

Dicyandiamide Analysis and Solubility in Epoxy Resins

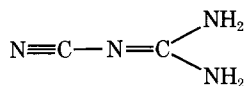
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Synopsis

A simple procedure is described for the rapid, quantitative analysis of dicyandiamide in epoxy resins and epoxy resin prepregs. High performance liquid chromatography is used to analyze for dicyandiamide and to investigate the solubility behavior of dicyandiamide and 3-(*p*-chlorophenyl)-1,1-dimethylurea (Monuron) in liquid epoxy resins. Solubility expressions and differential heats of solution are determined. The formation of soluble amine-epoxy reaction products and epoxy resin additives such as Monuron are found to enhance the solubility of dicyandiamide.

INTRODUCTION

The cyano substituted guanidine, dicyandiamide (dicy),

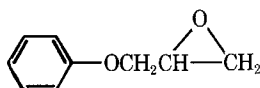


is widely used as a latent curing agent in heat-cured epoxy resins for laminates or prepreg fabrication, coatings, and adhesives. It is a white, crystalline solid (84.08 g/mole, 1.404 g/cm³, mp 208°C), soluble in water, alcohols, dimethylformamide, and dimethylsulfoxide but relatively insoluble in less polar solvents, including liquid epoxy resins.¹⁻³ Dicy is available in high purity, easy to store and handle, and relatively inexpensive. Nearly all areas of application rely upon the fact that dicy is not very reactive at temperatures below 100°C and cures epoxies rapidly at elevated temperatures (120–180°C). Dicy-epoxy resin formulations are relatively stable at room temperature and have long pot lives; and as a latent curing agent, dicy provides economical advantages in the manufacture of certain items where rapid curing, durability, and reliability are essential. Typically, 3–10 wt% dicy is used in epoxy resin formulations, and the dicy must be ground into a fine powder and dispersed or blended with the epoxy resins.

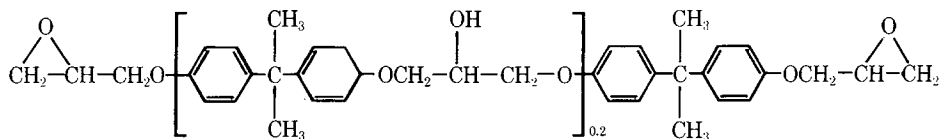
A major problem in the utilization of the curing agent is its poor solubility in epoxy resins and tendency to separate and form a white precipitate after cure has been affected. Large particle size and poor mixing adversely affect the mechanical properties of dicy-cured resins and sedimentation of dicy crystals affects the degree of crosslinking and ultimately surface hardness as demonstrated by Vickers microhardness measurements.⁴ Although the cure mechanism and effects of reaction conditions on mechanical properties of dicy-epoxy resins systems have been investigated in some detail,^{1,4-7} more information re-

lating to the solubility of dicy in epoxy resins and how the solubility of dicy changes with temperature and in the presence of other components is needed to understand more fully the curing behavior of dicy. Furthermore, a reliable, simple method is needed for the quality assurance of dicy not only in uncured resin formulations but also to ascertain whether unreacted dicy remains in cured resins.

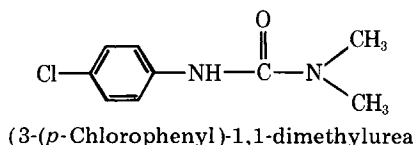
In this paper procedures using high performance liquid chromatography (HPLC) are described for the quantitative analysis of dicy in epoxy resins. A detailed procedure for analyzing the weight percentage of dicy in glass fiber-epoxy resin prepregs is given and a simple experiment is described to evaluate the solubility of dicy in liquid epoxy resins and to investigate the temperature dependence of dicy's solubility in phenyl glycidyl ether (PGE)



and in the diglycidyl ether of bisphenol A (DGEBA) resin Epon 828



The temperature dependence of the solubility of the resin accelerator Monuron (mp 172°C)



is also determined in PGE with and without dicy present to ascertain whether there are synergistic solubility effects. Differential heats of solution are evaluated.

EXPERIMENTAL

The dicy (Aldrich, 97%) was used as a finely divided powder. PGE (Miller-Stephanson Chemical Co., Lansbury, CT) was purified by recrystallization from methanol in an acetone-dry ice bath and Monuron (Pfaltz & Bauer, Stamford, CT) was purified by recrystallization from methanol. The Shell Chemical resin Epon 828 (Lot 11THJ19) was used as received.

