Glycol Ethers for Protective Coatings

Coatings Industry Background

Protective coatings are composed of pigments, resins, solvents (active and latent), and additives. Coatings are grouped into two categories: Water-based coatings which include emulsions and dispersions, and solvent-based coatings which include varnishes, enamels, and lacquers. The solvent based coatings are subdivided into high-solids and conventional (low-solids) systems.

The protective coatings area is the largest application for DOW glycol ethers and acetates. DOW glycol ethers are used by resin manufacturers, coating formulators, and coating applicators in many protective coatings. For example, such coatings are used in industrial, coil, wood, metal, and architectural applications.

A broad range of physical properties enables DOW glycol ethers to be used as general solvents, coupling agents, or coalescing agents with many coating resins.

The following features of DOW glycol ethers and acetates make them well suited for use in protective coatings:

- Compatibility with water and many organic chemicals, ranging from alcohols and esters to naphthas and aromatics.
- Active solvents for a wide range of resins.
- Powerful coalescing ability
- Superior coupling ability
- Wide range of evaporation rates for the best possible film formation.
- Low surface tension for improved wetting of substrate.
- Penetrating ability to promote adhesion to porous substrates.

The DOW glycol ether product line is composed of E-Series glycol ethers and P-Series glycol ethers and acetates. The Dow Chemical Company has concentrated on the development of glycol ethers and acetates for over 40 years. This development effort has lead to the current extensive line of products that find extensive use in water-borne and solvent-based coating systems.

Development work has centered on solvent property characterization, resin/solvent interactions, polymerization, and paint formulation and evaluation.

Dow's broad range of glycol ethers and acetates provides the resin manufacturer and paint formulator with options for selecting the product or blend of products providing optimum performance.

Dow glycol ether products can meet the challenges of formulating waterborne, high-solids, and conventional coating systems and help meet the application and quality standards of today's coating industry.

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As restrictions on emissions of volatile organic compounds (VOC) increase, technologies such as high-solids and water-borne coatings continue to grow. Dow glycol ethers and acetates have demonstrated to be key performance solvents for these technologies.

In addition to formulating assistance, Dow's CHEMCOMP Service Evaporation Rate computer program can assist formulators in selecting the appropriate DOW glycol ether or solvent blend for their coating formulation needs.

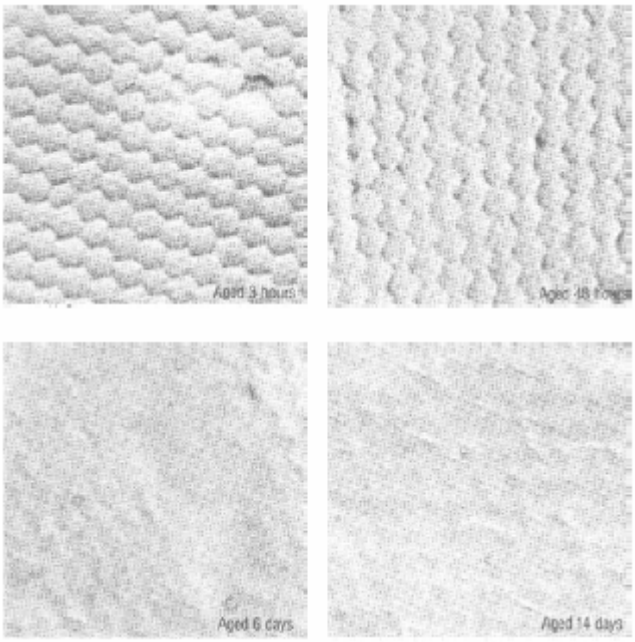
Glycol Ethers Coatings Technology

Water-Based The combination of higher solvent prices, increased energy costs and VOC emission regulations has led to increased emphasis on the development of new coating technologies. The purpose of these technologies is to reduce the presence of organic solvents.

In the coatings industry, this trend can be seen as a marked shift toward water-based systems. Although water doesn't dissolve polymeric or resinous components and therefore isn't considered a true solvent, it is used in these systems as a diluent or latent solvent in combination with an active solvent, such as a DOW glycol ether product. Waterbased systems can be either water-borne or water-reducible.

