Polyether Polyol Resins Compositions

Abstract:
The invention relates to compositions of polyether polyol resins (hydroxyfunctional oligo or poly ether) comprising a mixture of 9,9-branched alkane carboxylic glycidyl esters derived from butene oligomers characterized in that the sum of the concentrations of the blocked and of the highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.
POLYETHER POLYOL RESINS COMPOSITIONS

The present invention relates to a composition of polyether polyol resins comprising a mixture of $\alpha,\alpha$-branched alkane carboxylic glycidyl esters derived from butene oligomers characterized in that the sum of the concentration of the blocked and of the highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.

More in particular the invention relates to polyether polyol resins compositions comprising of aliphatic tertiary saturated carboxylic acids or $\alpha,\alpha$-branched alkane carboxylic acids, which contain 9 or 13 carbon atoms and which provide glycidyl esters with a branching level of the alkyl groups depending on the olefin feedstock used and/or the oligomerisation process therof, and which is defined as below.

The glycidyl ester derived from propene or containing 5 carbon atoms in the alkyl chain are used by the industry to introduce modified resins by reaction such a glycidyl ester with polyols. US 5,051,492 is about the process to prepare such a modified resins using metal salt to carry out the etherification reaction of a polyol and a 10 carbon chain alkyl glycidyl ester. The WO2007/041633 introduce the modification of C5 glycidyl ester, which as for effect to provide a coating composition with a low content of volatile organic compounds. The same technical approach was given in US 2007/0117938.
It is generally known from e.g. US 2,831,877, US 2,876,241, US 3,053,869, US 2,967,873 and US 3,061,621 that mixtures of \( \alpha,\alpha \)-branched alkane carboxylic acids can be produced, starting from mono-olefins, carbon monoxide and water, in the presence of a strong acid.

One of the more recent method has been disclosed in EP 1033360A1. The problem of providing better softening derivatives of \( \alpha,\alpha \)-branched acids, manufactured from alkenes, carbon monoxide and water and a nickel catalyst was solved therein by a process, which actually comprised:

(a) oligomerisation of butene;

(b) separation of butene dimers and/or trimers from the oligomerisate;

(c) conversion of the butene dimers and/or trimers into carboxylic acids;

(d) conversion of the carboxylic acids into the corresponding vinyl esters showing attractive softening properties when mixed into other polymers or if used as comonomers in coatings.

If the olefin feed is based on Raf. II or Raf III or any mixture rich in n-butene isomers on the total olefins, the subsequently mixture of neo-acid (C9 or C13 acids) derivatives will provide a mixture where the concentration of blocked and highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30%.

The glycidyl esters can be obtained according to PCT/EP2010/003334 or the US6433217.
We have discovered that well chosen blend of isomers of the glycidyl ester of mixture compositions of neo-acid (C9 or C13 acids) glycidyl ester, is providing for example a good leveling of a coating, is a mixture where the sum of the concentration of blocked and highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.

We have further discovered that well chosen blend of isomers of the glycidyl ester of, for example, neononanoic acids give different and unexpected performance in combination with some particular polymers such as polyether polyols.

The isomers are described in Table 1 and illustrated in Scheme 1.

We have found that the performance of the glycidyl ester compositions derived from the branched acid is depending on the branching level of the alkyl groups R1, R2 and R3, for example the neononanoic acid has 3, 4 or 5 methyl groups. Highly branched isomers are defined as isomers of neo-acids having at least 5 methyl groups.

Neo-acids, for example neononanoic acids (V9) with a secondary or a tertiary carbon atoms in the β position are defined as blocking isomers.

Mixture compositions of neononanoic (C9) acids glycidyl esters providing for example a good leveling of a coating, is a mixture where the sum of the concentration of the blocked and of the highly branched isomers derivatives is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.
Furthermore the above compositions of neononanoic acids glycidyl esters mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester or 2-methyl 2-ethyl hexanoic acid glycidyl ester or 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters.

Furthermore the above compositions of neononanoic acids glycidyl esters mixture is comprising 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) below 40%, preferably below 30% and most preferably below or equal 25% weight on total composition.

Furthermore the above compositions of neononanoic acids glycidyl esters mixture is comprising 2-methyl 2-ethyl hexanoic acid glycidyl ester above 10%, preferably above 30% and most preferably above 45% weight on total composition.

The above compositions of the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester and 2-methyl 2-ethyl hexanoic acid glycidyl ester and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) is above 40%, preferably 55% and most preferably 65% weight on total composition.

