Cyclic Organic Carbonates Serve as Solvents and Reactive Diluents

Their high polarity, high flash point, low toxicity and biodegradability exempt them from many air quality restrictions. They also plasticize and flexibilize.

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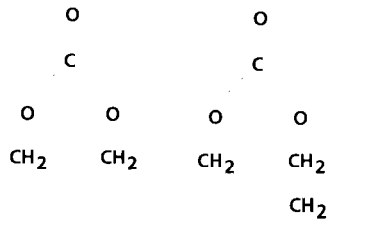
CYCLIC ORGANIC carbonate compounds, such as ethylene carbonate (EC) and propylene carbonate (PC), are now becoming more readily available on a worldwide basis. These polar materials are also finding a variety of applications as components of paint and coatings formulations. Such applications include solvents, additive modifiers and reactive diluents. The chemical structures of EC and PC are shown below and their physical properties are listed in Table 1.



Ethylene Carbonate (EC) Propylene Carbonate (PC)

The cyclic carbonate structure of EC and PC contributes to their high polarity[1], high flash points, low toxicity[2] and biodegradability[3]. As a result, these products are exempt from many air pollution ordinances, such as Rule 66. In addition, these physical characteristics contribute to the broad solvency power that enables these carbonates to function as diluents, compatilibizers and coalescing agents in coating systems.

Because of their relatively high boiling points, these cyclic carbonates are not commonly used as evaporative solvents, but are used along with other solvents and water to form safe solvent systems, which are employed in baked coatings that require a gradual removal of the solvent as the baking temperature is increased (example in Table 2[11]). In these formulations, the carbonates function as tail solvents or may remain in the coating as a plasticizer, flexibilizer or flow control aid. In addition, the carbonates are used with other solvents and water to produce safe paint-stripping and cleaning agents [4].

Many surface coating compositions contain bentonite or montmorillonite clay gellants to provide thixotropic properties. These gellants often resist wetting by most organic liquids used in the formulations. This may cause extended mixing times and poor gellant efficiency. In the past, polar additives, such as ethanol, methanol or acetone were used to improve clay gellant wetting. However, PC is superior to these additives with regard to its degree of polarity and resultant methanol. Since only one or two pounds of PC are required for each 100 gallons of surface coating, the cost of this additive is most efficient in terms of the decreased mixing times and improved gellant performance.

Propylene carbonate was used to lower the raw material cost of a low-VOC acrylic polyether modified urethane used as a topcoat over an epoxy primer, for a 10-mils total. The formulation shown in Table 3 is suitable for a high-gloss topcoat with good gloss and color retention.

Formulators of reactive amine-cured epoxy systems were able to reduce viscosity, decrease gel time and improve mechanical properties (tensile, flex strength and modulus) of the cured resin by adding an alkylene carbonate, such as EC, PC or glycerine carbonate. The HDT, Tg and chemical resistance were lowered, about the same as if the systems were modified with glycidyl ether.

TABLE 1 CARBONATE PROPERTIES

Property	Ethylene Carbonate	Propylene Carbonate
Density lb/gal.	10.9	10.0
Boiling point, °C	248.2	241.9
Flash point, °F	320	275
V.P> mm Hg, 20°C	<0.02	0.02
Melting point, °C	36.4	-49.2

Table 2 Epoxy Phenolic High Bake Coil Coating Formulation

Component	lbs.
Araldite 7097 Epoxy Resin	15.3
Duralite P-97 Phenolic Resin	30.7
Methyl Isobutyl Ketone	9.1
Propylene Carbonate	18.5
Toluene	13.2
n-Butanol	13.2
	100

Solids=30.8%

Cured 15 minutes @ 375°F

TABLE 3
2.07 LB/GAL VOC ACRYLIC POLYETHER MODIFIED URETHANE MANUFACTURE IN A MEDIA MILL

Part A	Lbs.	Gals.
Desmophen LS-2945 (Miles)	149.90	17.41
TT-400 Polyether (Huntsman Corp.)	39.76	4.62
TiPure R-902 (DuPont)	164.00	4.92
T-12 (1% in N.Butyl Acetate (Air Products)	2.10	.31
MPA 2000X (Rheox)	6.31	.86
JEFFSOL Propylene Carbonate (Huntsman)	9.80	.99
Grind above to 7+NS		
PM Acetate (Eastman)	31.67	3.93
Xylene	50.00	6.90
	453.54	39.94
Part B		
Desmodur N3390 (miles)	156.50	16.65
PM Acetate(Eastman)	23.93	2.97
	180.43	19.62

