656913

P/00/001
Section 29

AUSTRALIA
Patents Act 1990
PATENT REQUEST : STANDARD PATENT

We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Applicant: **HERBERTS GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG**
Address: Christbusch 25, D-5600 Wuppertal 2, Germany

Nominated Person: As above
Address: As above

Invention Title: "Partially Esterified Glycidyl Containing Polymers"

Name of Actual Inventor/s: Dr. Klaus BEDERKE, of Oststraße 36, 4322 Sprockhövel, Germany; Hermann KERBER, of Daniel-Schürmann-Weg 37, 5600 Wuppertal 21, Germany; Dr. Walter SCHUBERT, of Hintersudberg 91, 5600 Wuppertal 12, Germany; Dr. Thomas BROCK, of Kallweg 2, 5030 Hürth, Germany; Helmut LÖFFLER, of Parkstraße 15a, 5040 Brühl, Germany; and Dr. Fritz SADOWSKI, of Am Mühlenacker 35, 5024 Brauweiler, Germany.

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BASIC CONVENTION APPLICATION DETAILS
Application Number: P 40 27 259.1
Country: Federal Republic of Germany
Code: DE
Date of Application: 29th August, 1990

Dated this 28th day of August, 1991.

CARTER SMITH & BEADLE
Patent Attorneys for the Applicant

AUSTRALIAN PATENT OFFICE

Our Ref: #8436 BMH:WB 08-7her

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P/00/008
Section 29(1)
Regulation 3.1(2)

AUSTRALIA
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NOTICE OF ENTITLEMENT

I/We, **HERBERTS GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG**, of Christbusch 25, D-5600 Wuppertal 2, Germany, being the applicant in respect of Application No. 83440/91 , state the following:-

The person(s) nominated for the grant of the patent:

has entitlement from the actual inventor(s) by virtue of employment and therefore the nominated person would, on the grant of a patent on the application, be entitled to have the patent assigned to it

The person(s) nominated for the grant of the patent:

is/are the applicant(s) of the basic application(s) listed on the patent request form

The basic application(s) listed on the request form:

is/are the first application(s) made in a Convention country in respect of the invention

HERBERTS GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG

.... (Signature) .... 25/9/91 (Date)

ppa 25.9.91

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(12) **PATENT ABRIDGMENT** (11) Document No. **AU-B-83440/91**
(19) **AUSTRALIAN PATENT OFFICE** (10) Acceptance No. **656913**

(54) Title
PARTIALLY ESTERIFIED GLYCIDYL CONTAINING POLYMERS

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(56) Prior Art Documents
AU 38704/78 GO3C 1/68 C08F 20/32 8/14
US 4477610
US 4358477

(57) The ratio of epoxy : acryloyl groups in the binder is from 20 : 80 to 80 : 20, preferably from 30 : 70 to 70 : 30. That ratio is the total number of epoxy groups : the total number of acryloyl groups in a molecule.

The "equivalent weight" in this context means the weight in g containing 1 mol of the functional group. In the case of component (A), 1 mol is the sum of the functional groups of epoxy and acryloyl groups. In the case of component (B), the reference is to 1 mol of the amine groups.

CLAIM

1. A binder composition for solvent- and/or water-containing coating agents which comprises,

(A) one or more film forming components based on (meth)acrylic copolymers containing at least one acryloyl group and at least one epoxy group in the molecule, the acryloyl groups and the epoxy groups being present in a ratio of from 20 : 80 to 80 : 20, obtained by reacting one or more glycidyl group-containing (meth)acrylic copolymers having an average molecular weight (Mn) of from 1000 to 10000,

.../2

with α, ß-ethylenically unsaturated monocarboxylic acids containing from 2 to 10 carbon atoms and also optionally containing additional ethylene double bonds, and

(B) one or more polyamines containing activators in the form of at least two primary and/or secondary amine groups, optionally masked, in the molecule, as cross linking or curing agent,

the components (A) and (B) being in an equivalent-weight ratio of from 2 : 0.5 to 1 : 1.5.

3. A process for the production of the binder component (A) according to claim 1, characterised in that one or more di-or higher poly-epoxides based on glycidyl-group containing (meth) acrylic copolymers having an average molecular weight (Mn) of from 1000 to 10000 are reacted with one or more α, ß-ethylenically unsaturated monocarboxylic acids containing from 2 to 10 carbon atoms and also optionally containing additional ethylene double bonds.

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Regulation 3.2

AUSTRALIA
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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

Name of Applicant: HERBERTS GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG

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Invention Title: "Partially Esterified Glycidyl Containing Polymers"

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

Our Ref: #8436 BMH:WB 08-7her

AUSTRALIAN PATENT OFFICE

This invention relates to a binder composition suitable for the production of solvent- and/or water-based coating agents.

EP-A-0 002 801 describes two-component varnish binders, wherein the two components are cross-linked by reacting amido amides with acryloyl-unsaturated groups. A dry film of varnish forms very quickly at the surface, but does not set completely for a number of weeks. There is no mention of additional incorporation of glycidyl groups in the acryloyl-unsaturated compound.

