ABSTRACT

The global desire to reduce VOC emissions in solvent-borne coatings can be driven by environmental legislation, customer specifications, or by reasons related to performance and productivity. High solids binder systems are important to achieve these objectives, yet often come with the penalty of higher viscosity. This paper describes simple ways to produce low viscosity, high solids acrylic and polyester polyols based on glycidyl neodecanoate. This paper also discusses improvements in the properties of coatings formulated with polymers based upon this glycidyl ester.

INTRODUCTION

In the 1950's, Dr. Herbert Koch from the Max Plank Institute in Mülheim, Germany, found that olefins may react with carbon monoxide and water under the influence of strong acids to form tertiary branched neocarboxylic acids (Figure 1). Before the intermediate carbocation reacts with carbon monoxide, isomerization reactions are observed and, therefore, the resulting acid is composed of a number of isomers\textsuperscript{1, 2}.

![Figure 1. Koch reaction for the production of neo-acids.](image)

These neocarboxylic acids can be converted into their glycidyl esters by reaction with epichlorohydrin. Today, this monomer is marketed under the trade name Cardura™ E10P glycidyl ester and may also be referred to in industry as glycidyl versatate or glycidyl neodecanoate.

Cardura™ E10P glycidyl ester (Figure 2.) is a highly versatile molecule containing a reactive epoxy group, and a very hydrophobic and highly branched tertiary substituted α-carbon structure. The epoxy group is used to incorporate the molecule into the polymers in which it is used through reaction with carboxylic acid groups\textsuperscript{3}, and the neodecanoate group imparts outstanding performance characteristics. Enhancements that are realized by
incorporation of Cardura™ E10P glycidyl ester into polymers include excellent acid resistance, superior wet look appearance, very good weatherability, and low viscosity, which enables the production of polymers which are amenable to use in high solids, low viscosity coating systems.

Figure 2: Cardura™ E10P glycidyl ester, \( R^1 + R^2 = C_7H_{16} \)

**ACRYLIC POLYOL RESINS**

In order to manufacture acrylic polyol resins at high solids content and reasonable viscosity, the molecular weight of the acrylic polymer needs to be reduced. A very practical and economic way to produce a low molecular weight acrylic polyol polymer is to polymerize at high temperatures. Cardura™ E10P glycidyl ester can be used as a reactive solvent and processing medium for conducting the free radical polymerization of acrylic or methacrylic monomers, thus either replacing partly or entirely the solvent that would normally be used as a process medium in the reactor. Because of its very high boiling point (>250°C), the use of Cardura™ E10P glycidyl ester allows high polymerisation temperatures to easily be reached. The maximum achievable polymerisation temperature is a function of the ratio between the Cardura™ E10P glycidyl ester and the conventional solvent present in the initial reactor charge as shown in Figure 3.

Figure 3: Boiling point of the Cardura™ E10P glycidyl ester/solvent mixture as function of the composition of the initial reactor charge.
Cardura™ E10P glycidyl ester is incorporated into the polymer backbone by reacting its epoxy functionality with acrylic acid or methacrylic acid present in the monomer mixture. The glass transition temperature for the homopolymers of the adducts of Cardura™ E10P glycidyl ester with acrylic acid and methacrylic acid are 3°C and 33°C respectively.

During the synthesis of an acrylic polyol resin containing Cardura™ E10P glycidyl ester, two reactions occur simultaneously: a conventional radical polymerisation of the acrylic monomers and the reaction of the Cardura™ E10P glycidyl ester with acrylic or methacrylic acid present in the monomer mixture. Cardura™ E10P glycidyl ester is thus gradually incorporated into the polymer via the epoxy-acid reaction while peroxide or azo initiated radical polymerisation occurs as shown in Figure 4.

In addition, the reaction between Cardura™ E10P glycidyl ester and the carboxylic acid generates a hydroxyl group. In this way, Cardura™ E10P glycidyl ester allows for the partial replacement of other hydroxyl functional monomers. The hydroxyl groups generated by the epoxy opening reaction serve as reactive sites for subsequent crosslinking with materials such as isocyanates or aminoplasts.