A Waters Associates ALC/GPC-244 instrument, with 6000A solvent delivery system, 660 solvent programmer, 710A WISP auto injection system, and a Perkin Elmer LC75 variable ultraviolet (UV) absorbance detector was used for the liquid chromatographic analyses. A Spectra Physics SP4000 data system with SP4020 data interface and SP4050 printer/plotter was used for peak integration and data formatting. All analyses were run using a Waters Associates μ Bondapak C₁₈

(30 cm \times 3.9 mm ID) column. Freshly distilled solvents were used. Tetrahydrofuran (THF) was dried over molecular sieves and doubly distilled over calcium hydride. ASTM-type reagent grade water was prepared from distilled water using a Millipore Milli-Q2 water purification system. All solvents and solutions were filtered through 0.2- μ m Millipore membrane filters and, for the modified dicy analysis, prepreg solutions were filtered through Waters Associates Sep-PAK-A (μ Bondapak C₁₈) cartridges.

For the solubility study, saturated solutions were formed by mixing weighed amounts (0.5–6 g) of dicy and/or Monuron with epoxy resin (40–70 g) in a 100-ml, three-neck round-bottom flask suspended in a temperature-controlled oil bath. The components were stirred continuously using a glass vane-type impeller with an electric stirring motor and were mixed at least 18 h at 30°C before starting each experiment. The temperature was controlled within 0.1°C and monitored using a digital thermocouple indicator. Samples were obtained by transferring an aliquot (ca. 0.5 ml) of the mixture to a 2-ml syringe fitted with a Swinny filter holder maintained at the same temperature as the mixture; and 4–8 drops of sample were immediately filtered through a 0.2- or 5- μ m Millipore Teflon membrane filter into a preweighed 10-ml volumetric flask. Next, the flask was reweighed and the contents were diluted to volume and dissolved in THF in preparation for HPLC analysis. After each sampling, the temperature was elevated about 10°C and, with continued stirring, equilibrium was achieved within 15 min. Hence, samples were obtained within 4–6 h over the temperature range 30–150°C and the concentrations of epoxy resin-soluble components were monitored using HPLC. Membrane filtration removed insoluble dicy and/or Monuron from the epoxy resin mixture. Experiments were repeated several times starting with different component ratios and using different membrane filter porosities to optimize experiments and to ensure reproducibility.

PROCEDURES FOR DICY ANALYSIS

This procedure is designed for determining the weight percentage of dicy in a glass fiber-epoxy resin prepreg in which the formulation consists of dicy, Monuron, and three different types of epoxy resins. Solutions for HPLC analysis are prepared as follows: (1) A 8 \times 10-cm section (ca. 3 g) is cut from the prepreg, weighed, and placed in a 25-ml erlenmeyer flask. (2) THF is added to the flask and the contents are agitated for at least 30 min. (3) The solution is decanted into a 100-ml volumetric flask and more THF is added to extract the remaining resin from the fibers. This process is continued until the volumetric flask is filled to 100 ml. Dicy is fully soluble in the THF. (4) The glass fibers are dried overnight in a fume hood and weighed. (5) The fibers are placed in a muffle furnace (650–800°C) for 4–6 h and reweighed. (6) The contents of volumetric flask are mixed thoroughly and about 5 ml is filtered (0.2 μ m) into a clean, glass sample vial.

The solution concentration (ca. 10 μ g/ μ l) is calculated from the difference between the initial prepreg weight and final fiber weight. The difference between the dried, extracted fiber weight and final fiber weight equals sizing agent plus resin bonded to the glass fibers and is generally <0.06% of the prepreg weight.

The extracted prepreg solution contains dicy and other soluble prepreg components. Dicy is analyzed using the following conditions. Mobile phase: H₂O;

flow rate: 2 ml/min; injection volume: 20 μ l; column: μ Bondapak C₁₈; pump pressure: 1000 psi; detector: UV 230 nm; chart speed: 0.5 cm/min; and dicy retention time: 124 \pm 1 s. After dicy is eluted, the column should be purged (a step gradient may be programmed) with THF to dissolve and remove sample components insoluble in H₂O. Allowing time to reequilibrate the mobile phase, the total analysis time is about 30 min per sample.

