

SOLVENTS

Miscibility Characteristics of Glycol Ether/ Water Mixtures for Waterborne Coatings

Phase Equilibria of *Eastman* EB Solvent/Water

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Introduction

In solution-type waterborne coatings, a blend of organic solvents is used to solubilize the neutralized resin and couple it with water to keep the solution homogeneous. Organic solvents used in waterborne coatings also help control solution viscosity behavior and improve flow properties of the coating, control evaporation characteristics of the solvent/water system, keep the film open during drying, and control sagging and running. Glycol ethers or blends of glycol ethers with other solvents are used because they give these desired properties.

Water Miscibility of Glycol Ethers

Glycol ethers used in waterborne coatings are generally referred to in literature as being completely water soluble: i.e., miscible. However, in tests conducted in Eastman laboratories, certain glycol ethers have shown changes in degree of water solubility with increasing temperature. As indicated in Table 1, at 20 volume percent concentration, *Eastman* EB solvent and propylene glycol propyl ether solvent were miscible with water at room temperature, but both became immiscible with water when heated as exhibited by mixture

separation (two distinct layers). The other glycol ethers listed in Table 1 did not show phase separation over the temperature range investigated.

The temperature at which immiscibility first occurred was a function of the organic solvent/water volume percent ratio. The minimum point of the miscibility boundary curve determines the classical Lower Critical Solution Temperature and occurs at a specific solvent/water volume percent ratio.

Table 1

**Miscibility of Glycol Ethers and Water at Varying Temperatures
(20% Glycol Ether/80% Water)^a**

Glycol Ether	Miscibility	
	21°C (70°F)	77°C (170°F)
<i>Eastman</i> PM Solvent (Methyl ether of propylene glycol)	Miscible	Miscible
<i>Eastman</i> EP Solvent (Propyl ether of ethylene glycol)	Miscible	Miscible
<i>Eastman</i> EB Solvent (Butyl ether of ethylene glycol)	Miscible	Immiscible
<i>Eastman</i> DM Solvent (Methyl ether of diethylene glycol)	Miscible	Miscible
<i>Eastman</i> DE Solvent (Ethyl ether of diethylene glycol)	Miscible	Miscible
<i>Eastman</i> DB Solvent (Butyl ether of diethylene glycol)	Miscible	Miscible
Propylene Glycol Propyl Ether Solvent (Propyl ether of propylene glycol)	Miscible	Immiscible

^aAll data on solvent/water ratios in this publication are in volume percent.

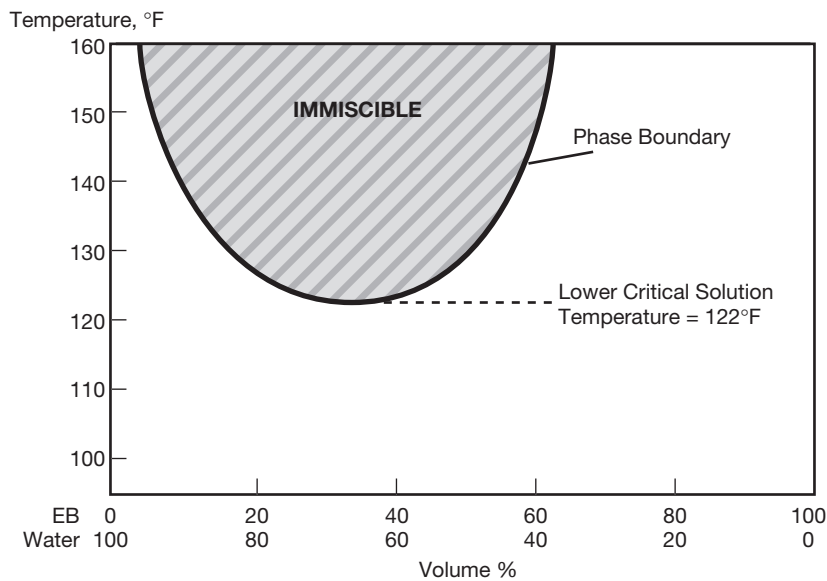
With *Eastman* EB solvent, as shown in Figure 1, phase separation or immiscibility at elevated temperature occurred over a wide range of glycol ether/water ratios (from approximately 7% *Eastman* EB/93% water to 65% *Eastman* EB/35% water). The temperature required to cause phase separation or immiscibility varied with the composition of the glycol ether/water mixtures. The lowest temperature at which immiscibility occurred (Lower Critical Solution Temperature)

was approximately 50°C (122°F). Samples of the glycol ether/water composition that existed as two phases at elevated temperature became homogeneous under slight agitation when cooled to a temperature below that required for separation to occur.