![Figure 4: Preparation of Cardura™ E10P glycidyl ester based acrylic polyol resin, simultaneous free radical polymerization and esterification reactions.](image)

The presence of the bulky ester group of Cardura™ E10P glycidyl ester grafted to the polymer backbone functions as a spacer between adjacent polymer chains and therefore weakens hydrogen bonds and other inter-molecular forces between them. Consequently, the resulting acrylic polyol resin will have a lower viscosity. The efficiency of viscosity reduction in a given acrylic polyol resin is a function of the amount of Cardura™ E10P glycidyl ester used in the composition.
To demonstrate the viscosity reducing effect of the incorporation of Cardura™ E10P glycidyl ester in acrylic polyols, a series of polymers with varying levels of Cardura™ E10P glycidyl ester content were synthesized at identical $T_g$'s and molecular weights. Levels of 0%, 20%, and 30% Cardura™ E10P glycidyl ester were evaluated in two different molecular weight regimes: 3000 daltons and 5500 daltons (weight average). The $T_g$'s for the polymers at 3000 daltons were ~15°C and the $T_g$'s for the polymers at 5500 daltons were ~27°C. Both sets of polymers were evaluated for viscosity at various solids levels and the dramatic viscosity reducing effect of Cardura™ E10P glycidyl ester can clearly be seen at all solids levels evaluated (Figures 5 and 6). Additionally, the viscosity reduction effect increases with increasing Cardura™ E10P concentration and is even more pronounced at higher molecular weights.

**Figure 5.** Viscosity of polymers with varying levels of Cardura™ E10P glycidyl ester with molecular weights of 3000 daltons shown at various solids levels.

**Figure 6.** Viscosity of polymers with varying levels of Cardura™ E10P glycidyl ester with molecular weights of 5500 daltons at various solids levels.
In addition to its viscosity reducing effect, Cardura™ E10P glycidyl ester also has a very pronounced effect on the solubility of polyols in which it is used, improving the compatibility with lower cost aliphatic solvents. To demonstrate this effect, two acrylic polyols containing different levels of Cardura™ E10P glycidyl ester were blended with odorless mineral spirits. The first acrylic polyol contains no Cardura™ E10P glycidyl ester and the second contains 30% Cardura™ E10P glycidyl ester on total monomer; both systems are 70% solids in aromatic 100 solvent. When 10 weight percent odorless mineral spirits is added to the two samples, the difference in solubility becomes very apparent (Figure 7).

![Figure 7. Post addition of mineral spirits to 70% NVM acrylic polyols with and without Cardura™ E10P glycidyl ester.](image)

**POLYESTER POLYOL RESINS**

Cardura™ E10P glycidyl ester is also a versatile building block for the synthesis of polyester-polyol resins and delivers a number of advantages in resin processing:

- Cardura™ E10P glycidyl ester can be used as an acid scavenger at the end of the reaction, thus reducing batch cycle time and narrowing the molecular weight distribution of the resulting polyester.

- The ring opening reaction between the epoxy group and the carboxyl group occurs at lower temperature and is therefore more selective compared to the reaction between a hydroxyl group and a carboxyl group.

- The ring opening reaction between the epoxy group and the carboxyl group will not generate water and consequently the batch cycle time can be reduced as there will be less or no water to be removed.

- Polyesters synthesized by sequential ring opening reactions between epoxy and carboxyls and anhydrides can be conducted in reactors without fractionating columns since no water is evolved during this process (Figure 8).
Polyesters synthesized with Cardura™ E10P glycidyl ester also have performance advantages over other polyesters. The bulky neodecanoate side group that is incorporated into the polyester by Cardura™ E10P glycidyl ester imparts excellent hydrolytic stability to the polymer by sterically shielding neighboring ester groups. This shielding effect also results in increased acid and environmental etch resistance, which is crucial for melamine cross-linked coatings that have stringent weathering requirements, such as those found in automotive OEM applications.