To reduce analysis time, the procedure may be modified as follows: (1) 1 ml of the extracted prepreg solution is pipetted into a 10-ml volumetric flask and diluted with H₂O to the calibration mark; (2) after the solution is mixed, about 4 ml is filtered through a 0.2- μ m filter and a μ Bondapak C₁₈ SepPAK-A cartridge into a clean sample vial.

Adding H₂O causes the prepreg solution to turn turbid. Filtration through the membrane filter removes the turbidity, which is due primarily to precipitated high-molecular-weight epoxy oligomers; while the SepPAK-A cartridge removes the remaining resin components except for dicy and some Monuron. Reverse-phase HPLC chromatograms of the prepreg solution before and after passage through a SepPAK-A cartridge are shown in Figure 1. Dicy is unretained and produces only a small peak at the monitoring wavelength 280 nm. The SepPAK-A cartridge effectively removes epoxy components and permits samples to be injected consecutively without changing the mobile phase. By modifying the procedure the analysis time is less than 5 min per sample.

The weight percentage of dicy may be calculated from either peak area or height measurements. A series of dicy solutions of different concentration are injected to obtain the calibration plot, as shown in Figure 2, where the mass (μ g) dicy injected is plotted versus integrated peak area (mV s). For this data, the calibration constant $k = 0.0109 \pm 0.0001 \mu\text{g}/\text{mV s}$ is calculated from the least-squares slope of the line. If C is the extracted prepreg solution concentration, A is the integrated area of the dicy peak [Fig. 3(a)] and V is injection volume,

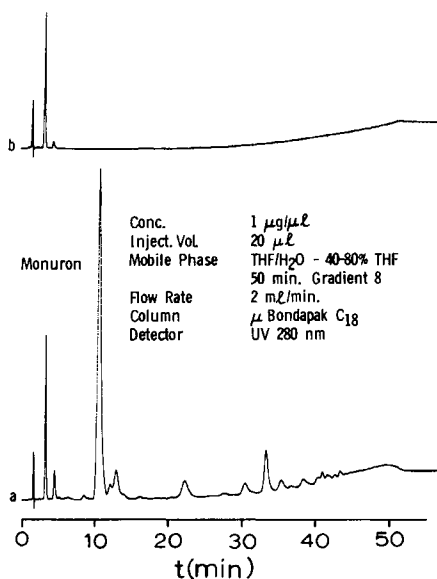


Fig. 1. Reverse phase HPLC chromatograms of epoxy resin prepreg solution (10% THF/90% H₂O) (a) before and (b) after filtration through a SepPAK-A cartridge.

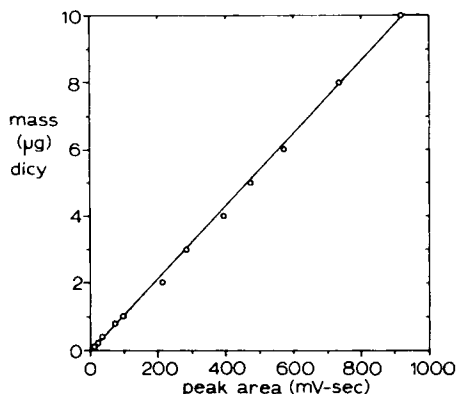


Fig. 2. Calibration plot for dicy analysis.

the weight percentage of unreacted dicy in the prepreg resin or in any sample may be calculated using the equation

$$\text{wt\% dicy} = \frac{Ak}{CV} 100\% \tag{1}$$

For the prepreg being considered, the resin portion is found to contain $7.14 \pm 0.06\%$ dicy. The cured prepreg is prepared for dicy analysis by grinding a sample to a fine powder on a cryogenic mill and extracting with THF. Upon analyzing the extract, no dicy is detected suggesting complete reaction of dicy.