EP-A-0 179 954 describes a two-component varnish binder in which epoxy group-containing compounds are cured by using cross-linking agents containing amine groups. These curing agents may also be masked by reacting the amine group with aldehydes or ketones to form a Schiff's base. This system also takes several days to form a hard petrol-resistant film. There is no description of additional incorporation of acryloyl-unsaturated groups in the compound containing epoxy groups.

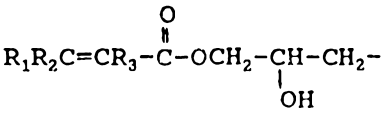
An object of the present invention is to provide two-component binders suitable for solvent-containing or aqueous coating agents which harden quickly at low temperatures, e.g. at room temperature, to form coatings which do not yellow and are resistant to solvents, in particular petrol.

It has been found that this problem may be solved by a binder system in which a film former, which contains epoxy and acryloyl groups in a ratio of from 20 : 80 to 80 : 20, is cross-linked with a curing agent containing an amine group, optionally masked. The combination of epoxy and acryloyl groups results in rapid drying and rapid cross-linking, and also ensures good evaporation of the solvent from the film containing the binder system.

The present invention therefore relates to a binder composition suitable for coating agents containing a solvent and/or water and having the composition specified in the claims.

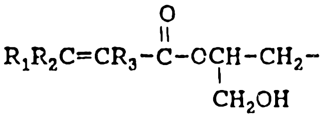
More particularly the present invention relates to a binder composition based on a component (A) containing glycidyl and acryloyl groups and a polyamine component (B) and in which, in a preferred embodiment, the binder component (A) is a glycidyl and acryloyl-group compound containing at least one functional group corresponding to the following general formulae:

(I)



$$R_1R_2C{=}CR_3{-}\overset{\overset{O}{\|}}{C}{-}OCH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_2{-}$$

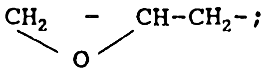
and/or



$$R_1R_2C{=}CR_3{-}\overset{\overset{O}{\|}}{C}{-}O\underset{\underset{CH_2OH}{|}}{CH}{-}CH_2{-}$$

and

(II)



wherein

R_1, R_2 and R_3 may independently represent a hydrogen atom or a straight or branched-chain alkyl radical containing from 1 to 10 carbon atoms and

(I) and (II) may be bonded to a radical of one or more of the following:

(a) polyols selected from straight- or branched-chain (cyclo)-aliphatic and/or aromatic di- or higher poly-ols containing from 2 to 12 carbon atoms having an average molecular weight (Mn) of up to 2000,

(b) polyesters having an average molecular weight (Mn) of from 500 to; 2000 and/or

(c) poly(meth)acrylic acid esters, optionally copolymerised with α,ß-unsaturated monomers and having an average molecular weight (Mn) of from 1000 to 10000;

the curing-agent component (B) being a polyamine component containing at least two functional groups corresponding to the following general formula:

RHN-,

wherein R represent a hydrogen atom or a straight or branched-chain alkyl radical containing from 1 to 10 carbon atoms or a cycloalkyl radical containing from 3 to 8, preferably 5 or 6, carbon atoms.

The ratio of epoxy : acryloyl groups in the binder is from 20 : 80 to 80 : 20, preferably from 30 : 70 to 70 : 30. That ratio is the total number of epoxy groups : the total number of acryloyl groups in a molecule.

The component of the present binder containing at least one glycidyl and one acryloyl group may be produced, e.g. by reacting di- or higher polye-poxides with α,ß-unsaturated carboxylic acids and opening the oxirane ring. The following are examples of suitable di- or higher poly-epoxides: polyglycidyl ethers based on diethylene glycol, dipropylene glycol or polypropylene glycol having an average molecular weight (Mn) of up to 2000, triglycidyl ethers of glycerol and/or di- or higher poly-phenols, such as bisphenol A.

Other examples of di- or higher poly-epoxides are based on di- or higher poly-glycidyl esters, e.g. reaction products of 1-hydroxy-2,3-epoxypropane with phthalic or terephthalic acid to form phthalic or terephthalic acid-bis-(2,3-epoxypropyl ester) or a diglycidyl ether of bisphenol A with trimellitic acid anhydride to form polyesters having an average molecular weight (Mn) of from 500 to 2000.

(Meth)acrylic polymers containing glycidyl groups may also be used, e.g. copolymers of glycidyl (meth)acrylate, 1,2-epoxybutyl acrylate or 2,3-epoxycyclopentyl acrylate. The copolymers may be esters of (meth)acrylic acid, e.g. methyl, ethyl, butyl, isobutyl, ethylhexyl, cyclohexyl, and/or laurylacryl, hydroxy group-containing esters of (meth)acrylic acid such as hydroxyethyl and/or hydroxypropyl esters, or styrene, vinyl toluene and/or methyl styrene. The average molecular weight may be from 1000 to 10000, preferably from 2000 to 5000. (Meth)allyl glycidyl ether or 3,4-epoxy-1-vinyl cyclohexane are other examples of copolymerisable glycidyl monomers. The copolymers are prepared by radical solvent polymerisation, which is known to those skilled in the art and need not be detailed.