A preferred composition is comprising a mixture of 2,2-dimethyl heptanoic acid glycidyl ester in 1 to 15 weight% and 2-methyl 2-ethyl hexanoic acid glycidyl ester in 40 to 70 weight% and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) in 8 to 32 weight% on total composition.

A further preferred composition is comprising a mixture of 2,2-dimethyl heptanoic acid glycidyl ester in 2 to 10 weight% and 2-methyl 2-ethyl hexanoic acid glycidyl ester
in 47 to 61 weight% and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) in 10 to 25 weight% on total composition.

The above glycidyl esters compositions can be used for example, as reactive diluent or as monomer in binder compositions for paints or adhesives.

The glycidyl esters compositions can be used as reactive diluent for epoxy based formulations such as exemplified in the technical brochure of Momentive (Product Bulletin: Cardura E10P The Unique Reactive Diluent MSC-512).

Other uses of the glycidyl ester are the combinations with polyester polyols, or acrylic polyols, or polyether polyols. The combination with polyether polyols such as could be used in the car industry coating leads to coating system with attractive coating appearance.

Methods used

The isomer distribution of neo-acid can be determined using gas chromatography, using a flame ionization detector (FID). 0.5 mL sample is diluted in analytical grade dichloromethane and n-octanol may be used as internal standard. The conditions presented below result in the approximate retention times given in table 1. In that case n-octanol has a retention time of approximately 8.21 minute.

The GC method has the following settings:
Column: CP Wax 58 CB (FFAP), 50 m x 0.25 mm, df = 0.2 µm
Oven program : 150°C (1.5 min) - 3.5°C/min - 250°C (5 min) = 35 min
Carrier gas: Helium
Flow : 2.0 mL/min constant
Split flow : 150 mL/min
Split ratio: 1:75
The isomers of neononanoic acid as illustrative example have the structure \((R^1 R^2 R^3)\text{C-COOH}\) where the three \(R\) groups are linear or branched alkyl groups having together a total of 7 carbon atoms.

The structures and the retention time, using the above method, of all theoretical possible neononanoic isomers are drawn in Figure 1 and listed in Table 1. The isomers content is calculated from the relative peak area of the chromatogram obtained assuming that the response factors of all isomers are the same.

| V901 | Methyl | Methyl | n-pentyl | 3 | No | 8.90 |
| V902 | Methyl | Methyl | 2-pentyl | 4 | Yes | 9.18 |
| V903 | Methyl | Methyl | 2-methyl butyl | 4 | No | 8.6 |
| V904 | Methyl | Methyl | 3-methyl butyl | 4 | No | 8.08 |
| V905 | Methyl | Methyl | propyl | 5 | Yes | 10.21 |
| V906 | Methyl | Methyl | propyl | 5 | Yes | 9.57 |
| V907 | Methyl | Methyl | propyl | 5 | No | 8.26 |
| V908 | Methyl | Methyl | 3-pentyl | 4 | Yes | 9.45 |
| V909 | Methyl | Ethyl | n-butyl | 3 | No | 9.28 |
| V910 K1 | Methyl | Ethyl | s-butyl | 4 | Yes | 9.74 |
| V910 K2 | Methyl | Ethyl | s-butyl | 4 | Yes | 9.84 |
| V911 | Methyl | Ethyl | i-butyl | 4 | No | 8.71 |
| V912 | Methyl | Ethyl | t-butyl | 5 | Yes | 9.64 |
| V913 | Methyl | n-propyl | n-propyl | 3 | No | 8.96 |
| V914 | Methyl | n-propyl | i-propyl | 4 | Yes | 9.30 |
| V915 | Methyl | i-propyl | i-propyl | 5 | Yes | 9.74 |
| V916 | Ethyl | Ethyl | n-propyl | 3 | No | 9.44 |
| V917 | Ethyl | Ethyl | i-propyl | 4 | Yes | 10.00 |

Table 1: Structure of all possible neononanoic isomers
The isomer distribution of glycidyl esters of neo-acid can be determined by gas chromatography, using a flame ionization detector (FID). 0.5 ml sample is diluted in analytical grade dichloromethane.

