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Review of Glycol Ether and Glycol Ether Ester Solvents Used in the Coating Industry

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Ethylene oxide-based glycol ether and glycol ether ester solvents have been used in the coatings industry for the past fifty years. Because of their excellent performance properties (evaporation rate, blush resistance, flow-out and leveling properties, solubility for coating resins, solvent activity, mild odor, good coupling ability, good solvent release) a complete line of ethylene oxide-based solvents of various molecular weights has been developed. These glycol ether and glycol ether ester solvents have better solvent activity for coating resin than ester or ketone solvents in their evaporation rate range. The gloss, flow and leveling, and general performance properties of many coating systems are dependent on the use of these products in the coating formula. Because of the concern about the toxicity of certain ethylene oxide-based solvents, other products are being evaluated as replacements in coating formulas.

Glycol ether solvents were first introduced as commercial products in the late 1920s. At a time when *n*-butyl acetate was the primary solvent for use in coatings, the introduction of the glycol ether solvents was a major step forward for the coatings industry. Even today when the coatings formulator has a wide range of solvents to work with, glycol ether and glycol ether ester solvents still fill a unique role in coatings formulations.

In the coatings industry, solvents are generally classified according to evaporation rate. To a large extent the evaporation rate of the solvent determines where and how it can be used. In determining the evaporation rate of solvents, *n*-butyl acetate is used as the standard and is assigned an evaporation rate value of 1. Other solvents are assigned evaporation rate values that indicate how they evaporate in relation to *n*-butyl acetate. For instance, a solvent that evaporates three times as fast as *n*-butyl acetate would be assigned a value of 3, whereas a solvent that evaporates half as fast as *n*-butyl acetate would be assigned a value of 0.5.

Solvents for the coatings industry are generally grouped into three classes—fast, medium or slow—according to their evaporation rate. In the fast-evaporating group, solvents with evaporation rates greater than 2.5 (*n*-butyl acetate = 1), the coatings formulator has a number of very active ester and ketone solvents to use. These include acetone, ethyl acetate, methyl ethyl ketone and isopropyl acetate. In the medium-evaporating group, solvents with evaporation rates between 0.8 and 2.5, there are products such as isobutyl acetate, *n*-butyl acetate, methyl isobutyl ketone and *n*-propyl acetate, all very active solvents. However, in the slow-evaporation rate range, solvents with an evaporation rate of less than 0.8, there are a limited number of ester and ketone solvents. Products that are available are methyl *n*-amyl ketone, a very active ketone solvent, and amyl acetate and isobutyl isobutyrate, two low activity ester solvents. All of these products have an evaporation rate around 0.4. It is in this slow evaporation rate area that the glycol ether and glycol ether ester solvents fill a void, particularly in the area from 0.3 to 0.05 evaporation rate.

Of the commercially available ethylene oxide-based glycol ether and glycol ether ester solvents (Table 1), ethylene glycol monomethyl ether (EGME), ethylene glycol monoethyl ether (EGEE), ethylene glycol monopropyl ether (EGPE), ethylene glycol monobutyl ether (EGBE), ethylene glycol monomethyl ether acetate (EGMEA), and ethylene glycol monoethyl ether acetate (EGEEA acetate), all have evaporation rates

Table 1. Evaporation rate of ethylene oxide-based glycol ethers.

Solvents	Relative evaporation rate (*n*-butyl acetate = 1)
Ethylene glycol monomethyl ether (EGME)	0.5
Ethylene glycol monoethyl ether (EGEE)	0.3
Ethylene glycol monopropyl ether (EGPE)	0.2
Ethylene glycol monobutyl ether (EGBE)	0.07
Ethylene glycol monomethyl ether acetate (EGMEA)	0.3
Ethylene glycol monoethyl ether acetate (EGEEA)	0.2

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Table 2. Comparison of properties of ester and ketone solvents with glycol ethers and ether esters.