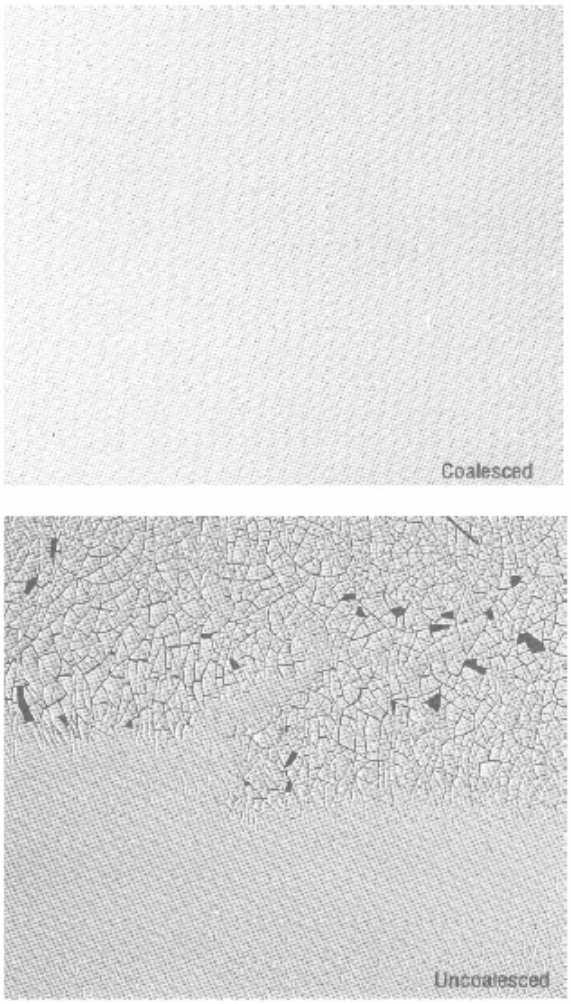
Water-Borne Water-borne coatings are latex emulsions used for both architectural and industrial applications. In most if not all cases, water-borne latex coatings must contain a coalescing agent to achieve proper film formation (see Figure 1).

Figure 1: Electronmicrographs of Latex Particle Coalescence as a Function of Time



By definition, a coalescing agent is a solvent that is left behind after the evaporation of water from a latex paint. The coalescent softens the latex particles, enabling them to fuse into a continuous film. Without the presence of a coalescing agent at the point of film formation, the latex particles may not fuse together to form a continuous, usable coating (see Figure 2). A film formed without a coalescing agent, may not have any inherent physical properties, e.g., scrubability. Therefore, the question is not usually whether a coalescent is needed, but which coalescent or combination of coalescents should be used.

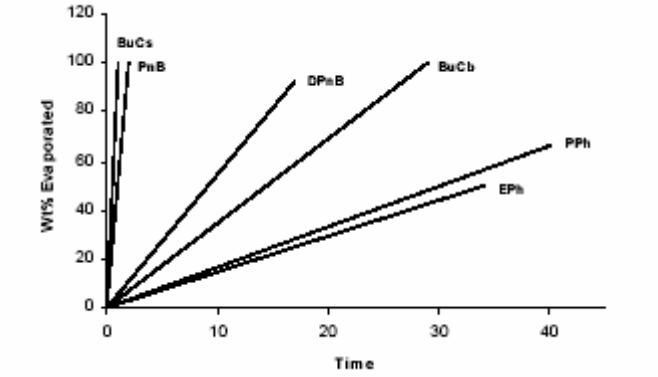
Figure 2: Coalesced vs. Uncoalesced Films



The DOW glycol ether family of coalescents offers a wide range of coalescents from which to choose. The breadth of this family is emphasized by two points:

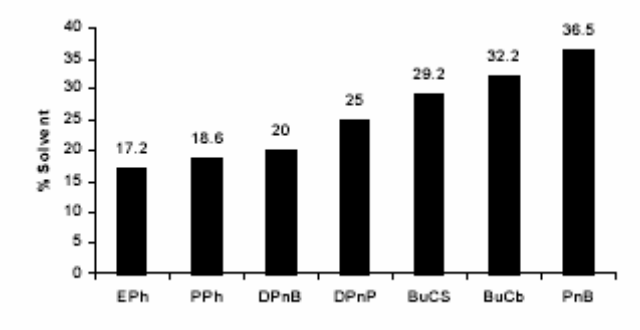
1. DOW glycol ether products offer the widest range of coalescent evaporation rates...from the relatively fast Butyl CELLOSOLVE™ And DOWANOL* PnB, to the moderately evaporating DOWANOL DPM and Butyl CARBITOL™, to the relatively slow evaporating DOWANOL PPh, DOWANOL EPh, or DALPAD A (see Figure 3).