In order to prepare the film-forming components of the binders, the di- or higher poly-epoxides may be reacted e.g. with mono- or poly-unsaturated monocarboxylic acids, e.g. containing from 2 to 10, preferably from 3 to 6, carbon atoms, such as cinnamic acid, crotonic acid, citraconic acid, sorbic acid or, preferably, acrylic and/or methacrylic acid.

In order to synthesise the compounds containing glycidyl and acryloyl groups, the reactants may be heated in a solvent, e.g. an aprotic organic solvent. Advantageously the process is carried out under an inert gas. The unsaturated monocarboxylic acid is used in such a quantity as to obtain the desired ratio of epoxy : acryloyl groups. The reaction is continued until the unsaturated monocarboxylic acid has been used up. The following is an example of synthesis of the compounds containing epoxy and acryloyl groups: the compound containing an epoxy group is dissolved, under an inert gas atmosphere, in an aprotic organic solvent and heated, e.g. to 80°C. The unsaturated monocarboxylic acid, which may be dissolved in an aprotic organic solvent, is then added over a period of e.g. 1 hour. The reaction solution is then agitated at 80°C until the acid number of the solution is less than 1 mg KOH/g solid resin.

The binder components containing acryloyl and epoxy groups are cross-linked with compounds bearing at least two primary or secondary amine groups. In order efficiently to cross-link the binder components (A) and (B), at least a portion of the components (A) and/or (B) should desirably be tri-functional. Another alternative is, of course to use tri- and higher multi-functional components (A) and/or tri- and higher multi-functional components (B).

Polyamines suitable as cross-linking agents may also have film-forming properties. The polyamines may be diamines or amines containing more than two amino groups, the amino groups being primary and/or secondary. The polyamines may also be adducts of polyamines containing at least two primary amino groups and at least one, preferably one, secondary amino group, with epoxy compounds, polyisocyanates and acryloyl compounds. Amino amides and adducts of carboxyl-containing acrylates and imines are also suitable.

Examples of suitable di- and higher poly-amines are described, e.g. in EP-A-0 240 083 and EP-A-0 346 982, e.g. aliphatic and/or cycloaliphatic amines containing from 2 to 24 carbon atoms and from 2 to 10, preferably from 2 to 4 primary amino groups and 0 to 4 secondary amino groups. The following are representative examples: ethylene diamine, propylene diamine, butylene diamine, pentamethylene diamine, hexamethylene diamine, 4,7-dioxa-decane-1,10-diamine, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, isophorone diamine, diethylene triamine, dipropylene triamine, 2,2-bis-(4-aminocyclohexyl)propane, polyether polyamines, e.g. those commercially known as "Jeffamines" and produced by Jefferson Chemical Company, bis-(3-aminopropyl)ethyl amines, 3-amino-1-(methylamino)-propane and 3-amino-1-(cyclohexylamino)propane.

Useful polyamines based on adducts of polyfunctional amine components containing di- or higher poly-functional epoxy compounds are obtained e.g. by using di- or higher poly-functional epoxy compounds such as di- or higher poly-glycidyl ethers of (cyclo)aliphatic or aromatic hydroxy compounds, such as ethylene glycol, glycerol, 1,2- and 1,4-cyclohexane diol, bisphenols such as bisphenol A, polyglycidyl ethers of phenol/formaldehyde novolaks, polymers of ethylenically unsaturated groups containing epoxy groups such as glycidyl(meth)acrylate, N-glycidyl(meth)acrylamide and/or allyl glycidyl ethers, optionally copolymerised with various other ethylenically unsaturated monomers, glycidyl ethers of fatty acids containing from 6 to 24 carbon atoms, epoxidized polyalkadienes such as epoxidized polybutadiene, hydantoin epoxy resins, glycidyl group-containing resins, such as polyesters or polyurethanes containing one or more glycidyl groups per molecule, and mixtures of the aforementioned resins and compounds.

The polyamines are added to the aforementioned epoxy compounds by opening the ring of the oxirane group. The reaction may be brought about, e.g. in a temperature range of from 20 to 100°C, preferably from 20 to 60°C. If required, from 0.1 to 2 wt.% of a Lewis base such as triethylamine or an ammonium salt, such as tetrabutyl ammonium iodide, may be used as a catalyst.