The GC method has the following settings:

Column: CP Wax 58 CB (FFAP), 50 m x 0.2 mm, df = 0.52 µm
Oven: 175°C (5 min) - 1°C/min - 190°C (5 min) - 10°C/min - 275°C (11.5 min)
Flow: 2.0 mL/min, constant flow
Carrier gas: Helium
Split ratio: 1:75
Injection volume: 1 µL
S/SL injector: 250°C

CP Wax 58 CB is a Gas chromatography column available from Agilent Technologies.

The isomers of glycidyl esters of neononanoic acid as illustrative example have the structure \((R^1 R^2 R^3)\cdot C\cdot COO\cdot CH_2\cdot CH(0)CH_2\) where the three R groups are linear or branched alkyl groups having together a total of 7 carbon atoms.

The isomers content is calculated from the relative peak area of the chromatogram obtained assuming that the response factors of all isomers are the same.

GC-MS method can be used to identify the various isomers providing that the analysis is done by a skilled analytical expert.
**Scheme 1: Structure of all possible neononanoic isomers**

![Diagram of Scheme 1: Structure of all possible neononanoic isomers](image-url)
Methods for the characterization of the resins

The molecular weights of the resins are measured with gel permeation chromatography (Perkin Elmer/ Water) in THF solution using polystyrene standards. Viscosity of the resins are measured with Brookfield viscometer (LVDV-I) at indicated temperature. Solids content are calculated with a function \((W_w - W_d) / W_w \times 100\%\). Here \(W_w\) is the weight of a wet sample, \(W_d\) is the weight of the sample after dried in an oven at a temperature 110 °C for 1 hour.

\(T_g\) (glass transition temperature) has been determined either with a DSC 7 from Perkin Elmer or with an apparatus from TA Instruments Thermal Analysis. Scan rates were respectively 20 and 10°C/min. Only data obtained in the same experimental conditions have been compared. If not, the temperature difference occurring from the different scanning rate has been proved not significant for the results compared.
Blocking isomers

Whereas the carbon atom in alpha position of the carboxylic acid is always a tertiary carbon atom, the carbon atom(s) in opposition can either be primary, secondary or tertiary. Neononanoic acids (V9) with a secondary or a tertiary carbon atoms in the p position are defined as blocking (blocked) isomers (Schemes 2 and 3).

Scheme 2: Example of a Non-blocked V9 Structure

Scheme 3: Example of a Blocked V9 Structure

The use of the glycidyl esters compositions, discussed here above, can be as monomer in binder compositions for paints and adhesives. These binders can be based on a polyether polyol resin comprising the above composition glycidyl.

The polyether polyl resins of the invention are based on a composition of hydroxyl functional polyether resins (polyether polyols) comprising a mixture of α,α-branched alkane carboxylic glycidyl esters derived from butene oligomers characterized in that the sum of the concentration of the blocked and of the highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.
A prefer composition is that the glycidyl ester mixture is based on neononanoic (C9) acid mixture where the sum of the concentration of the blocked and of the highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.

Further the neononanoic (C9) glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester or 2-methyl 2-ethyl hexanoic acid glycidyl ester or 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl ester.

An other embodiment is that the composition of the glycidyl ester mixture is comprising 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) below 40%, preferably below 30% and most preferably below or equal 25% weight on total composition.

A further embodiment is that the composition of the glycidyl ester mixture is comprising 2-methyl 2-ethyl hexanoic acid glycidyl ester above 10%, preferably above 30% and most preferably above 45% weight on total composition.

A further embodiment is that the composition of the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester and 2-methyl 2-ethyl hexanoic acid glycidyl ester and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) is above 40%, preferably 55% and most preferably 65% weight on total composition.

A further embodiment is that the composition of the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester in 1 to 15 weight% and 2-methyl 2-ethyl hexanoic acid glycidyl ester in 40 to 70 weight% and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) in 8 to 32 weight% on total composition.
A further embodiment is that the composition of the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester in 2 to 10 weight% and 2-methyl 2-ethyl hexanoic acid glycidyl ester in 47 to 61 weight% and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) in 10 to 25 weight% on total composition.