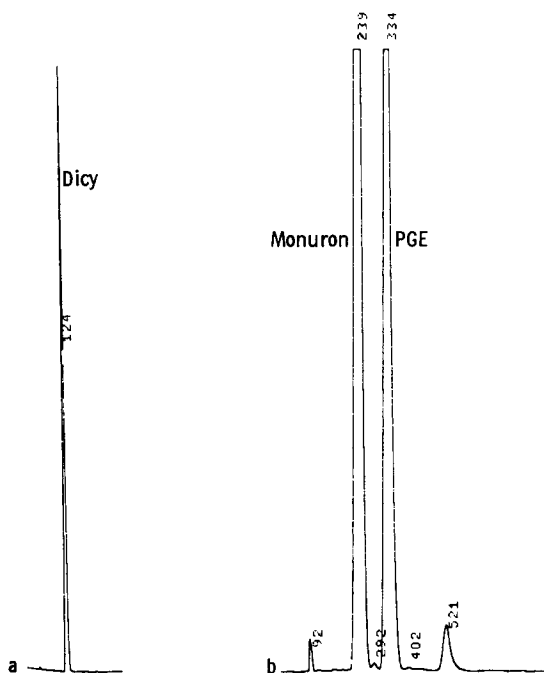


Fig. 3. HPLC chromatograms for analyzing (a) dicy and (b) Monuron and PGE.

SOLUBILITY STUDY

Since the epoxies selected for the solubility study were less complex than prepregs and therefore less likely to cause problems in HPLC analysis, neither SepPAK-A filtration nor column purging with THF were necessary. Dicy analyses were run consecutively and the column was purged only after a particular study was completed. Monuron and PGE were analyzed [Fig. 3(b)] using the HPLC conditions: mobile phase: 35% THF/65% H₂O; flow rate: 2 ml/min; injection volume: 20 μ l; column: μ Bondapak C₁₈; detector: UV 254 nm; chart speed: 0.5 cm/min; retention time: Monuron 239 s, PGE 335 s; and calibration constants: Monuron 0.00390 μ g/mV s, PGE 0.00138 μ g/mV s. Epon 828 was analyzed using the parameters shown in Figure 1.

In applying the filtration method, it is assumed that insoluble dicy particles are too large to pass through the membrane filters. In view of the fact that dicy with particle sizes less than 75 μ m produced by the whirl sinter process or the electrostatic spray process is used in epoxy resin laminates⁴ and that high-speed mixing might further reduce particle size, it was essential to ascertain whether very small (<5 μ m), insoluble dicy particles are present that might give rise to anomalously large solubility parameters. Hence, a slurry of dicy and isooctane (a nonsolvent for dicy) was stirred vigorously for 5 days, and aliquots were filtered through 0.2- and 5- μ m membrane filters for dicy analysis. In both cases, no dicy was detected demonstrating that undissolved dicy particles do not permeate the filters.

Solubility parameters for dicy and Monuron are plotted versus temperature in Figure 4. The concentration of dicy in PGE increases exponentially from 0.04 g dicy/100 g PGE at 30° to about 0.6 g/100 g PGE at 150°C. Identical solubility behavior is observed for dicy in Epon 828

$$\frac{\text{grams dicy}}{100 \text{ g (PGE or Epon 828)}} = 0.0227e^{0.0216T} \quad (2)$$

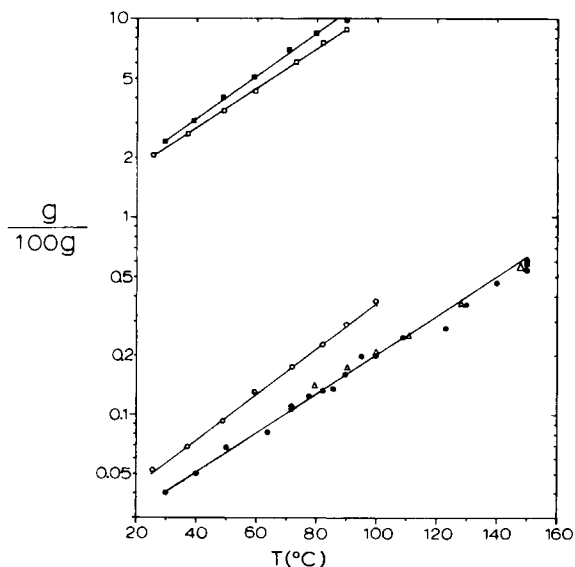
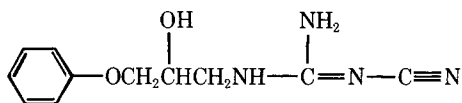


