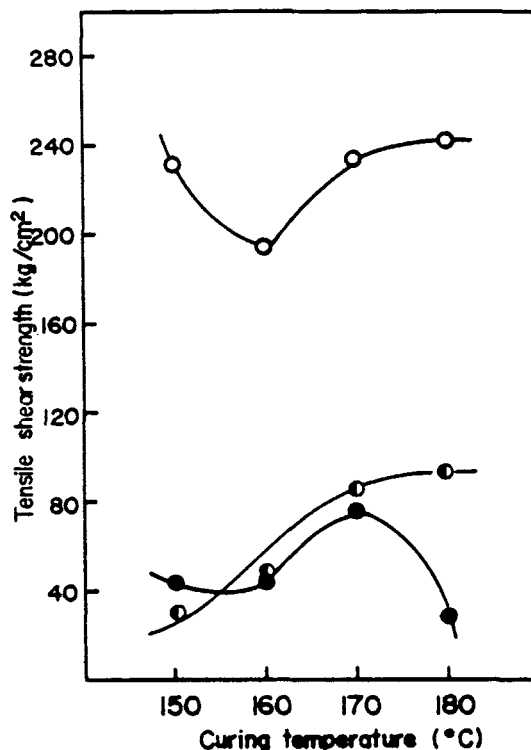


Fig. 3. Relationships between the curing temperature and the tensile shear strength for the cured compounds and the cured epoxide resin. Measuring temperature for the cured compounds: (○) 25°C; (●) 150°C. Measuring temperature for the cured epoxide resin: (◐) 25°C.

ature as the 2-oxazolidinone ring content in their cured structure increases. Therefore, tensile shear strength measured at 25°C decrease due to the reducing of the cohesive energy density as the curing temperature rises. But, at temperatures above 160°C, tensile shear strength increases due to the increasing of the crosslinking density of the cured compounds as the curing temperature rises. On the other hand, the values of tensile shear strength measured at 150°C showed a similar tendency to the values of the glass transition temperatures of the cured compounds. Due to the fact that the measuring temperatures of tensile shear strength are higher than the glass transition temperatures of the cured compounds, it is considered that tensile shear strength measured at 150°C takes the maximum value in the curing condition in which the glass transition temperatures of the cured compounds have the maximum value.

Peel strength measured at 25 and 150°C takes the maximum value at the curing conditions of 160 and 170°C for 60 min, respectively. Values of peel strength measured at 25°C showed a similar tendency to the glass transition temperature and tensile shear strength measured at 150°C. Due to the values of peel strength of epoxide resin polymerized with 2MA is almost zero, their values could not be written on the Figure 4.

In general, the electrical and thermal properties of epoxide resin polymerized with imidazole compounds are superior to those of the epoxide resin

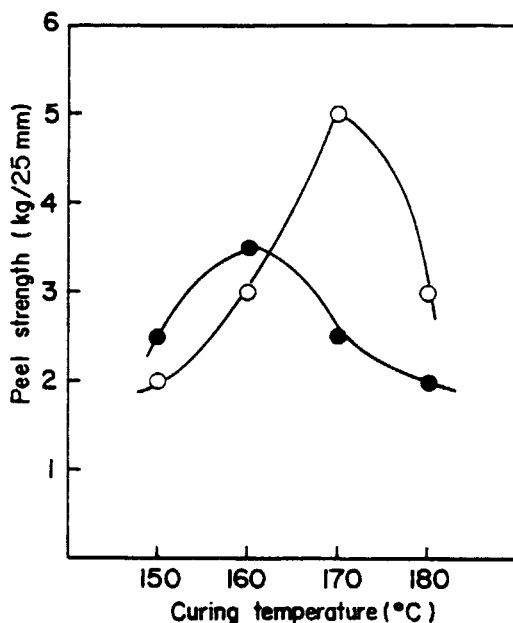


Fig. 4. Relationships between the curing temperature and the peel strength for the cured compounds. Measuring temperature: (○) 25°C; (●) 150°C.

