CONVENTION APPLICATION FOR A STANDARD PATENT

We, VIANOVA KUNSTHARZ AKTIENGESSELLSCHAFT, of 8402 Werndorf bei, Graz, Austria hereby apply for the grant of a standard patent for an invention entitled "KNOEVENAGEL REACTION PRODUCTS AS CROSSLINKING COMPONENTS FOR HARDENER COMPONENT FOR STOVING PAINT BINDERS AND PROCESS FOR PRODUCING SAME" which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION(S)

Number(s) of Basic Application(s): A 1235/86 and A 1236/86

Name of Convention Country in which Basic Application(s) were filed: Austria

Date(s) of Basic application(s): 9 May 1986 and 9 May 1986 respectively

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DATED this EIGHTH day of MAY 1987

VIANOVA KUNSTHARZ AKTIENGESSELLSCHAFT

By: Registered Patent Attorney.

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

SBR: ALB: 1F

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 23 - 8 - 90.
In support of the Convention Application made for a patent for an invention entitled:

HARDENER COMPONENT FOR STOVING PAINT BINDERS AND PROCESS FOR PRODUCING SAME

I/We, ..................................................

[full name of declarant(s)]

at ...........................................

[full address of declarant(s) - not post office box]

I/We do solemnly and sincerely declare as follows:--

1. I am/We are authorised by VIANOVA KUNSTHARZ AKTIENGESELLSCHAFT, the applicant for the patent to make this declaration on its behalf.

2. The basic applications as defined by Section 141 of the Act were made in AUSTRIA on 9 May, 1986 and 9 May, 1986 both by VIANOVA KUNSTHARZ AKTIENGESELLSCHAFT.

3. RUDOLF SCHIPFER, of Ernst Haeckelgasse 53, A8010 Graz; GERHARD SCHMOLZER of Eisteichgasse 37, A8010 Graz and WOLFGANG DAIMER of Rosenberggurtel 37, A8010 Graz, all in Austria [respectively] are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

VIANOVA KUNSTHARZ AKTIENGESELLSCHAFT is entitled by Contract of Employment between the inventors as employees and VIANOVA KUNSTHARZ AKTIENGESELLSCHAFT as employer, as a person who would be entitled to have the patent assigned to it if a patent were granted upon an application made by the inventors.

4. The basic applications referred to in paragraph 2 of this Declaration were the first applications made in a Convention country in respect of the invention(s) the subject of the application.

DECLARED at Graz this third day of Sept. 1987

[Signature of Declarant]

Robert PITTER

TO: THE COMMISSIONER OF PATENTS

AUSTRALIA
1. KNOEVENAGEL reaction products as crosslinking components for paint binders crosslinkable through transesterification and/or transamidation, characterised in that they have been obtained 
(a1) from oligomeric KNOEVENAGEL reaction products of the formula

\[
\begin{array}{c}
\text{X} \\
\text{C} \\
\text{COOR} \\
\end{array}
\begin{array}{c}
\text{R} \\
\text{C} \\
\text{R}_1 \\
\end{array}
\frac{1}{n}
\]

(I)

wherein X is –COOR, –CN or –COCH₃, 
R is an alkyl radical with from 1 to 8 carbon atoms 
R₁ is a hydrogen atom or an alkyl radical, and n is a factor multiplying the unit to a molecular weight of between 300 and 6000, 
through partial transesterification at 130°C to 185°C with from 0.1 to 1.4 hydroxy equivalents of a diol and/or polyol per mole of compound (I) 
or that they have been obtained
(a2) from compounds of the formula X-CH₂-COOR (II), wherein X and R have the abovementioned meaning, the ester groups of which having been partially transesterified to 5 to 80% with a diol and/or polyol; and the resulting precondensates having been reacted in a KNOEVENAGEL reaction with an aldehyde or ketone and having been polymerised; whereby products (a1) and (a2) have a molecular weight of between 1000 and 8000 (determined with gel permeation chromatography).
Complete Specification for the invention entitled:
"KNOEVENAGEL REACTION PRODUCTS AS CROSSLINKING COMPONENTS FOR HARDENER COMPONENT FOR STOVING PAINT BINDERS AND PROCESS FOR PRODUCING SAME"

The following statement is a full description of this invention, including the best method of performing it known to us.
Abstract.