Figure 3: Observed Evaporation Rates For Butyl CELLOSOLVE, DOWANOL PnB, DPM, DB, PPh, EPh or DALPAD A



2. DOW glycol ethers also offer a wide range of coalescent efficiencies. Studies have shown that DOWANOL PPh and DOWANOL EPh or DALPAD A are often the most efficient coalescents available, this is especially true for acrylic-based latexes (see Figure 4).

Figure 4: % Coalescent Required to Reach 50°F Minimum Film Formation Temperature (MFFT) in Rhoplex WL-911



Studies have shown that under varying atmospheric conditions such as humidity and temperature extremes, evaporation rates are very important to proper film formation.[2]

The coalescent should be the last component to evaporate from the latex coating. Since the coalescent is an organic compound, humidity will have little effect upon its evaporation rate. However, at the same time, humidity will have a drastic effect upon the evaporation rate of water. Thus, application of a latex paint under high humidity conditions can have a dramatic effect upon the final film properties of a coating. To compensate for the effect of high humidity, at least part of the coalescent package should contain a slow evaporating coalescent such as glycol ethers DOWANOL PPh, DOWANOL EPh, or DALPAD A.

Evaporation rates of the coalescents will also have a direct effect upon the hardness development rate of a latex coating, since the coalescent should be the last component to evaporate from a latex coating.

Temperature also plays an important role in latex film formation. Each latex resin has a specific minimum film formation temperature (MFFT), and a coalescent is added to ensure on MFFT of at least 40°F for the latex formulation. However, the amount of coalescent needed will vary, depending on how efficient the coalescent is in lowering the MFFT of the latex. As mentioned above, DOWANOL PPh, DOWANOL EPh, and DALPAD A glycol ethers have been extremely efficient in lowering the MFFT of most latex resins (see Figure 4). Other products such as DOWANOL DPnP, DPnB, and TPnB also offer excellent MFFT reduction, along with excellent final film properties.

Therefore, in order for a formulator to select the most efficient coalescent package, two of the most important properties to consider are evaporation rate and coalescent efficiency. All of this becomes even more important when working with industrial latex coatings, which often require large amounts of coalescents to ensure proper film formation and must have the fastest possible hardness development rate.

Water-Reducible Water-reducible coating formulations are finding greater acceptance as replacements for conventional solvent-based coating systems as pressure increases from both economic and environmental considerations. Water-reducible resins are solvent-borne resins which have been modified to increase their water solubility. Water-reducible resins, with the assistance of co-solvents such as alcohols, glycol ethers and neutralizing agents, can be diluted with water to form a homogeneous solution.

A typical water reducible formulation consists of approximately 15 percent solvent, 55 percent water and 30 percent solids. In addition to solubilizing the resin, glycol ethers find use in water reducible formulations as coupling agents. That is, they have the ability to create and maintain a homogeneous solution between the organic (resin) and aqueous phases.

Butyl CELLOSOLVE,DOWANOL PM, DPM and PnP glycol ethers and blends of these with alcohols are used as coupling agents in water reducible coatings.

If propylene based glycol ethers are desired blending C-4 alcohols such as n-butanol, isobutanol, and sec-butanol with DOWANOL PM, DOWANOL DPM and DOWANOL PnP significantly improves the coupling ability of the P-Series glycol ether. In some cases, these blends perform as well as Butyl CELLOSOLVE glycol ether. They perform effectively because the C-4 alcohol has good organic solubility but low water solubility, while DOWANOL PM, DOWANOL DPM and DOWANOL PnP glycol ethers are completely soluble in both the organic and water phases. The combination of hydrophobic and hydrophilic character contributed by the alcohols and glycol ethers produces a solvent blend with a high coupling performance.

DOWANOL DPM glycol ether may perform satisfactorily as the sole coupling agent in water-reducible coatings. However, if its evaporation rate is too slow, addition of DOWANOL PM or DOWANOL PnP, a faster evaporating glycol ether, may increase the evaporation rate of the blend sufficiently. If the coupling ability of DOWANOL DPM glycol ether is not sufficient, addition of C-4 alcohols will increase coupling performance. Table 1: Coupling Abilities of DOW glycol ethers and Alcohols is repeated here for easy reference.