The process to prepare the compositions of the polyether polyl resin is by reaction of a polyl selected from for example: trimethylolpropane, di(trimethylolpropane), pentaerythritol, dipentaerythritol, tripentaerythritol, neopentyl glycol, glycerine, ethyleneglycol, cyclohexane dimethylol 1,4, mannitol, xylitol, isosorbide, erythritol, sorbitol, ethylene glycol, 1,2-propylene glycol, 1,2-butylen glycol, 2,3-butylen glycol, 1,2-hexanediol, 1,2-dihydroxycyclohexane, 3-ethoxypropane-1,2-diol and 3-phenoxypropane-1,2-diol; neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butane diol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-phenoxypropane-1,3-diol, 2-methyl-2-phenylpropane-1,3-diol, 1,3-propylene glycol, 1,3-butylen glycol, 2-ethyl-1,3-octanediol, 1,3-dihydroxy cyclohexane, 1,4-butanediol, 1,4-dihydroxy cyclohexane, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 3-methyl-1,5-pentanediol, 1,4-dimethylolcyclohexane, tricyclodecanedimethanol, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate (an esterification product of hydroxy-pivalic acid with neopentyl glycol), 2,2,4-Trimethyl-1,3-pentanediol (TMPD), mixture of 1,3- and 1,4-cyclohexanedi methanol (= Unoxol diol ex Dow Chemicals), bisphenol A, bisphenol F, bis (4-hydroxyhexyl) -2,2-propane, bis (4-hydroxyhexyl)methane, 3,9-bis (1,1-dimethyl-2-hydroxyethyl) -2,4,8,10-tetroxa spiro [5,5]-undecane, di-ethylene glycol, triethylene glycol, glycerine, diglycerine, triglycerine, trimethylol-ethane and tris(2-
hydroxyethyl) isocyanurate. Either pure multifunctional polyol can be used or mixtures of at least two of them.
5 either pure multifunctional polyol can be used or mixtures of at least two of them, and the glycidyl ester mixture as define above.

The polyether polyol resins of the invention prepared according to the above processes will have a number average molecular weight \((M_n)\) lower than 4500 Dalton according the polystyrene standard, and/or the hydroxyl value is above 120 mg KOH/g solids on solid.

The invention is also related to a binder composition useful for coating composition comprising at least any hydroxyl functional polyether resins as prepared above and having a low VOC.

The said binder compositions are suitable for coating metal or plastic substrates.

Examples

Chemicals used
- Cardura™ E10: available from Momentive Specialty Chemicals
- Neononanoic glycidyl ester from Momentive Specialty Chemicals
- GE9S: neononanoic glycidyl ester of composition A (see Table 2)
- GE9H: neononanoic glycidyl ester of composition B (see Table 2)
- Neononanoic glycidyl ester of composition C (see Table 2)
- Neononanoic glycidyl ester of composition D (see Table 2)
- Neononanoic glycidyl ester of composition E (see Table 2)
<table>
<thead>
<tr>
<th>Glycidyl ester of acid V9XX (described in Table 1)</th>
<th>A (%)</th>
<th>B (%)</th>
<th>C (%)</th>
<th>D (%)</th>
<th>E (%)</th>
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<tr>
<td>V901</td>
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<td>3.7</td>
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**Table 2:** Composition of the neononanoic glycidyl ester (according to the described gas chromatography method for glycidyl esters of neo-acid)
- **GE5**: glycidyl ester of pivalic acid obtained by reaction of the acid with epichlorhydrin.
- Ethylene glycol from Aldrich
- Monopentaerythritol: available from Sigma - Aldrich
- 3,3,5 Trimethyl cyclohexanol: available from Sigma - Aldrich
- Maleic anhydride: available from Sigma - Aldrich
- Methylhexahydrophtalic anhydride: available from Sigma - Aldrich
- Hexahydrophtalic anhydride: available from Sigma - Aldrich
- Boron trifluoride diethyl etherate (BF3-OEt2) from Aldrich
- Acrylic acid: available from Sigma - Aldrich
- Methacrylic acid: available from Sigma - Aldrich
- Hydroxyethyl methacrylate: available from Sigma - Aldrich
- Styrene: available from Sigma - Aldrich
- 2-Ethylhexyl acrylate: available from Sigma - Aldrich
- Methyl methacrylate: available from Sigma - Aldrich
- Butyl acrylate: available from Sigma - Aldrich
- Di-t-Amyl Peroxide is Luperox DTA from Arkema
- tert-Butyl peroxy-3,5,5-trimethylhexanoate: available from Akzo Nobel
- Xylene
- n-Butyl Acetate from Aldrich
- Dichloromethane from Biosolve
- Thinner: A: is a mixture of Xylene 50wt%, Toluene 30wt%, ShellSolA 10wt%, 2-Ethoxyethylacetate 10wt%. Thinner B: is butyl acetate
- Curing agents, HDI: 1,6-hexamethylenediisocyanate trimer, Desmodur N3390 BA from Bayer Material Science or Tolonate
- HDT LV2 from Perstorp
- **Leveling agent**: 'BYK 10 wt%' which is BYK-331 diluted at 10% in butyl acetate
- **Catalyst**: 'DBTDL 1 wt%' which is Dibutyl Tin Dilaurate diluted at 1wt% in butyl acetate
- **Catalyst**: 'DBTDL 10 wt%' which is Dibutyl Tin Dilaurate diluted at 10wt% in butyl acetate