The invention is concerned with crosslinking components for hydroxy and/or primary and/or secondary amine groups containing cationic resins which can be used as binders for stoving paints, particularly for cathodically depositable electrodeposition paints. The crosslinking components are obtained through partial transesterification or transamidation of oligomeric KNOEVENAGEL reaction products of C-H-active esters and carbonyl compounds with di- or polyols or amines. The products can also be obtained through partial transesterification or transamidation of the C-H-active esters and subsequent KNOEVENAGEL reaction.
The invention disclosed in the present application is concerned with crosslinking components for stoving paint binders which owing to their structure can be crosslinked through transesterification and/or transamidation; it is also concerned with the process for producing these crosslinking components and their use, particularly in the formulation of cathodic electrodeposition paints.

EP-B1-0 131 127 discloses a process for producing crosslinking components for paint binders crosslinkable through transesterification and/or transamidation which is characterised in that compounds of the structure \( X - \text{CH}_2 - \text{COOR} \), wherein \( X \) is \(-\text{COOR}, -\text{CN} \) or \(-\text{COCH}_3 \) and \( R \) is an alkyl radical with from 1 to 8 carbon atoms, preferably the diesters of malonic acid with alkanols with from 1 to 4 carbon atoms, are reacted with a carbonyl compound, preferably formaldehyde, in particular paraformaldehyde, with separation of water in the sense of a KNOEVENAGEL reaction, and the resulting alpha-disubstituted alkylidene compound is polymerised to an oligomeric or polymeric compound with a molecular weight of between 300 and 6000.

When carrying on research with the aim of further improving the film properties obtainable with the use of these hardener components, it has now been found that the compounds obtained according to the reaction

\[
\begin{align*}
X & \quad R_1 \\
\text{CH}_2 & + O = C & \quad C & \quad C \quad C & \quad C \\
\text{COOR} & \quad R_1 & \quad \text{COOR} & \quad R_1
\end{align*}
\]
wherein X and R have the above mentioned meaning, \( R_1 \) is a hydrogen atom or an alkyl radical, and \( n \) is a factor which multiplies the unit to a molecular weight of between 300 and 6000, in the form of their partial transesterification products with diols and polyols lead to products which are improved with regard to their film-forming characteristics.

Thus the present invention is concerned with KNOEVENAGEL reaction products as crosslinking components for paint binders crosslinkable through transesterification and/or transamidation, characterised in that they have been obtained

(a1) from oligomeric KNOEVENAGEL reaction products of the formula

\[
\begin{array}{c}
X \\
\text{COOR} \\
R_1 \\
\text{C} \\
\text{C} \\
R_1 \\
\text{COOR} \\
\end{array}
\]

wherein \( X \) is \(-\text{COOR}\), \(-\text{CN}\) or \(-\text{COCH}_3\), \( R \) is an alkyl radical with from 1 to 8 carbon atoms, \( R_1 \) is a hydrogen atom or an alkyl radical, and \( n \) is a factor multiplying the unit to a molecular weight of between 300 and 6000, through partial transesterification with from 0.1 to 1.4 hydroxy equivalents of a diol and/or polyol per mole of compound (I) or that they have been obtained

(a2) from compounds of the formula \( X-\text{CH}_2-\text{COOR} \) (II), wherein \( X \) and \( R \) have the abovementioned meaning, the ester groups of which having been partially transesterified to 5 to 80\% with a diol and/or polyol; and the resulting precondensates having been reacted in a KNOEVENAGEL reaction with an aldehyde or ketone and having been polymerised; whereby products (a1) and (a2) have a molecular weight of between 1000 and 8000 (determined with gel permeation chromatography).
Furthermore the invention is concerned with a process for producing Knoevenagel reaction products as crosslinking components for paint binders cross-linkable through transesterification and/or transamidation characterised in that

(a1) oligomeric KNOEVENAGEL reaction products of the formula

\[
\begin{array}{c}
\text{X} \\
\text{C} \\
\text{COOR} \\
\text{C} \\
\text{R} \end{array}
\begin{array}{c}
\text{R} \_1 \\
\text{n}
\end{array}
\]

wherein \(X\) is \(-\text{COOR}, \ -\text{CN}\) or \(-\text{COCH}_3\)

R is an alkyl radical with from 1 to 8 carbonatoms

R\(_1\) is a hydrogen atom or an alkyl radical and

n is a factor multiplying the unit to a molecular weight of between 300 and 6000,

are transesterified at 130 to 185°C with from 0.1 to 1.4 hydroxy equivalents of a diol and/or polyol

(a2) 5 to 80% of the ester groups of a compound of the formula \(X - \text{CH}_2 - \text{COOR}\), wherein \(X\) and \(R\) have the above mentioned meanings, are transesterified at from 100 to 200°C with a diol and/or polyol and the thus obtained precondensates are reacted with a carbonyl compound in the sense of a KNOEVENAGEL reaction with a carbonyl polymerised, whereby in case (a1) as well as in case (a2) the reaction is carried out such that the products have a molecular weight of between 1000 and 8000 (determined by gel permeation chromatography).
The invention is further concerned with the use of the paint binders of the invention in combination with cationic resins carrying hydroxyl groups and/or primary and/or secondary amino groups for the formulation of stoving paints, in particular in cathodically depositable electrodeposition paints.