Depending on the specific job to be accomplished, several solvent systems are possible replacements for the above commonly used solvents. A list of several good alternate carbonate-containing binary systems are listed below:

1,1,1-TCE or Toluene/MEK or Toluene/MIBK Replacements

Solvent Compounds	*Wt.Rations*	
PC/PM	*PC (20-50)*	*PM (50-80)*
PC/DPM	*"""*	*DPM ""*
PC/TPM	*"""*	*TPM ""*
PC/DB	*"""*	*DB ""*
PC/DBE (DuPont)	*"""*	*DBE ""*
PC/DEC	*" (25)*	*DEC (75)*
PC/IBIB	*" (20)*	*IBIB (80)*
PC/PMA	*" (30)*	*PMA (70)*

PM=propylene glycol methyl ether
DPM=dipropylene glycol methyl ether
TPM=tripropylene glycol methyl ether
DB=diethylene glycol butyl ether
DBE=dibasic ester mixture from DuPont
DEC=diethyl carbonate
IBIB=isobutylisobutyrate
PMA=propylene glycol methyl ether acetate

Along with the above binary solvent system there are several three component solvent systems which will satisfactorily replace 1,1,1-TCE, toluene/MEK or toluene/MIBK. The d-limonene mentioned in these ternary system can be substituted with SCM Glidco's d-limonene 145 without loss of solvent power. The odor remains low.

In addition to being excellent solvents and compatibilizers for paints and coatings, the cyclic organic carbonates are also reactive with a number of active hydrogen compounds, including amines, alcohols, water and carboxylic acids. This permits use as additives to scavenge or reduce the levels of small quantities of such unwanted materials in paint and coating formulations. These general reactions are summarized in Fig.1.

Since the carbonates are not reactive with epoxy resins, isocyanates or polyesters, they may be used as diluents that will then be reactive with alcohols, water, amines or other materials in a second component. The resulting formulations may even have improved properties as a result of the compounds or resin extensions that are possible from the opening of the carbonate ring. Some specific examples are outlined below.

Alexander [5] has used both EC and PC as reactive diluent in epoxy resin systems. The carbonate is added to the epoxy resin or A component, thus lowering the viscosity as shown in Fig.2. This mixture is cured with aliphatic amines at an enhanced reaction rate due to the formation of hydroxyalkyl carbamates, which in turn cure the epoxy resin matrix in accelerated fashion. In some cases, resin properties are enhanced as well, but crosslink density is diminished. High-build coatings for floors and other applications could benefit from this application of carbonates, which are much less expensive and lower in toxicity than glycidyl ether diluents.

A development chemist has formulated an interesting polyurea spray coating that includes an alkylene carbonate in the A component containing a quasi-prepolymer prepared from an isocyanate and a polyol or other active hydrogen compound. The viscosity of the A component is reduced by a carbonate, such as PC, EC or butylene carbonate (BC). The cyclic carbonate also serves as a compatibilizer between the A component and a B component containing an amine-terminated polyether. In addition to these processing characteristics, the physical properties of the resulting coating are believed to be enhanced by the presence of the reaction products of the cyclic carbonate with the amine resin.