The two-phase compositions showed no tendency to revert to a single phase when heated to temperatures as high as 82°C (180°F).

Figure 1

Phase Equilibria of *Eastman* EB Solvent/Water



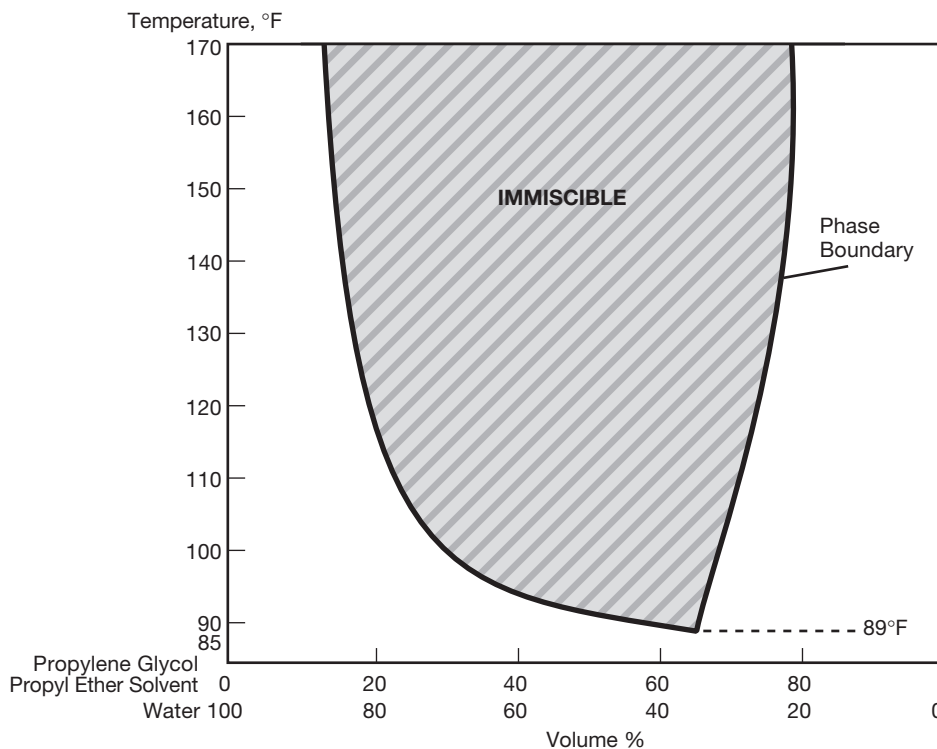
With propylene glycol propyl ether solvent, separation of the glycol ether/water system occurred over a range of approximately 13% glycol ether/87% water to 75% glycol ether/25% water. The Lower Critical Solution region occurred at a much lower temperature [31.7°C (89°F)] and higher solvent/water ratio than *Eastman* EB/water systems (see Figure 2).

Because of its solvency, evaporation characteristics, and low cost, the butyl ether of ethylene glycol (*Eastman* EB) is a widely used solvent in waterborne

coating systems. The inverse solubility with temperature of this glycol ether and water could cause problems with coating systems during resin hydrolytic stability aging tests and under drying conditions where the paint is baked at elevated temperatures. To learn how to control this inverse solubility phenomenon, the effect of different cosolvents on the water immiscibility of *Eastman* EB at elevated temperatures was studied. Similar concepts can be applied to other two-phase organic/aqueous systems.

Figure 2

Phase Equilibria of Propylene Glycol Propyl Ether Solvent/Water



Effect of Cosolvents

In a series of tests, a portion of the *Eastman* EB solvent in *Eastman* EB solvent/water mixtures was replaced with different cosolvents. Results are shown figuratively in this publication.