Contrary to the binder compositions obtainable with the crosslinking components of EP-B1-0 131 127 with the crosslinking components of the present invention it is possible to essentially influence the properties of the coating compositions prepared therefrom. This applies in particular to the characteristics for electrodeposition binders, e.g. film thickness and throwing power or formation of a perfect surface during the crosslinking process. Also, through judicious selection of the reaction partners the curing characteristics, the adhesion to the substrate and to the following coat can be governed.

In particular, according to the present process it is possible to introduce amide groups favourable for cathodic electrodeposition into the crosslinking components. Through modification of the alcohols and the amines with isocyanate compounds it is also possible to introduce urethane or urea groups.

The oligomeric KNOEVENAGEL reaction products of formula (I) used as the starting materials for method (a) are obtained according to EP-B1-0 131 127 through polymerisation of alpha-disubstituted alkylidene compounds, which are obtained through reaction of compounds of the structure X - CH₂ -
COOR, wherein X is COOR, -CN or -COCH₃ and R is an alkyl group with from 1 to 8 carbon atoms, with a carbonyl compound, preferably formaldehyde, with the separation of water.

For the methods of the present invention preferably the diesters of malonic acid (X is -COOR) with alkanols with from 1 to 4 carbon atoms are used, like dimethylmalonate, diethylmalonate, n- or isopropylmalonate. In the same way also the alkyl- or cycloalkylesters of cyanoacetic acid can be used, like methylcyanoacetate, ethylcyanoacetate, propylcyanoacetate, butylcyanoacetate, cyclopentylcyanoacetate, cyclohexylcyanoacetate or methylacetoacetate or ethylacetoacetate.

The carbonyl compound is formaldehyde, particularly the polymerised form (paraformaldehyde). Higher aldehydes can be used but are of little advantage compared to the cheap and readily available formaldehyde. Ketones, like methylisobutylketone or cyclohexanone are also suitable.

The oligomers are favourable prepared such that the paraformaldehyde is added in portions at 60 to 70°C to the ester and is dissolved therein. As a catalyst for the reaction a blend of piperidine and formic acid is added to the ester in a quantity of about 0.1 to 1 mole-%. Until the paraformaldehyde has not dissolved, the reaction temperature should not surpass 90°C. Then the temperature is slowly raised and the reaction water forming is entrained at 120 - 150°C through azeotropic distillation with an entraining agent, f. i. an aliphatic or aromatic hydrocarbon. The reaction is monitored by the amount of reaction water formed. The polymerisation reaction taking place at the same time is controlled by determining the refractive index or the rise in viscosity.
The polymerisation can optionally be completed by addition of peroxide initiators. After removing the entraining agent the crosslinking component can be used substantially solvent-free. Optionally it may be favourable to add inert solvents for easier handling and for better distribution of the basis resin in the crosslinker. The products have a molecular weight of between about 300 and about 6000.

These reaction products, in method (al) are reacted with 0.1 to 1.4 hydroxy equivalents of a di- and/or polyvalent alcohol per 1 mole of KNOEVENAGEL reaction product. For the increasing the molecular weight a transamidation reaction with 0.05 to 1.0 NH-equivalents of a primary and/or secondary amine per 1 mole of the reaction product can also be used. The starting materials are chosen such that the molecular weight (weight average) of the thus obtained crosslinking component lies between 1000 and 8000. The molecular weight is favourably determined by gel permeation chromatographie.

The reaction between this reaction product and the alkanol or amine component is carried out at 130 to 185°C, the reaction being monitored through the quantity of split alcohol and the intrinsic viscosity at 20°C in dimethylformamide.