The isocyanates for polyamine isocyanate adducts may be aliphatic, cycloaliphatic and/or aromatic di-, tri- or tetra-isocyanates, which may be ethylenically unsaturated. The following are examples thereof: 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, ω,ω'-dipropyl ether diisocyanate, 1,3-cyclopentane diisocyanate, 1,2- and 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanate cyclohexane, transvinylidene diisocyanate, dicyclohexyl methane-4,4'-diisocyanate, 3,3'-dimethyl-dicyclohexylmethane-4,4'-diisocyanate, toluidene diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene, 1,4-bis(1-isocyanato-1-methylethyl)-benzene, 4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, adducts of 2 mols of a diisocyanate, e.g. hexamethylene diisocyanate or isophorone diisocyanate with 1 mol of a diol, e.g. ethylene glycol, the adduct of 3 mols of hexamethylene diisocyanate and 1 mol of water (obtainable under the trade name "Desmodur" N from Bayer AG), the adduct of 1 mol trimethylol propane and 3 mols toluidene diisocyanate (obtainable under the trade name Desmodur L from Bayer AG) and the adduct of 1 mol trimethylol propane and 3 mols isophorone diisocyanate.

The polyamines are added to the aforementioned isocyanate compounds at a temperature of, eg. from 20 to 80°C, preferably from 20 to 60°C. If required, from 0.1 to 1 wt.% of a tertiary amine, such as triethylamine, and/or from 0.1 to 1 wt.% of a Lewis acid, such as dibutyl tin laurate, may be added as catalyst.

Examples of di- or higher poly-functional acryloyl-unsaturated compounds for producing polyamine adducts are described in US-PS 4,303,563, e.g. ethylene glycol diacrylate, diethylene glycol diacrylate, trimethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,6-hexamethylene glycol diacrylate, trimethylol propane diacrylate, pentaerythritol tetraacrylate and pentaerythritol triacrylate. The following are other examples of polyfunctional acryloyl-unsaturated acrylates:

(1) Urethane acrylates, obtained by reacting an isocyanate group of a polyisocyanate with a hydroxy acrylate, e.g. hexamethylene diisocyanate and hydroxyethyl acrylate; production is described in US 3,297,745;

(2) Polyether acrylates, obtained by transesterifying a hydroxy-terminated polyether with acrylic acid, described in US 3,380,831;

(3) Polyester acrylates, obtained by esterifying a hydroxyl-containing polyester with acrylic acid, described in US 3,935,173,

(4) Polyfunctional acrylates obtained by reacting a hydroxyl-containing acrylate, such as hydroxyethyl acrylate, with:

- (a) Dicarboxylic acids containing 4 - 15 carbon atoms,
- (b) Polyepoxides having terminal glycidyl groups, or
- (c) Polyisocyanates having terminal isocyanate groups, described in US 3,560,237;

(5) Acrylate-terminated polyesters obtained by reacting acrylic acid, a polyol containing at least three hydroxy groups and a dicarboxylic acid, described in US 3,567,494;

(6) Polyacrylates, obtained by reacting acrylic acid with an epoxidized oil containing epoxy groups, e.g. soya bean oil or linseed oil, described in US 3,125,592;

(7) Polyacrylates, obtained by reacting acrylic acid with epoxy groups of a diglycidyl ether of bisphenol A, described in US 3,373,075;

8) Polyacrylates, obtained by reacting acrylic acid with an epoxy-containing vinyl polymer, e.g. polymers with glycidyl acrylate or vinyl glycidyl ether, described in US 3,530,100;

(9) Polyacrylate, obtained by reacting acrylic acid anhydride with polyepoxides, described in US 3,676,398;

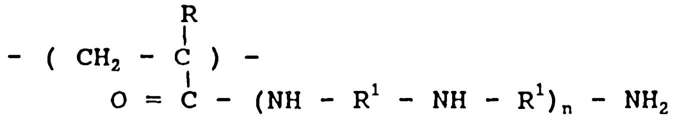
(10) Acrylate-urethane esters, obtained by reacting a hydroxyalkyl acrylate with a diisocyanate and a hydroxyl-containing alkyd resin, described in US 3,676,140,

(11) Acrylate-urethane polyesters, obtained by reacting a polycaprolactone diol or triol with an organic polyisocyanate and with a hydroxyalkyl acrylate, described in US 3,700,634; and

(12) Urethane polyacrylates, obtained by reacting a hydroxy-containing polyester with acrylic acid and a polyisocyanate, described in US 3,759,809.

The acryloyl terminal groups of the di- or higher poly-acrylic monomers or the polyacrylates in examples (1) to (12) may be provided with polyamine groups. The addition reaction may be brought about, e.g. at a temperature of 20 to 100°C, preferably from 40 to 60°C.

Another method of synthesizing a curing agent containing amine groups is described in EP 2801, wherein acrylic acid ester copolymers are amidised with diamines, splitting off alcohol. The resulting reactive group has the following structure:



$$-(\,CH_2 - \overset{\displaystyle R}{\underset{\displaystyle O = C - (NH - R^1 - NH - R^1)_n - NH_2}{C}}\,)-$$

wherein

R represents H or CH_3

R^1 independently represents alkylene groups containing 2 or 3 carbon atoms; and

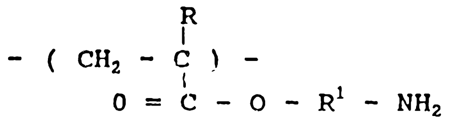
n represents 0, 1, 2 or 3; and

the radical $-(CH_2-\overset{R}{C})-$ originates from the acrylic acid ester copolymer skeleton.