FIGURE 1

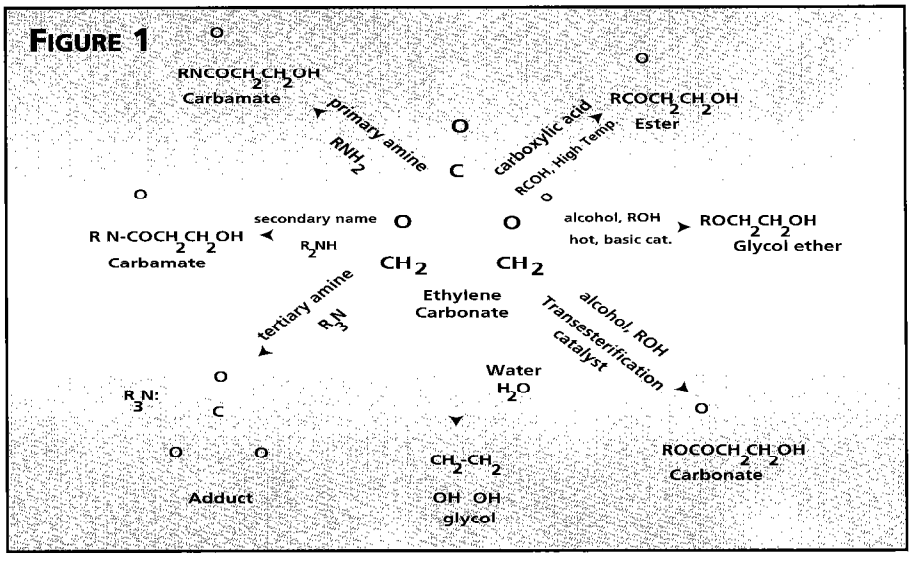
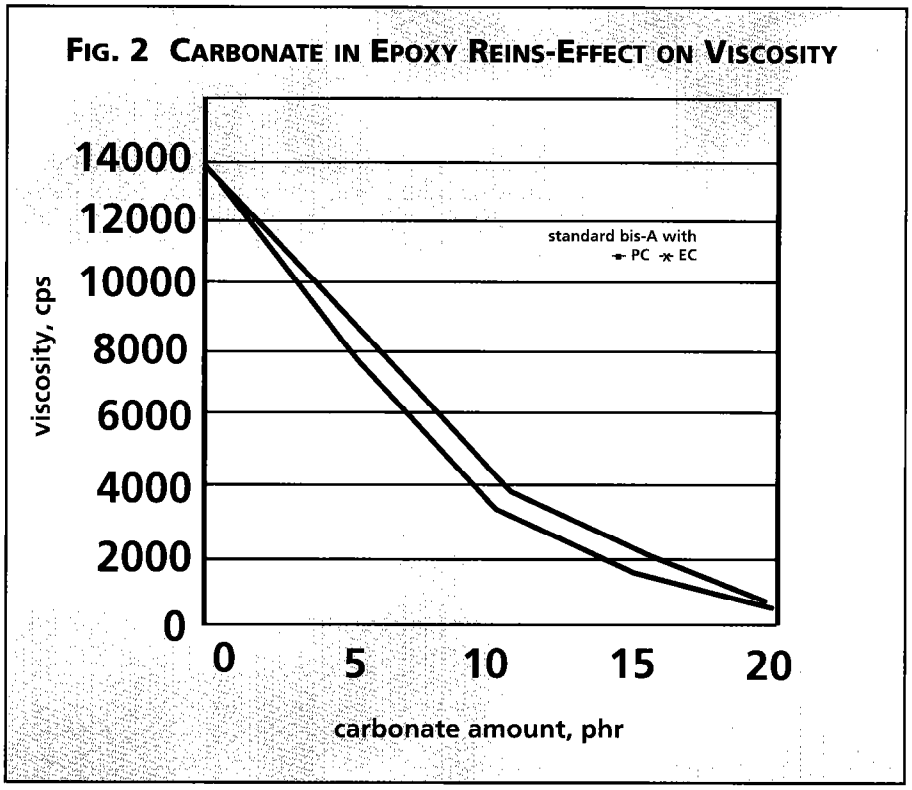


FIG. 2 CARBONATE IN EPOXY REINS-EFFECT ON VISCOSITY



Barker et.al.[9] have shown that the use of a cyclic carbonate as a reactive diluent and polar activator can be instrumental in improving the performance efficiency of polyurethane coatings and adhesives used on wood chip composites.[10] Such compositions provide good substrate adhesion, exhibit a desirable re-gel time and can be more easily spray applied. Cyclic carbonates have also been cited as coalescing agents in latex paint formulations.

There are several other products that may be used with the cyclic carbonates in coating applications. These include dibasic esters (DBE, isophorone, glycol ether acetates, N-methyl pyrrolidone (NMP) and dimethylformamide (DMF). However, none of these solvents has all the qualities of solvent power, low toxicity, biodegradability and cost effectiveness of the cyclic carbonates discussed here. In some cases, a combination of solvents will give the best fit for an existing solvent that for some reason is not desirable for a particular situation or circumstance. ■

References:

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