Suitable dihydric alcohols are straight chain or branched alkane diols like ethylene glycol, its homologues and their isomers. Polyether diols can be used likewise such as di- or polyalkylene glycols or polycaprolactone diols or diols with ring structures, such as 1,1'-isopropylidene-bis-(p-phenylene-oxy)-di-ethanol-2 (DIANOL 22) or tricyclodecane-dimethanol (TDC-alcohol DM).
Suitable polyhydric are trimethylol alkanes or pentaerythritol. Other suitable di- oder polyols can be prepared through simple reactions, e.g. by reaction of monoepoxy compounds with secondary alkanol amines or hydroxy carboxylic acids, such as dimethylol propionic acid, or of diamines with alkylene carbonates. Similar reactions leading to di- or polyols are known to the expert.

For the introduction of urethane groups, as the diol or polyol component also reaction products of isocyanate compounds and the mentioned alcohols can be used.

For transamidation, in particular, primary and secondary aliphatic amines are used. Besides these, also primary and secondary alkanol amines, like monomethylethanolamine, 2-amino-2-ethylpropanediol, monoethanolamine, etc. and cyclic polyamines, like hydroxyethyl piperazine or aminoethylpiperazine can be used in the transamidation reaction.

In the preparation of the crosslinking components of the invention according to method (a2), in a first reaction step, 5 to 80% of the ester groups of the esters carrying active methylene groups, of formula X—CH2—COOR, wherein X and R have the meaning as claimed, are reacted at 100 to 200°C with di- and/or polyols and/or di- and/or polyamines with transesterification or transamidation. The reactions take place with the separation of the alcohol R-OH, which is favourable removed from the reaction blend with a bubble tray column. The course of the reaction can be monitored via the quantity of distillate or the refractive index of the reaction product.
The alcohol components are the same compounds as are used in method (al). The amines are straight-chain or branched alkylene diamines or polyamines, as long as they have primary and/or secondary amine groups. Further, the corresponding alkanolamines can be used for the process of the invention. Examples are ethylene diamine and its homologues, isophorone diamine, diethylene triamine, or similar substances. Reaction products of the mentioned amines with isocyanate compounds can be used for the introduction of urea groups into the crosslinking component.

Just like in method (al) the reaction product is reacted in the presence of catalysts (normally a blend of piperidine or dicyclohexylamine and formic acid) with the carbonyl compound, preferably formaldehyde in the form of paraformaldehyde with a content of from about 90 to 100 % CH₂O, in the sense of a KNOEVENAGEL reaction. Advantageously, the ester catalyst blend is added in portions to paraformaldehyde at 60 to 90°C. The reaction temperature should not surpass 90°C until the paraformaldehyde has dissolved completely. Then the temperature is raised to 100°C and held, until the content of free formaldehyde has fallen below 0.5 %. Then the reaction water is distilled off, using an entraining agent, and the reaction temperature is held, until the desired viscosity and refractive index is attained. The reaction is carried on to a molecular weight of the crosslinking components of about 1000 to 8000 (determined by gelpermeation chromatography).

It was surprising that the KNOEVENAGEL reaction, also when using these precondensates, takes place in a trouble free and controllable manner.
The crosslinking components prepared according to the invention are used in combination with basis resins capable of transesterification and transamidation reactions. In particular, the products produced according to the invention can be used in water dilutable paint systems. The crosslinking components proved particularly useful in cathodically depositable coating compositions, the high reactivity of the crosslinking components in many cases allowing the reduction of the stoving temperature to 130 to 160°C.

The suitable basis resins are products carrying a sufficient number of groups capable of esterification and amidation in order to guarantee a satisfactory crosslinking of the film. Resins of this type are disclosed in EP-00 12 463 or AT 372 099. The preferred resins are based on epoxy resins, in particular epoxy resin amine adducts, optionally modified in the sense of inner flexibilisation being specially suited for cathodic electrodeposition. Other preferred basis resins are copolymers carrying a sufficient number of protonable groups, either through the use of adequate monomers or through subsequent modification.

In order to secure a satisfactory dilutability with water upon partial or total neutralisation with acids, the basis resins have an amine value of between 20 and 150 mg KOH/g. The number of groups capable of transesterification or transamidation should correspond to between 40 to 500 mg KOH/g.

In a special embodiment of the invention the basis resin and the crosslinking component are subjected to a partial pre-condensation at from 80 to 140°C. Through this measure the compatibility between the components can be considerably
improved and phase separation can be avoided, even on prolonged storage of the binders or coating compositions.

The components are combined in a ratio of from 60 to 95 % b.w. of the basis resin and of from 5 to 40 % b.w. of the crosslinking component of the invention. The preferred mixing ratios are from between 70 to 85 % b.w. of the basis resin and between 15 to 30 % b.w. of the crosslinking component.