**Example 01 comparative**
The following constituents were charged to a reaction vessel:
- 2.5500 grams of a neononanoic glycidyl ester of composition D,
- 1.1571 grams of dichloromethane,
- 0.0137 grams of boron trifluoride diethyl etherate.
The reaction took place for 3 days at room temperature and the solvent was then thoroughly removed by evaporation. The polyether had a molecular weight (Mw) of 1900 Daltons and a Tg of -40.5°C.

**Example 02**
The following constituents were charged to a reaction vessel:
- 2.5438 grams of a neononanoic glycidyl ester of composition C,
- 1.0150 grams of dichloromethane,
- 0.0128 grams of boron trifluoride diethyl etherate.
The reaction took place for 3 days at room temperature and the solvent was then thoroughly removed by evaporation. The polyether had a molecular weight (Mw) of 1500 Daltons and a Tg of -51.1°C.

**Observations**: Tg of the modified polyether resin is impacted by the composition of the neononanoic glycidyl ester (see examples 01, 02).

**Example 03**
Polyether resin
The following constituents were charged to a reaction vessel equipped with a stirrer, a thermometer and a condenser:
- 134 grams of di-Trimethylol propane (DTMP),
- 900 grams of glycidyl neononanoate, GE9S,
- 135.5 grams of n-butylacetate (BAC) and 2.5 grams of Tin 2 Octoate. The mixture was heated to its reflux temperature of about 180° C. for about 4 hours till the glycidyl neononaoate was converted to an epoxy group content of
less than 0.12 mg/g. After cooling down the polyether had a solids content of about 88%.

**Example 04 Comparative**

Polyether resin

The following constituents were charged to a reaction vessel equipped with a stirrer, a thermometer and a condenser: 28.8 grams of monopentaerythritol, 201.5 grams of Cardura E10P, 19.4 grams of n-butylacetate and 0.3552 grams of Tin (II) 2-ethylhexanoate. The mixture was heated to a temperature of about 180° C for about 6 hours till the Cardura E10P was converted to an epoxy group content of about 25 mmol/kg. After cooling down the polyether had a solids content of about 94%.

**Example 05**

Polyether resin

The following constituents were charged to a reaction vessel equipped with a stirrer, a thermometer and a condenser: 28.8 grams of monopentaerythritol, 187.1 grams of GE9S, 18.3 grams of n-butylacetate and 0.3550 grams of Tin (II) 2-ethylhexanoate. The mixture was heated to a temperature of about 180° C for about 5.5 hours till the GE9S was converted to an epoxy group content of about 29 mmol/kg. After cooling down the polyether had a solids content of about 95%.

**Example 06 Comparative**

Polyether resin

The following constituents were charged to a reaction vessel equipped with a stirrer, a thermometer and a condenser: 28.8 grams of monopentaerythritol, 189.4 grams of GE9H, 18.5 grams of n-butylacetate and 0.3572 grams of Tin (II) 2-ethylhexanoate. The mixture was heated to a temperature of about 180° C for about 4 hours till the GE9H was converted to an epoxy group content of about 27 mmol/kg. After cooling down the polyether had a solids content of about 95%.
Formulation of the Clear Coats

A clear coat is formulated with one of the polyether (from examples 04, 05, or 06, the curing agent (HDI, Desmodur N3390), the thinner (Methyl Amyl Ketone), the levelling agent (BYK-331) and the catalyst (dibutyltin dilaurate, DBTDL) according to the amounts indicated in Table 3.