With n-butyl alcohol replacing 10% of the *Eastman* EB solvent (Figure 3), phase separation occurred at a much lower temperature than when *Eastman* EB was used alone in the solvent/water system; that is, immiscibility of the system increased with incorporation of n-butyl alcohol. (Compare Figure 3 with Figure 1.)

The range of solvent/water ratios over which immiscibility occurred at elevated temperatures was about the same.

The Lower Critical Solution Temperature was 40°C (103°F) and occurred at a cosolvent/water composition of 40/60. It should be noted that n-butyl alcohol has limited solubility in the presence of an aqueous phase.

With tertiary butyl alcohol replacing 10% of the *Eastman* EB solvent (Figure 4), the lowest temperature at which immiscibility occurred increased slightly compared to the value for *Eastman* EB. The range of solvent/water ratios over which phase separation occurred was lightly contracted.

Figure 3

**Phase Equilibria of Eastman EB Solvent
(10% n-Butyl Alcohol)/Water**

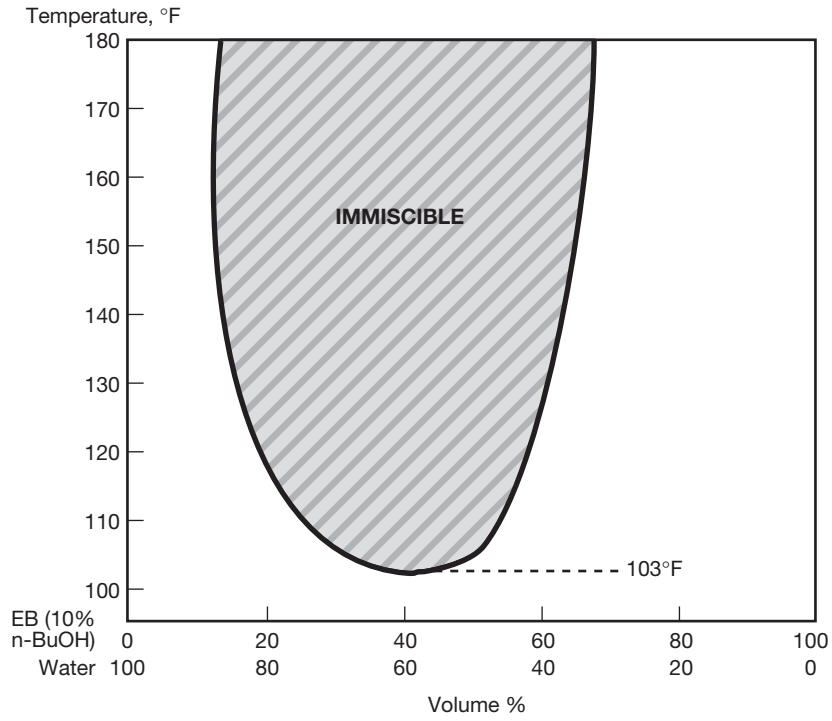
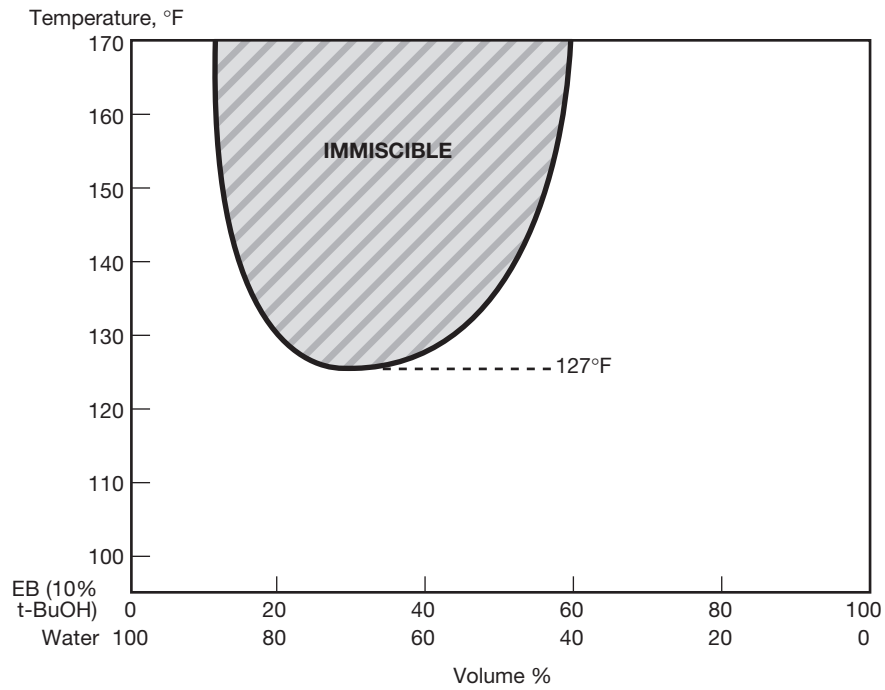