The acrylic acid ester copolymer has an average molecular weight (Mn) of from 1000 to 20000, preferably from 2000 to 5000. The comonomers may, e.g. be esters of (meth)acrylic acid, e.g. methyl, ethyl, butyl, cyclohexyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, or (meth)acrylic acid, styrene or vinyl toluene.

Methyl acrylate is particularly preferred, since this monomer is particularly easily accessible for aminolysis. The proportion of methyl acrylate in the copolymers is from 2 to 35 wt.%. The copolymer is produced by polymerisation in conventional solvents, such as toluene, xylenes, acetates, e.g. butyl acetate or ethyl glycol acetate, ethers, such as tetrahydrofuran, or aromatic mixtures, such as the commercial product "Solvesso 100". The synthesis of the copolymers is known to those skilled in the art and need not be further described. The polyamines used in aminolysis must contain at least two primary or secondary amine groups and have already been described.

The curing agents may be products of a reaction between a (meth)acrylic acid copolymer and alkylene imines as described in EP-A-0 179 954. The resulting functional groups have the structure:



$$\begin{array}{l} -(\,CH_2-\overset{\displaystyle R\atop |}{C}\,)- \\ \qquad O=\overset{|}{C}-O-R^1-NH_2 \end{array}$$

wherein
R represents H or CH_3;
R^1 represents an alkylene group having from 2 to 4 carbon atoms; and

the radical $-(CH_2-\overset{\displaystyle R\atop |}{C})-$ is as defined previously.

In addition to (meth)acrylic acid, the copolymer may contain esters of (meth)acrylic acid or vinyl compounds. The comonomers have already been described elsewhere. Propylene or butylene imine are examples of alkylene imines.

The terminal amino groups of the polyamine curing-agent component (B) may be masked, e.g. with ketones or aldehydes to form Schiff's bases.

All the polyamines described hitherto have very high reactivity towards the binder according to the present invention, resulting in a very short pot-life. For this reason, it may be advantageous to react the terminal amine groups of the aforementioned polyamines with aldehydes or ketones, splitting off water to form Schiff's bases or aldimines or ketimines. Under humidity-free atmosphere, mixtures of the binder according to the present invention and the thus-protected curing agent have a very long pot-life of several days or weeks. The aldehydes and ketones used for masking may be, e.g. C_3-C_{10}- compounds, such as hexyl aldehyde, octyl aldehyde, diisopropyl ketone and/or methyl isobutyl ketone. The last two compounds are particularly preferred because they have only a slight tendency to side-reactions.

In the present binders, according to the invention, the equivalent weight ratio of components (A) and (B) is from 2 : 0.5 to 1 : 1.5, preferably from 2 : 0.5 to 1.

The "equivalent weight" in this context means the weight in g containing 1 mol of the functional group. In the case of component (A), 1 mol is the sum of the functional groups of epoxy and acryloyl groups. In the case of component (B), the reference is to 1 mol of the amine groups.

The binder compositions according to the present invention may be formulated in conventional manner to form coating agents, e.g. varnishes. This is usually done by adding solvents, water or solvent/water mixtures. Optionally, a mixture of components (A) and (B) may be prepared and converted in conventional manner to coating agents by adding solvents and/or water and conventional additives. Alternatively, component (A) or (B) may firstly be prepared by adding solvents, water or solvent/water mixtures and conventional additives, followed by the second component.

The organic solvents used for producing the individual components (A) and (B) are also suitable for producing coating agents, such as varnishes. The solvents may be organic solvents, e.g. aliphatic and aromatic, such as aliphatic and aromatic hydrocarbons, e.g. toluene, xylenes, mixtures of aliphatic and/or aromatic hydrocarbons, esters, ethers and alcohols. These are conventional varnish solvents. The coating agents may also be produced from the binders according to the present invention in aqueous solvents, e.g. emulsifiers as conventionally used in the varnish sector.

The coating agents may be produced by using additives which are conventional in the varnish sector.

The additives may be e.g. pigments, e.g. colour-yielding pigments, such as titanium dioxide or carbon black, or ornamental pigments, such as metal-flake pigments and/or pearlescent pigments. The binder compositions according to the present invention are particularly advantageous for coating agents containing the aforementioned decorative pigments. Preferably, they contain decorative pigments together with colour-yielding pigments, or colour-yielding pigments together with fillers. The additives may also be fillers, such as talc, silicates, plasticizers, light-excluding agents, stabilizers and levelling agents, such as silicone oils.

The binder compositions according to the present invention are "two-component" systems, i.e. components (A) and (B) are stored separately and mixed to form the coating agents just before or when used.

The coating agents produced from the binders according to the present invention are then brought to the desired viscosity for application by suitably adjusting the amount of solvents and/or additives.

Depending on the equivalent weight and the ratio of component (A): component (B), the coating agents may be adjusted to pot lives from 1 to 24 hours, resulting in a long time for processing the coating agents produced from the two-component binder system. The resulting coating agents may be applied in conventional manner, e.g. by immersion, spraying, painting or by electrostatic means.