Table 1: Coupling Abilities of DOW Glycol Ethers and Alcohols[1]

Composition of Titrant, Volume %										
PM	**DPM**	**TPM**	**PnP**	**BuCs**	**BuCb**	**MeCb**	**sec-butanol**	**isobutanol**	**n-butanol**	**ml to couple[1]**
				100						32.8
				75			25			34.2
				50			50			37.9
50									50	41.0
	25						75			42.1
					100					42.5
			100							45.0
				25			75			48.8
			75						25	49.0
25									75	51.0
			50						50	54.0
	50							50		58.3
							100			60.9
	25							75		61.8
			25						75	62.0
	50						50			63.9
75									25	64.0
		100								67.0
									100	71.0
	75							25		78.8
100										80.0
	75						25			82.1
	100									95.8
								100		104.6
						100				230.0

[1]Milliliters of product required to titrate 10 ml of mineral spirits and 10 ml of water to a clear homogeneous solution at 25°C.

Solvent-Based

Solvent-based coatings – which can include lacquers, varnishes, and enamels – are divided into two categories: high-solids and conventional (low-solids). An active solvent such as a DOW glycol ether or acetate used in a solvent-based coating formulation dissolves the film-forming components, e.g. resin and cross-linking agents, and holds them in solution with the pigments and additives.

High-Solids For the purpose of this discussion, high-solids coating formulations are defined as all types of solvent-based coatings with at least 60% solids content by volume. Although there is less solvent use in high-solids coatings than in conventional coatings, high-solids systems put greater demands on solvent performance.

As active solvents, DOW glycol ethers and acetates are powerful solvents capable of solubilizing a wide range of resin types for high-solids applications. Table 2: Solubility of Resins in DOW glycol ethers is repeated on the facing page for your convenience.

Formulators are seeking solvents that impart low viscosities to the coating systems. DOW glycol ethers with hydrogen bonding parameters ranging from 10.9 to 16.6 and solubility parameters ranging from 8.7 to 11.4 are compatible with a wide range of resins having similar parameters. The DOW glycol ether products are, therefore, very effective in providing low viscosity systems.

DOW glycol ether products are classified as medium to slow evaporating solvents, with evaporation rates ranging from 0.7 to <0.001 (where butyl acetate = 1). This evaporation range allows formulators to select the appropriate glycol ether or acetate for the coating formulation and application conditions to ensure that the DOW glycol ether product is the last component out of the curing film. This reduces the possibility of solvent popping, resin blush, and orange peel, while providing excellent flow and leveling.

Glycol ethers exhibit low surface tensions. When they are incorporated into coating systems,
they enhance the “wettability” of the coating and thus improve adhesion to the substrate.

DOW glycol ether products are powerful solvents, and can accommodate dilution with large quantities of latent solvent before losing their ability to maintain the resin and diluents in solution. Because latent solvents are usually less expensive than active solvents, the high dilution ratios of DOW glycol ether products can translate into lower costs to the formulator.

A wide range of DOW glycol ether products finds use in high-solids coatings. The selection of the appropriate DOW glycol ether product for a coating typically depends on the resin type, final use for the coating, application technique, and curing procedure. DOWANOL PM, DPM, TPM, PMA, DPMA, PnP, DPnP, PnB, Butyl CELLOSOLVE, Butyl CARBITOL, Butyl CELLOSOLVE Acetate, Butyl CARBITOL acetate, and Methyl CARBITOL glycol ethers all find use in high-solids, solvent-based coatings.

Table 2: Solubility of Typical Coatings Resins in DOW Glycol Ether and PROGLYDE* Products

RESIN SOLUBILITY†																	
	DOWANOL*																
COMPOUND	PM	DPM	TPM	PMA	DPMA	PnP**	DPnP**	TPnP**	PnB**	DPnB**	TPnB**	PPh	DMM**	Eph	BuCs[1]	BuCb[2]	MeCb[3]
Acrylic Acryloid[4] B-66	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Acryloid B-72	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Acryloid B-82	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Elvacite[5] 2010	•	*	■	•	*	°	°	°	°	°	°	*	°	*	°	*	•
Alkyd Plexal[6] P65**	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Cellulosic CAP-482-0.5[7]	•	•	•	•	•	•	°	°	•	°	°	■	°	■	•	•	•
Elastomer Hycar[8] 1052**	°	°	°	•	•	°	°	°	°	°	°	•	°	•	°	•	°
Epoxy D.E.R.* 331	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
D.E.R. 661	•	•	°	•	•	•	°	°	•	°	°	•	°	•	•	•	•
Melamine Cymel[9] 300**	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Isocyanate Desmodur[10] N100	•[12]	•[12]	•[12]	•	•	•[12]	•[12]	•[12]	•[12]	•[12]	•[12]	•[12]	•	•[12]	•[12]	•[12]	•[12]
Nitrocellulose R.S. ½ sec.	•	•	•	•	•	•	°	°	•	°	°	■	°	■	•	•	•
Phenoxy UCAR[11] PKHH**	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Polyamide Versamid 930**	°	•	•	°	°	•	•	•	•	•	•	•	°	•	•	•	•
Polyester Desmophen[12] 850**	•	•	°	•	°	•	°	°	•	°	°	•	°	•	•	•	•
Cargill 5781[13]	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Vinyl UCAR VYHH	°	°	°	•	■	°	°	°	°	°	°	■	°	*	°	°	■