The expert knows how the binder compositions are processed to water dilutable coating compositions, i.e. neutralisation with acids, dilution to application viscosity and incorporation of pigments and extenders as well as possible forms of application. The preferred end use of the coating compositions containing the crosslinking components of the invention is cathodic electrodeposition.

The coating compositions are cured at between 120 and 180 °C for 15 to 30 minutes, optimum resistance characteristics being obtained already at from 130 to 160 °C.

The following examples illustrate the invention without limiting the scope of it. Parts and percentages are by weight and refer to resin solids of the resin components, unless otherwise stated.

The following abbreviations for raw materials are used in the examples:
ACEE Ethylacetoacetate
MDM Dimethylmalonate
MDE Diethylmalonate
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDIP</td>
<td>Diisopropylmalonate</td>
</tr>
<tr>
<td>MDBE</td>
<td>Di-n-butylmalonate</td>
</tr>
<tr>
<td>MEBE</td>
<td>Ethyl-n-butylmalonate</td>
</tr>
<tr>
<td>PG</td>
<td>Propyleneglycol-1,2</td>
</tr>
<tr>
<td>NPG</td>
<td>Neopentylglycol</td>
</tr>
<tr>
<td>BD</td>
<td>Butanediol-1,4</td>
</tr>
<tr>
<td>HD</td>
<td>Hexanediol-1,6</td>
</tr>
<tr>
<td>TPG</td>
<td>Tripropyleneglycol</td>
</tr>
<tr>
<td>CAP</td>
<td>Polycaprolactonediol (molecular weight ca. 200)</td>
</tr>
<tr>
<td>D 22</td>
<td>1,1' -Isopropylidene-bis-(p-phenylene-oxy)-di-ethanol-2 (DIANOL 22)</td>
</tr>
<tr>
<td>TMP</td>
<td>Trimethylolpropane</td>
</tr>
<tr>
<td>CE</td>
<td>Glycidylester of a C&lt;sub&gt;9&lt;/sub&gt;-C&lt;sub&gt;11&lt;/sub&gt;-tert.-monocarboxylic acid</td>
</tr>
<tr>
<td>MEOLA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>DOLA</td>
<td>N,N-diethanolamine</td>
</tr>
<tr>
<td>EHA</td>
<td>2-Ethylhexylamine</td>
</tr>
<tr>
<td>HMDA</td>
<td>Hexamethylenediamine-1,6</td>
</tr>
<tr>
<td>IPDA</td>
<td>Isophoronediamine</td>
</tr>
<tr>
<td>DCHA</td>
<td>Dicyclohexylamine</td>
</tr>
<tr>
<td>DETA</td>
<td>Diethylenetriamine</td>
</tr>
<tr>
<td>DEAPA</td>
<td>N,N-diethylpropanediamine-1,3</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethylamine</td>
</tr>
<tr>
<td>FA</td>
<td>Formaldehyde (100 %)</td>
</tr>
<tr>
<td>ECT</td>
<td>Ethylenecarbonate</td>
</tr>
<tr>
<td>PCT</td>
<td>Propylenecarbonate</td>
</tr>
<tr>
<td>TDI</td>
<td>Toluyleneisocyanate</td>
</tr>
<tr>
<td>DMPS</td>
<td>Dimethylolpropionic acid</td>
</tr>
<tr>
<td>AMS</td>
<td>Formic acid</td>
</tr>
</tbody>
</table>
Examples 1 - 16: The crosslinking components type (al) are prepared in the described manner from the raw materials listed in Table 1.

In a suitable reaction vessel equipped for azeotropic distillation and a bubble tray column for the separation of the alcohol component formed on partial transesterification or transamidation, a mixture of the ester component and catalyst blend (each 0.5 to 1.0 mole-%, calculated on ester,
of piperidine and formic acid) is heated to 70 to 80°C and paraformaldehyde is added in portions. The reaction is exothermic and the temperature should not surpass a maximum of 90°C. The temperature is held until the paraformaldehyde has dissolved completely. Then the temperature is slowly raised to 110 to 120°C and the reaction water formed is separated from the reaction mixture with the aid of a suitable entraining. After vacuum-stripping the entraining agent, the polyol component or the amine component is added and the temperature is raised until distillation starts (about 140 to 180°C). The separation of the alcohol component is preferably made with the aid of a bubbly tray column. The obtained reaction products have a solids content of between 90 and 96 % (120°C, 30 minutes).