cured with curing agents such as amines, polyamide resins, or acid anhydrides. But the flexibility of the cured epoxide resin polymerized with imidazole compounds is poor. It is well known that the cured epoxide resins have generally high tensile shear strength, but have often poor peel strength. Peel strength depend on the flexibility of the cured compounds. In order to increase the flexibility of the cured epoxide resins, liquid rubber as a carboxy-terminated copolymer of butadiene-acrylonitrile has been added to epoxide resins. But this method, because of the compounds have high viscosity, cannot be practically applied as adhesives and solder resist inks for printed circuit boards. Moreover, the glass transition temperature is reduced by the addition of liquid rubber to epoxide resin.¹⁰

One of the most important characteristics of the cured epoxide resin containing VT · ICA is that its mechanical properties can be varied from hard to flexible by forming a 2-oxazolidinone ring in its molecular structures without reducing the glass transition temperature. The amounts of a 2-oxazolidinone ring in its cured structure increases as the curing temperature rises. As a result of increasing the 2-oxazolidinone ring content, the peel strength of the cured compounds increased.

The preparation of the cured epoxide resins containing a 2-oxazolidinone ring was also obtained by reacting a polyisocyanate with epoxide in the presence of a selected catalyst. Although the products prepared therein exhibit good shear strength, they exhibit poor peel strength. Therefore, the above uncured compound is unstable in the storage life.

On the other hand, the compounds of epoxide resin and VT · ICA are as stable as mentioned before and simultaneously cured compounds exhibit good shear and peel strengths. The increasing of peel strength without reducing the

glass transition temperature, which is caused by the formation of a 2-oxazolidinone ring in their cured structures, is very significant.

CONCLUSIONS

The epoxide resin containing the intermolecular compound of 2,4-diamino-6-vinyl-s-triazine and isocyanuric acid can be thermally cured to form the cured compound which has isocyanurate and 2-oxazolidinone rings in their molecular structures. Adhesive strengths of the steel/steel bonded with the above cure compound were superior to those of epoxide resin polymerized with imidazole compound. Especially, the peel strength of the cured compound exhibited high values.

References

1. K. F. Muller and S. J. Heiber, *J. Appl. Polym. Sci.*, **27**, 4043 (1982).
2. K. C. Frisch, D. Klempner, and H. L. Frisch, *Polym. Eng.*, **22**, 1143 (1982).
3. J. M. Widmaier and L. H. Sperling, *J. Appl. Polym. Sci.*, **27**, 3513 (1982).
4. D. J. Hourston and Y. Zia, *J. Appl. Polym. Sci.*, **28**, 2139 (1983).
5. K. C. Frisch, D. Klempner, and H. X. Xiao, *Polym. Eng.*, **25**, 758 (1985).
6. K. Kamagata, S. Yoshida, and M. Kinoshita, *Kobunshi Ronbunshu*, **42**, 899 (1985).
7. K. Kamagata, M. Kinoshita, and S. Yoshida, *Polym. J.*, **18**, 193 (1986).
8. K. Kamagata, S. Yoshida, and T. Mizui, *Kobunshi Ronbunshu*, **42**, 273 (1985).
9. K. Kamagata, S. Kawata, and T. Yamada, *Denshi Tsushin Gakkai Ronbunshi*, **J69-C**, 126 (1986).
10. N. Kinjo, S. Numata, T. Koyama, and T. Narahara, *J. Appl. Polym. Sci.*, **28**, 1729 (1983).
11. J. A. Clarke, *Rubber-Modified Thermoset Resins*, C. K. Riew and J. K. Gillham, Eds., *Advances in Chemistry Series No. 208*, Am. Chem. Soc., Washington, DC, 1984, p. 51.
12. K. Kamagata and T. Mizui, *Nippon Kagaku Kaishi*, **1985**, 2081.
13. K. Kamagata, *Nippon Kagaku Kaishi*, **1985**, 2073.

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