Figure 4

**Eastman EB Solvent
(10% tert-Butyl Alcohol)/Water**



With denatured ethyl alcohol (*Tecsol C* solvent) replacing 10% of the *Eastman EB*, the profile in which separation occurred was altered and the Lower Critical Solution Temperature was increased to 54°C (130°F)—see Figure 5.

It may be concluded that modification of the water/*Eastman EB* solvent blend with water-soluble alcohols will raise the value of the Lower Critical Solution Temperature and decrease the region of phase separation.

With *Eastman DB* solvent replacing 30% of the *Eastman EB* (Figure 6), the minimum temperature at which separation occurred was 154°F (68°C). Phase separation occurred over a range of approximately 12% to 55% organic solvent.

With *Eastman DE* replacing 20% of the *Eastman EB* (Figure 7), the organic solvent/water compositions did not separate under the test conditions: *Eastman DE* solvent appears to have excellent elevated temperature solubility and coupling activity with *Eastman EB*/water combinations.

Additional work has revealed that parameters such as type and level of coating resin or other organic insoluble phase present and degree of neutralization of a carboxyl functional waterborne coating binder drastically affect the shape of the phase boundaries and thus the composition at which the Lower Critical Solution Temperature occurs. In the selection of organic cosolvents for waterborne coatings, the formulator must be aware of chemical phase separation and methods available to control such phenomenon in a favorable manner.