Examples 17 – 25: From the raw materials listed in Table 2 crosslinking components type (a2) are prepared in the following way:

In a suitable reaction vessel equipped for azeotropic distillation and a bubble tray column for separating the alcohols formed on partial transesterification and transamidation, the blend of ester and transesterification or transamidation component is heated to 120°C and with the temperature rising to 180°C, the alcohol set free from the ester is separated through the bubble tray column. The course of the reaction is monitored through the quantity of distillate. The course of reaction can also simply be controlled by determining the refractive index of the reaction mass.

After cooling to 60°C, the catalyst blend, and then, paraformaldehyde is added in portions; the reaction is exothermic and the temperature should not surpass 90°C. When the
formaldehyde has completely dissolved, the temperature is raised to 100°C and held, until the content of free formaldehyde has fallen to below 0.5 %. The reaction water formed is vacuum-stripped with an entraining agent, f. i. a hydrocarbon solvent with adequate stoving range. Then the temperature is held, until the final values are attained. The reaction products have a solids content of over 90 %, dried for 30 minutes at 120°C.

Use of the crosslinking agents prepared according to the invention

The crosslinking agents prepared according to the invention are combined with various basis resins at the conditions listed in Table 3.

The components are mixed or partially reacted as 70 % solution in PM.

Preparation of test paints

Of the listed binder compositions each 100 g of resin solids are milled with 29.5 g titanium dioxide, 0.5 g carbon black, 17 g aluminium silicate and 3 g basic lead silicate. In addition, transesterification catalysts are admixed homogeneously. Lead octoate with an effective metal content of 0.5 %, calculated on resin solids, is used.

After the dispersion of the pigments, the paints are neutralised with formic acid and diluted with deionised water to a solids content of 15 %.
For the combinations, 2, 8, 20 and 24 a white pigmentation is chosen. 100 g resin solids, 37 g titanium dioxide and 3 g basic lead silicate are milled and 0.5 % of lead, as lead octoate, are admixed homogeneously.

Test for acetone resistance

The acetone resistance is tested by applying an acetone-soaked cotton swab to a pigmented paint film deposited cathodically and stoved for 30 minutes at 160°C. The period of time is recorded, after which the film can be wounded by scratching with a finger nail.

The products used as basis resins are prepared as follows:

MEQ-Value = Milliequivalents of unreacted epoxide groups + milliequivalents of amine groups per gram of sample (solids).

**Basis Resin A 1:** 190 g of a bisphenol-A-epoxy resin (1 epoxy equivalent) and 1425 g of a bisphenol-A-epoxy resin (3 epoxy equivalents) are dissolved at 100°C in 597 g of EGL. The solution is cooled to 60°C and 126 g DOLA are added. The temperature is slowly raised within 2 hours to 80°C and 169 g DEAPA are added. The temperature is raised within 2 hours to 120°C. At this temperature, 478 g CE are added and 130°C are held for 5 hours while stirring. The batch is diluted with EGL to 65 % resin solids. The amine value of the resin is 91 mg KOH/g; the hydroxyl value is 265 mg KOH/g.

**Basis Resin A 2:** 2 g azobisisobutyronitrile are dissolved in 40 g isopropanol with warming. To the clear solution at reflux temperature (at ca. 84°C) a monomer blend of 20 g glycidylmethacrylate, 20 g hydroxyethylmethacrylate, 20 g methyl
methacrylate and 40 g 2-ethylhexylacrylate, in which 2 g azobisisobutyronitrile are clearly dissolved, is added continuously within 2 hours. The reaction mass is stirred at reflux temperature for another 3 hours. At 85°C a homogeneous solution of 16 g diisopropanol amine in 20 g BUGL is quickly added to the reaction mass which is stirred for another 2 hours at 90°C. The product is diluted at 90°C with 13 g EGL and, at 40°C, with 10 g acetone.

The resin has a solids content of 57 %, an amine value of 58 mg KOH/g and a hydroxyl value of 250 mg KOH/g.

**Basis Resin A 3:** 380 g of an epoxy novolak resin (epoxy equivalent ca. 190) are dissolved in 354 g DEGM and reacted at 80°C with 269 g of a semi-ester of THPSA and HEOX, as well as with 37 g DEA and 140 g TOFS to an acid value of below 3 mg KOH/g. Then the resin is blended with 10 mMoles acetic acid (3-N) per 100 g resin solids and stirred for 3 hours. The product has a hydroxyl value of 270 mg KOH/g.

**Basis Resin A 4:** 1627 g (3.43 Val) of an epoxy resin based on bisphenol-A (epoxy equivalent weight about 475) are reacted with 226 g (0.24 COOH-Val) of a polyester of 3 moles TMP, 2 moles AS, 1 mole INS and 1 mole THPSA (acid value 65 mg KOH/g, carboxy equivalent 942 g) in an 85 % solution of PM at 110°C to an acid value of below 5 mg KOH/g.