The coatings produced from the coating agents may set at a relative air humidity of from 20 to 90% and over a wide temperature range of from 10 to 180°C, preferably from 20 and 80°C.

The binders according to the present invention may be used to produce various types of coating agents, e.g. varnishes which may be prepared as pigmented coating varnishes or clear varnishes. They are also of use, e.g. for producing fillers.

The coating agents produced from the binders according to the present invention are suitable for coatings which adhere to a number of substrates, such as wood, textiles, plastics, glass, ceramics and particularly metal. The coating agents may also be applied in a number of layers, e.g. on primers, foundation varnishes, fillers or on existing coating layers. They may be applied either to the previous layers after hardening or wet-on-wet, after which the multi-layer coatings are stoved together. All conventional pre-coatings are suitable.

One preferred application of the binders according to the present invention is the production of coating agents for varnishing in the vehicle sector. Owing to the favourable setting conditions, they are particularly suitable for vehicle-repair varnishing.

The present invention accordingly relates to a method of producing coatings on various substrates, in which a coating agent made from the binders according to the present invention is applied to the substrate, dried and set. The present invention also relates to use of the binder composition according to the invention in clear varnish, fillers or coating varnish.

In all cases, the coating agents produced from the binders according to the present invention yield films having a good gloss, good hardness and good resistance to water and solvents, more particularly supergrade petrol. The substances set very quickly, e.g. are dry to handle within a few minutes, e.g. 10 minutes.

The following Examples illustrate the invention. All parts are by weight.

Synthesis of glycidyl and acryloyl-unsaturated resin

Example 1

(a) 1000 parts of xylene were placed in a 4-litre three-necked flask equipped with an agitator, thermometer, dropping funnel and reflux condenser, and were heated to 90°, with agitation. A mixture of:

380 parts	glycidyl methacrylate
128 parts	butyl methacrylate
252 parts	butyl acrylate
200 parts	styrene and
40 parts	<u>t</u>-butyl peroctoate

was added dropwise over five hours. The resulting epoxy-containing resin had a viscosity of 70 mPas (25°C) and contained 50.1% non-volatile matter (1h/150°C).

(b) 2000 parts of this resin were heated to 90°C, with agitation, with 4.8 parts of triphenyl phosphite, 500 parts butyl acetate 98/100 and 0.9 parts methyl hydroquinone in a 4-litre flask equipped with agitator, thermometer, dropping funnel and reflux condenser. A mixture of 93 parts acrylic acid and 200 g butyl acetate 98/100 was added dropwise at 90°C over 5 hours and was then reacted until reaching an acid number of 1. The resin was distilled until it contained 60% non-volatile matter, when it had a viscosity of 435 mPas.

Example 2

2000 parts of the glycidyl containing resin in Example 1(a) were heated, with agitation, to 90°C with 4.8 parts triphenyl phosphite, 0.9 parts methyl hydroquinone and 500 parts butyl acetate 98/100 in a 4-litre flask equipped with agitator, thermometer, dropping funnel and reflux condenser. A mixture of 110 g acrylic acid and 250 g butyl acetate 98/100 was added dropwise at 90°C over 5 hours and then reacted until the acid number was 1. The resin was distilled until the content of non-volatile matter was 60%, when it had a viscosity of 520 mPas.

Example 3

3000 parts of the glycidyl-containing resin from Example 1(a) were heated to 90°C, with stirring, with 6.3 parts triphenyl phosphite, 1.2 parts methyl hydroquinone and 670 parts butyl acetate (98/100) in a 6-litre flask equipped with stirrer, termometer, dropping funnel and reflux condenser. A mixture of 186 g acrylic acid and 370 g butyl acetate (98/100) was added dropwise at 90°C over 5 hours and then reacted until the acid number was 1. The resin was distilled until the content of non-volatile matter was 80%. To obtain an aqueous solution, 708 g of deionised water was mixed with 0.56 g of a commercial polysiloxane anti-foaming agent and heated to 45°C. 1520 g of the acrylic resin obtained as above was mixed with 60.80 g of a polyoxyethylene-polyoxypropylene alkylphenol emulsifier and heated to 75°C. The resin was sheared, using a rotor/stator homogenizer, and emulsified in the mixture of water and polysiloxane. The proportional amounts were added over 8 minutes. The rotor speed was 10,000 rpm.

During the addition process, the receiver was cooled with water at 45°C. The resulting cloudy white emulsion had a content of non-volatile matter of 55.8%, a viscosity of 57 mPas and an average particle size of 626 nm, determined by photon correlation spectroscopy.

Synthesis of cross-linking agents:

Example 4

568 parts of triethylene tetra-amine and 1000 parts methyl isobutyl ketone were placed under an inert gas atmosphere in a 2-litre flask equipped with agitator, thermometer, dropping funnel and reflux condenser. The reaction mixture was heated to boiling and agitated until separation of water ceased (138 g H_2O = 96% of the theoretical amount).