**ACRYLIC POLYOL / STAR POLYESTER POLYOL BLENDS**

Currently, there is a trend to formulate high quality high solids clearcoats and pigmented topcoats for transportation and industrial applications to comply with ever more stringent VOC regulations. These high solids formulations require the use of high solids acrylic polyol resins which exhibit adequate hardness development upon curing and excellent appearance characteristics as well as resistance to weathering. These properties
can be achieved by blending a high solids acrylic polyol resin with a specific type of polyester resin, referred to as a star polyester. The polymer depicted in Figure 8 is an example of one such star polyester. This molecule is synthesized from 1 mole of pentaerythritol, 3 moles of hexahydrophthalic anhydride, and 3 moles of Cardura™ E10P glycidyl ester.

Star polyester resins are characterized by a combination of low molecular weight (<2000 Daltons) and a relatively high hydroxyl value. These star polyesters combine ideal properties to lower the VOC without significantly affecting the drying speed of 2K polyurethane systems, as they exhibit low molecular weight and a very homogenous distribution of primary hydroxyl groups. Therefore, star polyesters are an ideal choice of for blending with acrylic polyols for high solids clearcoats and pigmented top coats.

**ACRYLIC POLYOL AND POLYESTER POLYOL – HYBRIDS**

In addition to being excellent blending resins, star polyesters can be used in the initial reactor charge for the synthesis of acrylic polyol resins. The resulting hybrid polyol polymers show a good balance of properties.

As can be seen in Figure 9, the average molecular weight peak of these hybrids is lower than that of similar products prepared by blending the acrylic and the polyester resin. The molecular weight peak values of the acrylic polyol and of the polyester shift to lower and higher values respectively because of the hybrid polymerisation.

![Figure 9: Molecular weight of resins as a function of the synthetic technique.](image)

**CLEARCOAT PERFORMANCE**

Starting formulations for 2K urethane refinish clearcoats were tested and the results are presented in Figure 10. In case of blends or hybrids, the ratio between the acrylic polyol resin and the star polyester resin was 75/25 on weight solids.
One can see that blending allows a reduction of VOC at the same viscosity in the clearcoat formulation when compared to the use of acrylic polyol resin alone. Moreover, the hybrid technology enables the resin producer to use even lower amounts of solvent. In the case of hybrid technology, the dust-free time increases and hardness after 24 hours decreases. These effects can be easily controlled by the appropriate design of an acrylic polyol with higher $T_g$ and a polyester with higher $T_g$.

A higher value of distinctness of image (DOI) of the clearcoat is observed for the blending technology compared to the use of the acrylic polyol resin alone. In addition, even higher DOI values can be achieved by using the hybrid technology instead of blending.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Cardura™ based acrylic polyol</th>
<th>Cardura™ based acrylic polyol / star polyester blend</th>
<th>Cardura™ based acrylic polyol / star polyester hybrid</th>
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<td>Leveling agent</td>
<td>BYK™ 331 at 0.07% on solids</td>
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<td>Clearcoat properties</td>
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<td>DOI at 60 µm</td>
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![Figure 10. Clearcoat formulation and properties as function of the technology.](image-url)
CONCLUSION

Cardura™ E10P glycidyl ester is the ideal choice for the production of high performance acrylic and polyester polyols for high solids clearcoats and pigmented topcoats for transportation and industrial applications.

The use of Cardura™ E10P glycidyl ester simplifies the process of synthesizing high solids acrylic polyols and polyester resins with low molecular weights and narrow molecular weight distributions, thereby making it easier to produce market competitive high solids polymers. The advantages of producing resins with lower molecular weight and higher solids content can be maximized through physical blending of acrylic polyols and star polyesters or by chemical grafting.

In addition to the advantages in resin processing, the use of Cardura™ E10P glycidyl ester containing resins allows the coatings formulator to develop long lasting finishes with outstanding properties including excellent weathering and environmental etch resistance, broader solvent solubility, very high DOI and appearance, and more - all at high solids and reduced VOC.

REFERENCES

1. “Production of carboxylic acids from olefins”, Herbert Koch. US patent 2,831,877, filed 17 March 1952,

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