After dilution of the batch with PM on a solids content of 70 % a blend consisting of 94.5 g (0.9 Val) DOLA, 67.5 g (0.9 Val) MEOLA, 78 g (1.2
Val) DEAPA and 240 g PM is added at 60°C within 2 hours. Then the temperature is raised to 90°C and held for one hour. Then the solids content is adjusted to 70 % with PM.

**Basis Resin A 5**: 570 g (3 Val) of an epoxy resin based on bisphenol-A (epoxy equivalent about 190) and 317 g PM are heated to 60°C and reacted for 2 hours to an MEQ-value of 2.06 with a blend of 116 g (0.9 Val) EHA and 163 g (0.15 NH-Val) of a polymeric amine (see below). Then, 1330 g (2.1 Val) of a 75 % solution of a bisphenol A-epoxy resin (epoxy equivalent weight about 475) in PM are added. At 60°C, within 1 hour, a solution of 189 g (1.8 Val) DOLA in 176 g PM is added and the reaction is carried to an MEQ-value of 1.57. After addition of a solution of 78 g (1.2 Val) DEAPA in 54 g PM within 1 hour, the reaction is carried on at 60°C to an MEQ-value of 1.46. The temperature is raised to 90°C and, within another hour, to 120°C. When a viscosity of 1 - J (Gardner-Holdt; 6 g resin + 4 g PM) is reached, the solids content is adjusted to 65 % with PM. The product has an amine value of 117 mg KOH/g and a hydroxyl value of 323 mg KOH/g.

The polymeric amine is obtained through reaction of 1 mole of DETA with 3.1 moles of 2-ethylhexylglycidylether and 0.5 moles of a bisphenol-A epoxy resin (epoxy equivalent about 190) as an 80 % solution in PM. The product has a viscosity of 60 to 80 s (DIN 53 211; 100 g resin + 30 g PM).

**Basis Resin A 6**: A modified epoxy-amine adduct as described as basis resin A 4 is mixed in the last phase with 5 % b. w. of polypropylene glycol diglycidylether at 90°C and reacted at 120°C until all glycidyl groups have reacted. The product has an amine value of 76 mg KOH/g and a hydroxyl value (primary OH) of 89 mg KOH/g.
Basis Resin A 7: To a solution of 570 g (3 Val) of a bisphenol-A-epoxy resin in 173 g PM, a blend of 96.8 g (0.75 Val) EHA, 326 g (0.3 NH-Val) of the polymeric amine used in A 5 and 160 g PM is added at 60°C within 2 hours and reacted to an MEQ-value of 2.15. Then, 1330 g (2.1 Val) of a 75% solution of a bisphenol-A-epoxy resin (epoxy equivalent weight 475) in PM are added, and, at 60°C, within 30 minutes 210 g (2 Val) DOLA. On attaining an MEQ-value of 1.72, 138 g (0.5 NH-Val) of a diketimine (see below), dissolved in 245 PM are added and reacted to an MEQ-value of 1.60. The product has a solids content of 70% and a viscosity (Gardner-Holdt, 10 g resin + 4 g PM) of L – M. The amine value is 117 mg KOH/g.

Preparation of the diketimine: 103 g DETA are reacted with 200 g MIBK at 120°C with the separation of 36 g water through azeotropic distillation. The solvent is vacuum-stripped. The reaction product has a refractive index n 20/D of 1.4672.
<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>MOLES DIOLESTER</th>
<th>MOLES CH₂O</th>
<th>MOLES POLYOL</th>
<th>ESTER EQUIVALENTS (1)</th>
<th>OH-VALUE</th>
<th>INTRINSIC VISCOSITY 20°C/DMF ETA</th>
<th>REFRACTIVE INDEX n 20/D</th>
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(1) g resin / 1 estergroup
Table 2

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<th>REACTIONS-PARTNER MOLES</th>
<th>FORM-ALDEHYDE MOLES</th>
<th>KATALYST</th>
<th>REFRACTIVE INDEX n 20/D</th>
<th>INTRINSIC VISCOSITY 20°C / DMF ETA</th>
<th>ESTER-EQUIVALENTS (2)</th>
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(1) Basis resin A 1 neutralised with 40 mEq formic acid per 100 g resin solids
(2) g Resin / 1 Ester group
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<th>COMBINATION A + B</th>
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<tr>
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<td>90</td>
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<td>100</td>
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<td>22</td>
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<td>60</td>
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<tr>
<td>23</td>
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</table>
The claims defining the invention are as follows:

1. KNOEVENAGEL reaction products as crosslinking components for paint binders crosslinkable through transesterification and/or transamidation, characterised in that they have been obtained
   (a1) from oligomeric KNOEVENAGEL reaction products of the formula
   \[
   \text{X} \quad \text{R} \quad \text{C} \quad \text{C} \quad \text{COOR} \quad \text{R} \quad \text{n}
   \]
   wherein \(X\) is \(-\text{COOR}, -\text{CN}\) or \(-\text{COCH}_3\), \(R\) is an alkyl radical with from 1 to 8 carbon atoms, \(R_1\) is a hydrogen atom or an alkyl radical, and \(n\) is a factor multiplying the unit to a molecular weight of between 300 and 6000, through partial transesterification at 130°C to 185°C with from 0.1 to 1.4 hydroxy equivalents of a diol and/or polyol per mole of compound (I) or that they have been obtained
   (a2) from compounds of the formula \(X-\text{CH}_2-\text{COOR}\) wherein \(X\) and \(R\) have the abovementioned meaning, the ester groups of which having been partially transesterified to 5 to 80% with a diol and/or polyol; and the resulting precondensates having been reacted in a KNOEVENAGEL reaction with an aldehyde or ketone and having been polymerised; whereby products (a1) and (a2) have a molecular weight of between 1000 and 8000 (determined with gel permeation chromatography).

2. Crosslinking components according to claim 1, characterised in that in the compounds of formula (I) and (II) the radical \(X\) is \(-\text{COOR}\) and radical \(R\) is an alkyl radical with from 1 to 4 carbon atoms.

3. Crosslinking components according to claims 1 or 2, characterised in that the aldehyde is formaldehyde.

4. Crosslinking components according to claim 1 or claim 2 wherein the aldehyde is paraformaldehyde.

5. Process for producing KNOEVENAGEL reaction products as crosslinking components for paint binders crosslinkable through transesterification and/or transamidation characterised in that
   (a1) oligomeric KNOEVENAGEL reaction products of the formula
wherein X is -COOR, -CN or -COCH₃
R is an alkyl radical with from 1 to 8 carbon atoms
R₁ is a hydrogen atom or an alkyl radical and
n is a factor multiplying the unit to a molecular weight of between 300 and 6000,
are transesterified at 130 to 185°C with from 0.1 to 1.4 hydroxy
equivalents of a diol and/or polyol per mole of compound (I) or
(a2) 5 to 80% of the ester groups of a compound of the formula X –
CH₂ –COOR, wherein X and R have the above mentioned meanings, are
transesterified at from 100 to 200°C with a diol and/or polyol and the thus
obtained precondensates are reacted with an aldehyde or ketone in the sense
of a KNOEVENAGEL reaction and are polymerised; whereby in case (a1) as well
as in case (a2) the reaction is carried out such that the products have a
molecular weight of between 1000 to 8000 (determined by gel permeation
chromatography).

6. Process according to claim 5, characterised in that as the
compounds with the structure X – CH₂ – COOR and for the preparation of
the oligomeric KNOEVENAGEL reaction products (formula I) diesters of
malonic acid with alkanols with 1 to 4 carbon atoms are used.

7. Process according to claims 5 or 6, characterised in that the
aldehyde is formaldehyde.

8. Process according to claim 5 or claim 6, characterised in that the
aldehyde is paraformaldehyde.

9. Use of the crosslinking components according to any one of
claims 1 to 4, in combination with hydroxy and/or primary and/or secondary
amino group containing cationic resins.

10. Use of the crosslinking components prepared according to claims
1 to 4 in a partially precondensed form with the cationic resin.

11. KNOEVENAGEL reaction products as crosslinking components for
paint binders crosslinkable through transesterification and/or transamidation, substantially as hereinbefore described with reference to any one of the Examples.

12. Cathodically depositable electrodeposition paints containing as binder blends or partial condensation products of hydroxy and/or primary and/or secondary amine group containing resins and crosslinking agents according to any one of claims 1 to 4 or 11.

13. A process for producing KNOEVENAGEL reaction products as crosslinking components for paint binders crosslinking through transesterification and/or transamidation, substantially as hereinbefore described with reference to any one of the Examples.

DATED this EIGHTEENTH day of APRIL 1990
Vianova Kunstharz Aktiengesellschaft

Patent Attorneys for the Applicant
SPRUSON & FERGUSON