Solvent	Relative evaporation rate (*n*-butyl acetate = 1)	Solubility			
		Nitrocellulose (0.5 sec RS grade)	Epoxy (high molecular weight)	Acrylic (methyl methacrylate)	Phenoxy
Glycol ether, EGEE	0.3	Soluble	Soluble	Soluble	Soluble
Ether ester, EGEEA	0.2	Soluble	Soluble	Soluble	Soluble
Ester solvent	0.2	Soluble	Insoluble	Insoluble	Insoluble
Ketone solvent	0.2	Soluble	Hazy solution	Insoluble	Insoluble

Table 3. Ethylene oxide-based glycol ether solvents commercially available.

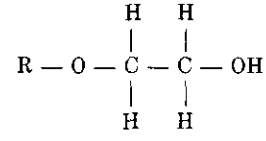
Solvents	Relative evaporation rate (*n*-butyl acetate = 1)
Ethylene glycol monohexyl ether (EGHE)	<0.01
Ethylene glycol mono-2-ethylhexyl ether (EGEEHE)	<0.01
Ethylene glycol monophenyl ether (EGPhE)	<0.01
Diethylene glycol monomethyl ether (diEGME)	0.02
Diethylene glycol monoethyl ether (diEGEE)	0.02
Diethylene glycol monopropyl ether (diEGPE)	<0.01
Diethylene glycol monobutyl ether (diEGBE)	<0.01
Ethylene glycol monobutyl ether acetate (EGBEA)	0.03
Diethylene glycol monoethyl ether acetate (diEGEEA)	<0.01
Diethylene glycol monobutyl ether acetate (diEGBEA)	<0.01

between 0.5 and 0.07. The use of EGME and EGMEA is generally limited to specialty applications in coatings, but the other products (EGEE, EGPE, EGBE and EGEEA) all find a broad range of use in coatings applications.

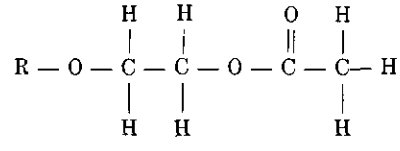
The blush resistance, flow-out and leveling properties, handling properties, and gloss of many coatings systems depend on the presence of these glycol ethers and esters in the formulation. When compared to ketones and ester solvents of a similar evaporation rate (Table 2), the glycol ether and ether ester solvents have a much broader range of solvent activity for polymers used in coating systems. The combination of the ether and alcohol group on the glycol ethers and of the ether and ester group on the glycol ether esters give these products solvent characteristics which cannot be obtained with the simpler ester and ketone solvents. In addition, the glycol ethers and the glycol ether esters are noted for their mild odor, good coupling ability, and good solvent release in coating systems.

It is the combination of desirable properties that causes these products to be widely used in coatings. While there are some other types of solvents with evaporation rates in the same range as the glycol ethers, none of these products have the combination of attractive properties for use in coatings.

A number of other glycol ether and glycol ether ester solvents based on ethylene oxide are commercially available (Table 3). These are all high-boiling, very slow-evaporating solvents. While they find use in such applications as tail solvents in coating systems, active solvents in coil coatings, slow solvents in waterborne finishes, coupling agents in different coatings systems, coalescing aids in latex paints, and coupling solvents in electrodeposition finishes, they are not used in the same large volumes as EGEE, EGBE and EGEEA.



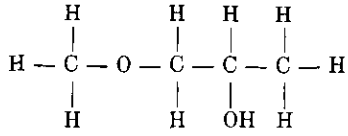
Glycol Ether
R = 1–8 carbons



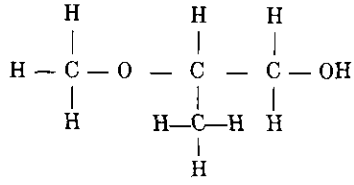
Glycol Ether Ester
R = 1–8 carbons

Glycol ether solvents based on propylene oxide have also been available commercially for many years. The

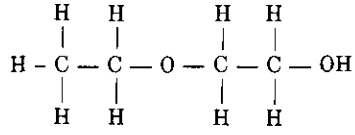
propylene oxide-based products are generally mixtures of two components. The major component contains a secondary hydroxyl, while the minor component has a primary hydroxyl group, but a branch structure. In contrast, the ethylene oxide-based products have a linear structure with a primary hydroxyl. The ethylene oxide-based products are considered to be better solvents and have dominated the coatings market.