† METHOD: Solubility observations were made after 0.5 g resin and 4.5 ml solvent were agitated for 24 hours. Exceptions, which were calculated via Chemcomp are noted by **.

*Trademark of The Dow Chemical Company

[1] Butyl CELLOSOLVE™

[2] Butyl CARBITOL™

[3] Methyl CARBITOL™

[4] Acryloid Trademark of Rohm & Haas Company

[5] Elvacite Trademark of I.C.I.

[6] Plexal Trademark of Polyplex Polymers Corporation

[7] Available from Eastman Chemical Company

[8] Trademark of BF Goodrich

[9] Trademark of CYTEC Industries Inc.

[10] Trademark of Bayer Corporation

[11] Trademark of Union Carbide Corporation

[12] Trademark of Henkel Corporation

[13] Product no longer available

[14] Soluble, but use reccomended only with non-reactive aprotic solvents, DOWANOL PMA, DOWANOL DPMA, or PROGLYDE DMM.

• Soluble

* Partially soluble, some undissolved gel particles

■ Partially soluble, many undissolved gel particles

° Insoluble

Conventional Solids For the purpose of this discussion, conventional (low-solids) solventbased coating systems are defined as coatings containing less than 60% solids by volume. A variety of resin types (e.g. alkyd, epoxy, polyester) can be formulated as conventional coatings.

The major uses for conventional solvent-based coatings are in coil coatings, metal and wood furniture, automotive coatings, machinery finishes, and refinishing.

Conventional coatings may be classified as thermoplastic or thermoset. Thermoplastic coatings dry solely by evaporation of the solvent from the coating. Thermoset coatings cure by a chemical or physical change such as air oxidation or crosslinking reactions during film formation.

The most significant thermoplastic coating systems are made from nitrocellulose and acrylic ester resins. Thermoset coatings are typically made from polyester, acrylic, epoxy, or polyurethane resins.

Selection of the right DOW glycol ether product for a conventional coating depends heavily on the way the system will be cured. For ambient systems, DOWANOL PM, DPM, PMA, Butyl CELLOSOLVE acetate and Butyl CELLOSOLVE glycol ethers are predominantly used. Butyl CARBITOL, Butyl CARBITOL Acetate and DOWANOL DPMA, glycol ethers may find use as tailing solvents in some conventional coatings (for example, coil coatings) that are cured at very high oven temperatures.

All of these solvents are excellent solubilizers for the range of resins used in conventional coating formulations. In addition, they offer moderate evaporation rates, which make them appropriate for coatings applied under either ambient or force-dried conditions.

All of the above-mentioned DOW glycol ether products have high dilution ratios. Alone or in blends, they can accommodate dilution by large volumes of low cost hydrocarbon solvents and still maintain complete resin solubility.

Because of their high solvency, moderate evaporation rates, and surface tension lowering capability, the DOW glycol ether products help prevent coating defects such as moisture and resin blush, pinholing, orange peel, cracking, and popping.

Acrylic Polymerization Acrylic coatings are widely used in metal finishing and other applications that require high durability and toughness, UV stability, water resistance, and high gloss.

Preliminary research findings show that DOWANOL PMA aids in producing acrylic polymers. Experiments have shown that excellent results are possible with only slight system modifications when using DOWANOL PMA.[4]

DOWANOL PMA glycol ether provides the following benefits in acrylic polymerizations:

- Broad range of solvency for most resin types (fewer solvents to inventory).
- Moderate evaporation rate.
- Commercial availability.
- Moderate price.
- Favorable toxicity characteristics.

[4] N.T. Hebert and N.H. Morris. “Propylene Glycol Methyl Ether Acetate as a Solvent for Acrylic Solution Polymerization,”
presented at Federation of Societies for Coatings Technology, Nov. 5-7, 1986, Atlanta, GA.