Fig. 4. Semilogarithmic plot of the temperature dependence of dicy solubility in PGE (●), Epon 828 (Δ), and PGE/Monuron (○) and of Monuron solubility in PGE (■) and PGE/dicy (□).

over the temperature T range 25–150°C. No chemical reactions are evident; however, reaction products form if the PGE/dicy mixture is maintained at 150°C. According to HPLC analysis, 10 wt% PGE is consumed and dicy solubility increases to 0.91 g/100 g PGE after 2 h at 150°C. The products do not interfere with the analysis of dicy. Dicy and PGE probably react to form epoxy-amine addition products such as



The products are soluble in PGE and thereby may enhance dicy solubility by providing a more favorable solvent environment (i.e., higher dielectric constant, hydrogen bonding).

Monuron is more soluble than dicy with solubility increasing from 2.0 g/100 g PGE at 25° to nearly 10 g/100 g PGE at 90°C.

$$\frac{\text{grams Monuron}}{100 \text{ g PGE}} = 1.24e^{0.0237T} \quad (3)$$

Below 100°C, in the time allowed for the study, no chemical reactions were evident; however, above 100°C both Monuron and PGE react and anomalous solubility parameters are obtained.

Significant changes in dicy and Monuron solubility behavior are observed in the three-component system dicy/Monuron/PGE. Dicy is more soluble in PGE saturated with Monuron than in PGE alone and the difference in solubility increases with temperature. Dicy however tends to decrease slightly the solubility of Monuron. Dicy's enhanced solubility may be the consequence of physical changes in the solvent phase (e.g., dielectric constant), which appreciates with temperature due to Monuron's increasing solubility. Also, the effect may be synergistic in that specific interactions (e.g., dipole–dipole or hydrogen bonding) between Monuron and dicy may promote the dissolution of dicy. Upon heating the mixture to 100°C and cooling to 25°C, no chemical changes are apparent. However, after 1 month at room temperature, HPLC analysis reveals chemical changes and, after 2 months, no Monuron remains, less than 0.01 wt% dicy is present and 88 wt% PGE has reacted. If the dicy/Monuron/PGE mixture is not first heated to 100°C, no reaction is evident after 3 months at room temperature.

The reversibility of dicy and Monuron solubility was examined by allowing the various mixtures to cool to room temperature after heating to 100 or 150°C and periodically analyzing the components. Monuron's solubility is completely reversible; however dicy behaves differently depending upon whether PGE is saturated with Monuron or no Monuron is present. After heating the dicy/PGE mixture to 150°C, the solubility of dicy at 30°C is 0.126 g/100 g PGE, over three times greater than the value before heating. After 1 month, the solubility levels off at 0.076 g/100 g PGE. Conceivably, the higher value may be a result of supercooling or perhaps of the recrystallization of extremely small particles that pass through the membrane filter.

In considering the change in solubility with temperature, differential heats of solution may be calculated from the slopes of the plot $\ln X$ (dicy or Monuron)

versus $1/T$ (Fig. 5) using the equation:⁸

$$\Delta\bar{H} = -R \frac{\partial \ln X}{\partial(1/T)} \quad (4)$$

where X is the mole fraction of dicy or Monuron in solution, T is the temperature in degrees Kelvin, and $R = 1.9872$ cal/mole deg. For dicy in PGE and Epon 828:

$$\Delta\bar{H}(\text{dicy}) = 5.72 \pm 0.08 \text{ kcal/mol}$$

but in PGE/Monuron

$$\Delta\bar{H}(\text{dicy}) = 5.94 \pm 0.13 \text{ kcal/mol}$$

For Monuron

$$\Delta\bar{H}(\text{Monuron}) = 5.12 \pm 0.15 \text{ kcal/mol}$$

in PGE and

$$\Delta\bar{H}(\text{Monuron}) = 4.79 \pm 0.16 \text{ kcal/mol}$$

in dicy/PGE. For ideal solutions, the differential heat of solution is constant and equal to the heat of fusion. If $\Delta\bar{H}$ is assumed to be independent of temperature, the mole fraction X of dicy and Monuron may be calculated at various temperatures using the integrated equation

$$\ln X = -\frac{\Delta\bar{H}}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (5)$$

where T_m is the melting temperature (K) of the solute. Upon substituting the appropriate parameters determined for dicy and Monuron, the calculated X values are considerably larger than those obtained experimentally at the same temperature. Evidently, the solutions are not ideal and the temperature dependence of the heat of fusion should be considered.