Figure 5

**Phase Equilibria of *Eastman EB* Solvent
(10% *Tecsol C* Anhydrous Alcohol)/Water**

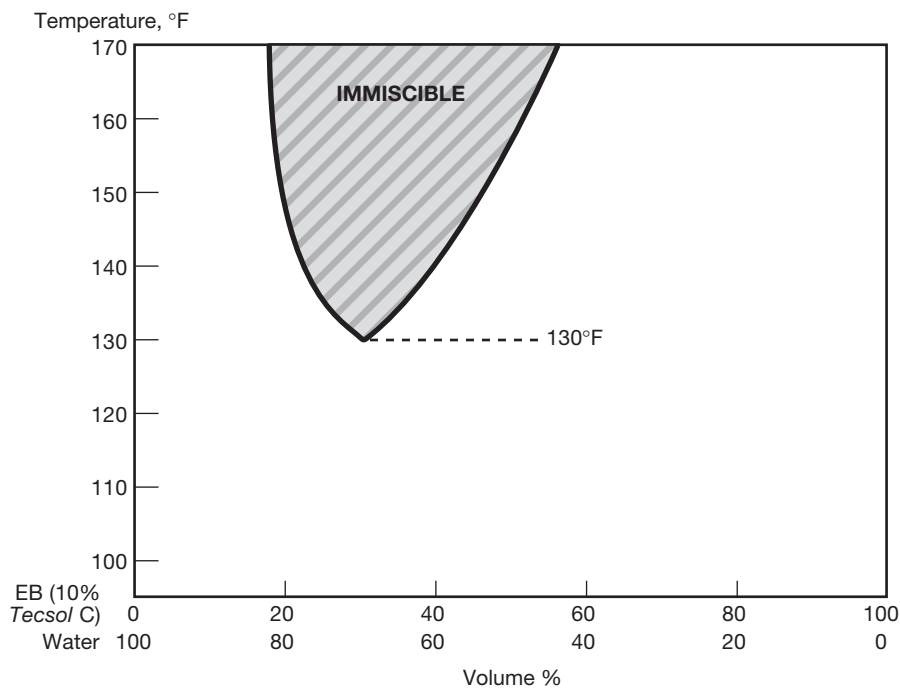


Figure 6

**Phase Equilibria of Eastman EB Solvent
(30% Eastman DB Solvent)/Water**

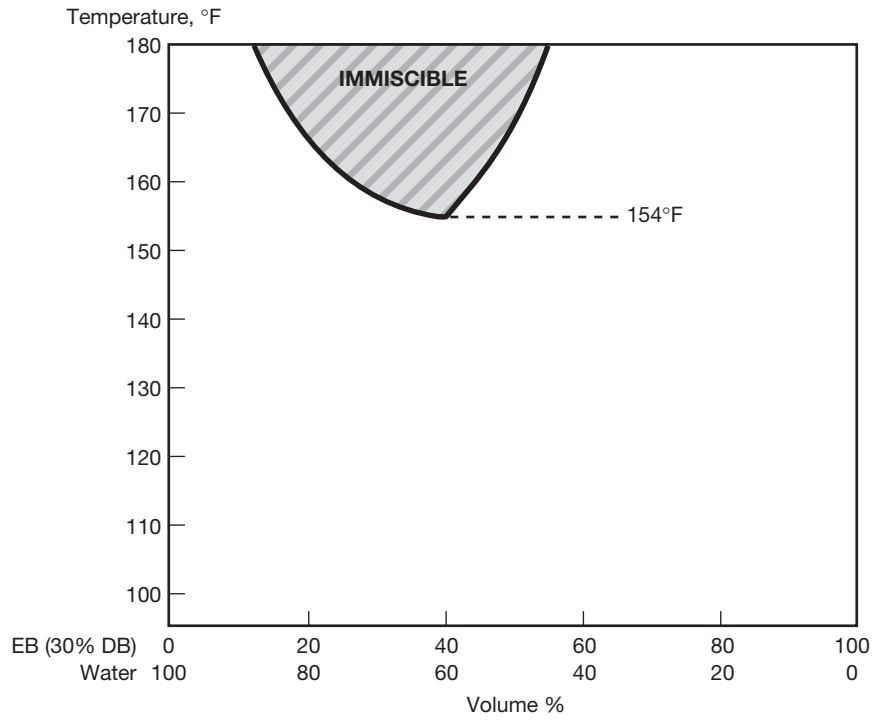
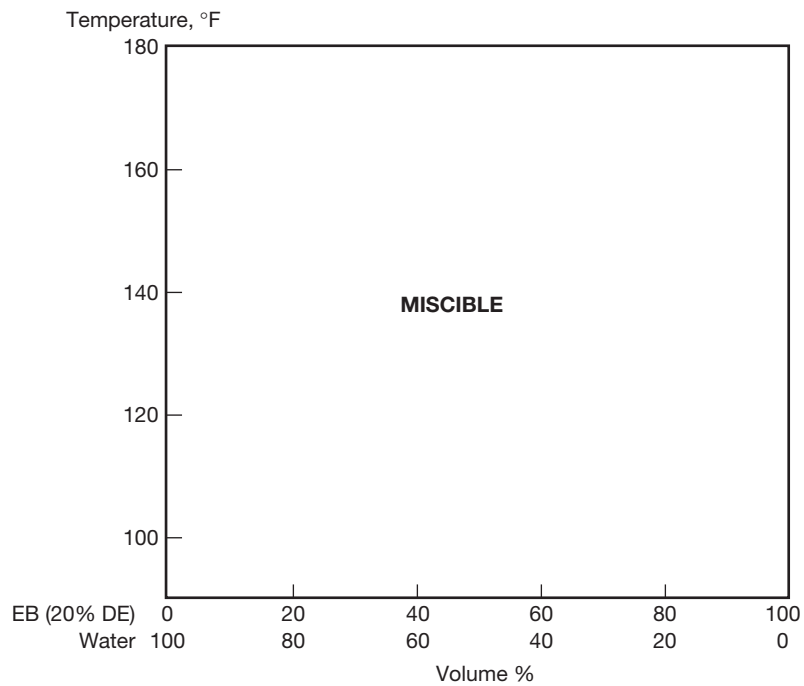


Figure 7

**Phase Equilibria of Eastman EB Solvent
(20% Eastman DE Solvent)/Water**



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