Example 5

142.5 g of deionised water, 7.5 g of an emulsifier based on a polyoxypropylene-polyoxyethylene sorbitan acid diester of unsaturated fatty acids and 0.1 g of a conventional polysiloxane anti-foaming agent were placed in a 1-litre flask at 25°C. The mixture was agitated by an agitator rotating at a speed of about 7500 rpm. Next, 162 g of a cycloaliphatic amine (amine number 265 mg/KOH/g, viscosity 300 mPas) was added at 25°C over 3 minutes. The resulting milky-white emulsion had a content of non-volatile matter of 55.0% and a viscosity of 47 mPas. The average particle size, determined by photon correlation spectroscopy, was about 631 nm.

Production of varnishes

Example 6

(a) Production of the base varnish:

90 parts of the glycidyl and acryloyl-containing resin in Example 1(b),
0.7 parts of levelling agent based on a conventional silicone oil (10% in butyl acetate 98/100),
0.4 parts of a steric-hindrance amine (UV stabilizer),
0.4 parts of a benzotriazole derivative (UV stabilizer), and
8.5 parts of the following diluent:

25% butyl acetate (98%)
20% methoxypropyl acetate
25% xylols
20% ethoxypropanol acetate
10% butyl glycol acetate

were homogeneously mixed.

(b) Production of the curing-agent solution:

28.0 parts of the polyketimine from Example 4 and
72.0 parts of diluent (composition as hereinbefore)

were homogeneously mixed.

c) Production of varnish:

The base varnish in Example 6(a) and the curing-agent solution in Example 6(b) were homogeneously mixed and, using the previously-mentioned diluent, were brought to a viscosity of 17 to 20'' to DIN 53211 for spraying and were applied wet-on-wet on to a conventional base varnish based on organic solvents, in two or three spraying operations, the thickness of the dry film being from 40 to 100 μm.

Example 7

The process was as in Example 6(a) - (c), except that the glycidyl and acryloyl-containing resin was as in Example 2.

Example 8

20 g of the aqueous resin solution from Example 3 and 5 g of the aqueous curing-agent solution from Example 5 were mixed and spread on a glass plate. After stoving at 60°C for 30 minutes, the clear varnish film had a thickness of 40 μm.

Comparative Example 9

Commercial clear varnish:

Basis: acryloyl-unsaturated resin and ketimine.

The conventional clear varnish system, consisting of clear varnish, curing agent and diluent, was mixed in the formulation given by the manufacturer and applied as described in Example 6(c).

Comparative Example 10

Commercial clear varnish:

Basis: glycidyl-containing resin and amino acrylic resin.

The conventional clear varnish system was mixed in the formulation given by the manufacturer and applied as described in Example 6(c).

The varnishes from Examples 6 to 10 were thermo-set at 60°C for 30 minutes. The varnish films 6 to 8, 1 hour after stoving, had very good resistance to petrol, a good slip and low sensitivity to scratching.

Comparative Examples 9 and 10, even 24 hours after stoving, were loosened by supergrade petrol, were very sensitive to scratches.

The binder compositions of the present invention can also be used for producing pigmented base varnishes and base coats. They can be used as base coats for multilayer coatings which base coats can be covered with usual transparent clear coats.

It is also possible to prepare transparent clear coats from the binders of the invention. Such clear coats can be used for the preparation of multi-layer coatings. They are coated on layers of base coats which may be aqueous or non-aqueous. The clear coats can be applied to the base coat layers after hardening of the base coat layers, drying or wet-in-wet possibly after short airing. In the latter case base coats and clear coat can be hardened together by heating.

In the following, several examples of base coats are furnished which base coats can e.g. be covered by clear coats prepared from the binder compositions of the present invention:

Waterborne base laquers on the basis of 50 to 95% wt. of an aqueous epoxide functionalized emulsion polymerisate and 95 to 5% wt. of an anionic polyurethane dispersion having an acid value of 5 to 10. In such waterborne base laquers pigments can be used which are ground with grinding resins on the basis of poly(meth)acrylate resins (e.g. in an amount of up to 20% wt.). Examples of such waterborne base laquers are described in published DE-A-3 628 124.

Base laquers on the basis of polyesters having a glass transition temperature of > 30°C, melamine resins (e.g. partially butylated melamine resin), polyurea-plasticisers (e.g. on the basis of an addukt from butyl-urethane and formaldehyde) and a copolymer of polyethylene (85% wt.) - vinylacetate (15% wt.) as a wax dispersion. Such base laquers can contain usual additives, such as cellulose acetobutyrate (e.g. having different molecular weights). Examples of such base laquers are described in published EP-A-187 379.

Water base coats which can e.g. be used for vehicle-repair varnishing (especially for repairing metallic-coatings) contain e.g. 50 to 90% wt. polyurethane having carbonate groups and a number average molecular weight of 70000 to 500000 on the basis of reaction products from polyisocyanates and polyhydroxy compounds containing polyhydroxy polycarbonates and 10 to 50% wt. polyurethane having a number average molecular weight of 20000 to 30000. Examples for such laquers are described in published DE-OS 41 15 015.