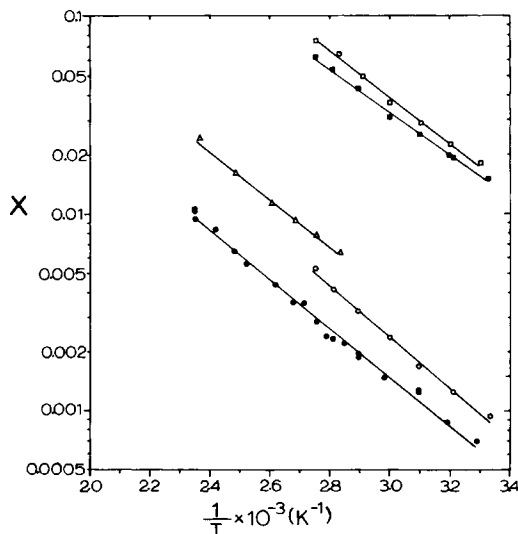


Fig. 5. Semilogarithmic plot of the mole fraction of dicy in PGE (●), Epon 828 (Δ), and PGE/Monuron (○) and of Monuron in PGE (■) and PGE/Dicy (□) versus $1/T$ (K^{-1}).

DISCUSSION

A simple procedure has been developed for the quantitative analysis of dicy in epoxy resin prepregs. Using water as the mobile phase and an alkylated, microporous (ca. 60-Å pore size) silica column packing for HPLC, dicy is unretained eluting at or near the column's exclusion limit. A reverse phase separation mechanism is likely considering the high dipole moment (8.16D) and amphoteric nature of dicy.³ Also, size exclusion may contribute to the early elution, since it is conceivable that dicy molecules may be associated by polar or ionic interactions to form polymolecular species. To determine whether the size exclusion mechanism is operative, dicy was analyzed using a set of Waters μ Bondagel E-linear columns (ca. 60–2000-Å pore sizes) with water as the mobile phase and was found to elute as a sharp, symmetrical peak at about the same retention time as benzyl alcohol. No associated species were present indicating that reverse phase rather than size exclusion is the preferred mechanism.

In a previous paper,⁹ a differential refractive index (RI) detector was used to monitor dicy. The present procedure using a 230-nm UV detector is more accurate and about 500 times more sensitive than the RI method. As a tetra-functional reactant dicy's concentration is of critical importance in forming crosslinked networks; and considering that dicy is seldom formulated at concentrations over 10 wt%, a sensitive analytical technique is most desirable. As in any chromatographic method, other compounds may elute with dicy; and if such compounds also absorb at 230 nm, dicy cannot be analyzed directly. Peak areas or heights obtained using different wavelengths or different types of detectors may be ratioed and compared with dicy standard values to determine whether other compounds are present. By monitoring at several wavelengths, it also may be possible to correct the dicy peak area for contributions from other compounds.

The solubility study shows that only about 0.05 wt% dicy and 2.0% Monuron are soluble in PGE and Epon 828 at room temperature. Since the prepreg resin discussed in the Procedures section consists of 7.14 wt% dicy and 4.0 wt% Monuron, 99.3% of the dicy and 50% of the Monuron are insoluble at room temperature. To what extent insolubility affects prepreg processability and properties of the cured resin is unknown. Eyerer attributes the poor tensile tests behavior of a cured DGEBA resin to the formation of boundary layers by sedimentation of dicy crystals.⁴ For curing temperatures below 150°C, he proposes that dicy continues to dissolve in the epoxy resin matrix after crosslinking is completed. In this study, it was determined that the formation of soluble reaction products and the addition of components such as Monuron significantly enhance dicy solubility. Finally, it was observed that heating the mixture dicy/Monuron/PGE to 100°C promotes room temperature epoxy reactions. Such behavior is similar to the room temperature aging of "staged" epoxy prepregs formulated with dicy and Monuron. Techniques described in this paper may be applied to monitoring the extent of dicy reaction and solubility during resin curing affording thereby a better understanding of reaction mechanisms and the role of dicy in network formation.

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