<table>
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<tr>
<th>CEP-Example</th>
<th>Binder (g)</th>
<th>HDI (g)</th>
<th>BYK 10 wt% (g)</th>
<th>DBTDL 1wt% (g)</th>
<th>Thinner (g)</th>
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<td>&gt; 12.5</td>
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<td>32.5</td>
<td>0.48</td>
<td>1.06</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Table 3: Clear coats, formulations

Characterization of the Clear Coats

The clearcoat formulations (from table 3) are barcoat applied on degreased Q-panel, optionally on basecoated Q-panel. The panels are dried at room temperature after a preliminary stoving at 60°C for 30 min. Clear coats have been characterized among others by measuring the Koenig hardness development (see Table 4).
Example 07
Polyester-ether resin

The following constituents were charged to a reaction vessel equipped with a stirrer, a thermometer and a condenser: 456g of GE9S, 134g of dimethylolpropionic acid and 0.35g of stannous octoate.

The mixture was heated to a temperature of about 110°C for about 1 hour and then steadily increased to 150°C in 3 hours and then cooled down.

This polyester-ether was then formulated in high solids and very high solids 2K polyurethane topcoats either as sole binder or as reactive diluent for an acrylic polyol.

<table>
<thead>
<tr>
<th></th>
<th>CEP-04</th>
<th>CEP-05</th>
<th>CEP-06</th>
</tr>
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<tbody>
<tr>
<td><strong>1°/ Koenig Hardness</strong> (Degreased Q panels) (sec)</td>
<td></td>
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<tr>
<td>6 hours</td>
<td>8</td>
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<td>24 hours</td>
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<td>7 days</td>
<td>18</td>
<td>20</td>
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<tr>
<td><strong>2°/ Koenig Hardness</strong> (Basecoated Q panels) (sec)</td>
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<td>6 hours</td>
<td>7</td>
<td>8</td>
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</tr>
<tr>
<td>24 hours</td>
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<td>14</td>
</tr>
<tr>
<td>7 days</td>
<td>12</td>
<td>13</td>
<td>34</td>
</tr>
</tbody>
</table>

**Table 4:** Clear coats, drying (curing) properties
CL A I M S

1. A composition of polyether polyol resins (hydroxyfunctional oligo or poly ether) comprising a mixture of $\alpha, \alpha$-branched alkane carboxylic glycidyl esters derived from butene oligomers characterized in that the sum of the concentration of the blocked and of the highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.

2. The composition of claim 1 characterized in that the glycidyl ester mixture is based on neononanoic (C9) acid mixture where the sum of the concentration of the blocked and of the highly branched isomers is maximum 55%, preferably below 40%, and most preferably below 30% weight on total composition.

3. The composition of claim 2 characterized in that the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester or 2-methyl 2-ethyl hexanoic acid glycidyl ester or 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters.

4. The composition of claim 2 characterized in that the glycidyl ester mixture is comprising 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) below 40%, preferably below 30% and most preferably below or equal 25% weight on total composition.

5. The composition of claim 2 characterized in that the glycidyl ester mixture is comprising 2-methyl 2-ethyl hexanoic
acid glycidyl ester above 10%, preferably above 30% and most preferably above 45% weight on total composition.

6. The composition of claim 2 characterized in that the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester and 2-methyl 2-ethyl hexanoic acid glycidyl ester and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) is above 40%, preferably 55% and most preferably 65% weight on total composition.

7. The composition of claim 2 characterized in that the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester in 1 to 15 weight% and 2-methyl 2-ethyl hexanoic acid glycidyl ester in 40 to 70 weight% and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) in 8 to 32 weight% on total composition.

8. The composition of claim 2 characterized in that the glycidyl ester mixture is comprising 2,2-dimethyl heptanoic acid glycidyl ester in 2 to 10 weight% and 2-methyl 2-ethyl hexanoic acid glycidyl ester in 47 to 61 weight% and 2-methyl 2-ethyl 3-methyl pentanoic acid glycidyl esters (sum of stereoisomers) in 10 to 25 weight% on total composition.

9. The process to prepare the compositions of claims 1 to 8 characterized in that the polyether polyol resin is obtained by the reaction of at least one polyol having at least three hydroxyl groups and a mixture of the $\alpha,\alpha$-branched alkane carboxylic glycidyl esters.

10. The composition of the claim 9 characterized in that the number average molecular weight ($M_n$) is lower than 4500 Dalton according the polystyrene standard, and/or the hydroxyl value is above 120 mg KOH/g solids on solid.
11. A binder composition useful for coating application with a low VOC and comprising at least any polyether polyol resin from claims 1 to 8.

12. A metal or plastic substrate coated with the binder of claim 11.

13. A polyester-ether resin characterized in that it is the reaction product of the composition of any claims 1 to 8 and dimethylol propionic acid.