An example for waterborne base varnish useful for vehicle-repairing (especially uni-colors) contains 50 to 90% wt. of polyurethane having carbonate groups, having a glass transition temperature of < 0°C on the basis of reaction products from polyisocyanates with polyhydroxyl compounds containing polyhydroxyl carbonates and 10 to 50% wt. of reaction products of carboxyl-functional polycondensates and α,β-olefinic unsaturated monomers having a glass transition temperature of > 0°C in the form of an aqueous dispersion. Examples of such waterborne base varnishes are described in published DE-A-41 15 042.

An example for a solvent containing base coat which is particularly useful for vehichle-repairing, contains physically drying binders on the basis of thermoplastic polyester resins and/or acrylic resins in mixture with cellulosic ethers, cellulosic esters and/or polyvinyl acetals. Further, such varnishes contain self-curing binders on the basis of acrylic resin which contain color pigments and which have hydrogen atoms which are reactive with isocyanates. Such varnishes contain additionally mixtures of cellulosic ethers and/or cellulosic esters and/or cellulosic halfesters dissolved in solvents. Examples for such varnishes are described in published DE-OS 29 24 632.

All of the above examples for base varnishes can contain additives which are usual on the varnish field, such as usual fillers and coloring pigments as well as metallic pigments, such as aluminium flakes and steel flakes or other effect pigments.

Further examples for base coatings which can be covered with clear coats on the basis of the binder compositions of the present invention are powder laquers such as described in "Products Finishing", April 1976, pages 54 to 56.

The claims defining the invention are as follows:

1. A binder composition for solvent- and/or water-containing coating agents which comprises,

(A) one or more film forming components based on (meth)acrylic copolymers containing at least one acryloyl group and at least one epoxy group in the molecule, the acryloyl groups and the epoxy groups being present in a ratio of from 20 : 80 to 80 : 20, obtained by reacting one or more glycidyl group-containing (meth)acrylic copolymers having an average molecular weight (Mn) of from 1000 to 10000, with α, β-ethylenically unsaturated monocarboxylic acids containing from 2 to 10 carbon atoms and also optionally containing additional ethylene double bonds, and

(B) one or more polyamines containing activators in the form of at least two primary and/or secondary amine groups, optionally masked, in the molecule, as cross linking or curing agent,

the components (A) and (B) being in an equivalent-weight ratio of from 2 : 0.5 to 1 : 1.5.

2. A coating agent containing the binder composition according to claim 1, and also one or more organic solvents and/or water and, if required, one or more pigments and/or fillers and conventional varnish additives if required.

3. A process for the production of the binder component (A) according to claim 1, characterised in that one or more di-or higher poly-epoxides based on glycidyl-group containing (meth) acrylic copolymers having an average molecular weight (Mn) of from 1000 to 10000 are reacted with one or more α, β-ethylenically unsaturated monocarboxylic acids containing from 2 to 10 carbon atoms and also optionally containing additional ethylene double bonds.

4. A process for the production of a coating agent according to claim 2, characterised in that the binder component (A) is produced according to claim 3 and mixed with one or more polyamines containing at least two primary and/or secondary amine groups, optionally masked, in the molecule and with one or more organic solvents, optionally water, one or more pigments and/or fillers if required, and conventional varnish additives if required.

5. Use of the binder composition according to claim 1 for producing pigmented coating varnishes.

6. Use of the binder composition according to claim 1 for producing pigment-free clear varnishes.

7. Use according to claim 5 or 6 for producing coating or clear varnishes which may set at temperatures of from 20 to 80°C.

8. Use of the binder composition according to claim 1 for producing solvent-resistant coatings.

9. Use of the coating agent according to claim 2 for multi-layer varnishing.

10. A coating agent according to claim 2 for the preparation of base coats.

11. A process for the preparation of multi-layer coatings by applying a coating agent containing the binder composition according to claim 1 on a base coat layer either after curing or drying of the base coat layer or after airing of the base coat layer wet-in-wet and curing of the obtained clear coat layer optionally together with the base coat layer.

12. A binder composition, coating agent, process for the production of binder components, and the use of said binder composition or coating agents substantially as hereinbefore described with reference to any one or more of the non-comparative examples.

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ABSTRACT

"Binder composition, production thereof, coatings containing same and use thereof"

1. A binder composition for coating agents.

2.1 The description relates to a binder composition for solvent-containing or aqueous coating agents which set at low temperatures to form coatings which do not yellow and are resistant to solvents.

2.2 The binder composition contains components based on polyethers, polyesters, polyether/polyesters and/or (meth)acrylic copolymers containing at least one acryloyl group and at least one epoxy group in the molecule, the acryloyl groups and epoxy groups being in a ratio of from 20 : 80 to 80 : 20, together with one or more activators in the form of polyamines in the equivalent-weight ratio of from 2 : 0.5 to 1 : 1.5.

2.3 A binder for pigmented and pigment-free varnish.