Propylene Oxide-Based Product
Glycol Ether PM
Major Component



Glycol Ether PM
Minor Component



Ethylene Oxide-Based Product
Glycol Ether EE

As an example, when comparing the properties of ethylene glycol monoethyl ether with the properties of a propylene oxide product of the same molecular weight (propylene glycol monomethyl ether), the evaporation rate with the propylene oxide-based product is about twice that of the ethylene oxide-based product; the flash point is much lower, and the solution viscosity with coatings resins is very similar (see Table 4). If the methoxy group on the propylene oxide-based products is replaced with ethoxy or propoxy groups (see Table 5), the evaporation rate of the solvent is reduced and the flash point increased, but the solution viscosity with coatings resins also increases.

It is not possible to match both solvent activity and evaporation rate of an ethylene oxide-based glycol ether with a propylene oxide-based product. This is one of the reasons it is difficult to replace ethylene oxide-based solvents in coatings systems with propylene oxide-based products. In most coatings systems, ethylene oxide-based products have better solvent activity, better coupling ability, and give better solvent release from a coating than the propylene oxide-based products.

Presently, there are five propylene oxide-based glycol ethers and one ether ester commercially available (Table 5). These are: propylene glycol monomethyl ether (PGME), propylene glycol monopropyl ether (PGPE), propylene glycol, monobutyl ether (PGBE), propylene glycol monophenyl ether (PGPhE), dipropylene glycol monomethyl ether (diPGME) and propylene glycol monomethyl ether acetate (PGMEA). Because of the concern about the toxicity of the ethylene oxide-based products, the number of propylene oxide-based products available may increase. There are currently eight domestic manufacturers of ethylene oxide-based glycol ether solvents (Eastman Chemical Products Inc., Union Carbide Co. Inc., Dow Chemical Co., Shell Chemical Co., Olin Chemical Corp., Texaco Chemical Co., ICI

Table 4. Comparison of properties of ethylene oxide- and propylene oxide-based glycol ethers.

Solvent	Base chemical	Mol. wt.	Relative evaporation rate (*n*-butyl acetate = 1)	Flash point TCC, °F	Solution viscosity (40% nonvolatile epoxy resin), cP
Glycol ether EGEE	Ethylene oxide	90.12	0.3	110	175
Glycol ether PGME	Propylene oxide	90.12	0.7	89	175

Table 5. Effect of molecular weight on properties of propylene oxide-based glycol ethers.

Solvent	Base chemical	Mol. wt.	Evaporation rate (*n*-butyl acetate = 1)	Flash point TCC, °F	Solution viscosity (40% epoxy resin), cP
Glycol ether EGEE	Ethylene oxide	90.12	0.3	110	175
Glycol ether PGME	Propylene oxide	90.12	0.7	89	175
Glycol ether PGEE	Propylene oxide	104.15	0.5	100	210
Glycol ether PGPE	Propylene oxide	118.17	0.25	121	305

Corp. and PPG Industries Inc.), and three domestic manufacturers of the glycol ether esters (Eastman Chemical Products Inc., Union Carbide Co. and ICI Corp.). These products are supplied under a number of different trade names (Table 6).

Total consumption of ethylene oxide-based glycol ethers in 1982 for all uses (coatings, inks, cleaners, chemical intermediates, process solvents, brake fluids, deicers, and so forth) was around 600,000,000 pounds. Over half of this volume goes into the coatings industry.

Table 6. Trade names for glycol ether solvents.

Trade name	Company
Cellosolve solvent	Union Carbide
Carbitol solvent	Union Carbide
Ektasolve solvent	Eastman
Dowanol solvent	Dow
Oxitol solvent	Shell
Dioxitol solvent	Shell
Polysol solvent	Olin
Jeffersol solvent	Texaco