LOW VISCOSITY ALLOPHANATES CONTAINING ACTINICALLY CURABLE GROUPS

Inventors: Jan Weikard, Oldenthal (DE); Christophe Detrembleur, Liege (BE); Dorota Greszta-Franz, Erkrath (DE); Frank Richter, Leverkusen (DE); Wolfgang Fischer, Meerbusch (DE); Jörg Schmitz, Köln (DE); Holger Mundstock, Wermelskirchen (DE)

Assignee: Bayer MaterialScience AG, Leverkusen (DE)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 671 days. This patent is subject to a terminal disclaimer.

App. No.: 11/217,207
Filed: Sep. 1, 2005

Prior Publication Data
US 2006/0052526 A1 Mar. 9, 2006

Foreign Application Priority Data
Sep. 9, 2004 (DE) 10 2004043540

Int. Cl. C08G 18/22 (2006.01)
C08G 18/30 (2006.01)
C08G 18/67 (2006.01)
C08G 18/79 (2006.01)
C08G 18/80 (2006.01)

U.S. Cl. 528/73; 522/90; 522/97; 522/98; 522/147; 528/45; 528/49; 528/55; 528/75; 564/44; 564/45; 564/46; 252/182.18

Field of Classification Search 522/90; 522/97, 98, 174; 528/45, 49, 55, 73, 75; 564/44, 45, 46; 252/182.18

See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS
4,160,080 A 7/1979 Köning et al. 528/59
5,672,736 A 9/1997 Braham et al.
5,790,251 A 4/1998 Venham et al. 528/49
5,777,024 A 7/1998 Kilblea et al. 524/590
5,917,083 A 6/1999 König et al. 560/157
5,951,911 A 9/1999 Venham et al. 252/182.2
6,392,001 B1 5/2002 Mertes et al. 528/59
6,417,413 B1 9/2003 Benschmann et al. 528/75

FOREIGN PATENT DOCUMENTS
GB 904890 6/1965
JP 5401492 A 2/1979
JP 59074112 A 4/1984
JP 07042724 A 11/1995
JP 08345544 A 9/1996
JP 2002533542 T 10/2002
JP 2003046927 A 2/2003
JP 2005513149 A 4/2005
WO WO/2005/092942 10/2005

OTHER PUBLICATIONS
B. Vollmer, Synthesis of Polymers with C-C Chains by the Polymerization of Olefinically Unsaturated Compounds, Grundriss der makromolekularen Chemie, (1979), vol. 1, Section 2.1 and Table 55, pp. 52-55.

* cited by examiner

Primary Examiner — Rabon Sergent
Attorney, Agent, or Firm — Connolly Bove Lodge & Hutz LLP

ABSTRACT

The present invention relates to a process for preparing radiation-curing binders containing allophanate groups by reacting at temperatures of ±130°C. A) one or more compounds containing uretdione groups with B) one or more OH-functional compounds which contain groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation (radiation-curing groups).

C) optionally NCO-reactive compounds other than B), in the presence of
D) a catalyst containing at least one zinc compound, to form allophanate groups by opening the uretdione ring.

10 Claims, No Drawings
LOW VISCOSITY ALLOPHANATES CONTAINING ACTINICALLY CURABLE GROUPS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to low viscosity reaction products of alcohols with polyisocyanates, the alcohols containing activated groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, to a process for preparing them and to their use in coating compositions.

2. Description of Related Art

The curing of coating systems which carry activated double bonds by actinic radiation, such as UV light, IR radiation or electron beams, is known and is established in industry. It is one of the most rapid curing methods in coating technology. Coating compositions based on this principle are thus referred to as radiation- or actinically curing or curable systems.

Because of the environmental and economic requirements imposed on modern coating systems, i.e., that they should use as little organic solvents as possible, or none at all, for adjusting the viscosity, there is a desire to use coatings raw materials which are already of low viscosity. Known for this purpose are polyisocyanates having allophanate groups as described, inter alia, in EP-A 0 682 012.

In industry these substances are prepared by reacting a monohydric or polyhydric alcohol with excess aliphatic and/or cycloaliphatic diisocyanate (cf. GB-A 994 890, EP-A 0 000 194 or EP-A 0 712 840). This is followed by removal of unreacted diisocyanate by means of distillation under reduced pressure. According to DE-A 198 60 041 this procedure can also be carried out with OH-functional compounds having activated double bonds, such as hydroxystyryl acrylates, although difficulties occur in relation to the preparation of particularly low-monomer products. Since the distillation step has to take place at temperatures up to 135°C, in order to be able to lower the residual isocyanate content sufficiently (<0.5% by weight of residual monomer), it is possible for double bonds to react, with polymerization, under thermal initiation, even during the purification process, meaning that ideal products are no longer obtained.

The preparation of low-monomer-content, allophanate-containing, polyurethane-based, radiation-curing binders is described in EP-A 0 867 457 and U.S. Pat. No. 5,739,251. These binders, however, do not carry activated double bonds but instead carry inert allyl ether groups (structure R—O—(CH₂)ₓ—CH=CH₂). It is therefore necessary to add reactive diluents (low molecular weight esters of acrylic acid), which introduce the required UV reactivity.

EP-A 0 825 211 describes a process for synthesizing allophanate groups from oxadiazinetriones, although no radiation-curing derivatives having activated double bonds are known. All that is mentioned is the use of maleate- and/or fumarate-containing polymers; the possibility of radiation curing is not described. U.S. Pat. No. 5,777,024 describes the preparation of low-viscosity radiation-curing allophanates by reacting hydroxy-functional monomers which carry activated double bonds with isocyanate groups of allophanate-modified isocyanurate polyisocyanates. The allophanate-bound radicals are saturated as a result.

The formation of allophanate compounds by ring opening of isocyanates with alcohols is known in principle as a crosslinking mechanism in powder coating materials (cf. Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium 2001, 28th, 405-419, and also US-A 2003/0153713). Nevertheless, the reaction temperatures required for this purpose are too high (>130°C) for a targeted preparation of radiation-curing monomers based on allophanate with activated double bonds.

Historically the direct reaction of urethane rings with alcohols to allophanates was first investigated for solvent-borne, isocyanate-free, 2K [2-component] polyurethane coating materials. Without catalyst this reaction is of no technical importance, due to the low reaction rate (F. Schmitt, Angew. Makromol. Chem. (1989), 171, pp. 21-38). With appropriate catalysts, however, the crosslinking reaction between HDI-based uretdione curatives and polyols is said to begin at 60 to 80°C. (K. B. Chandala, R. A. Englebacht, S. L. Goldstein; R. W. Good; S. H. Harris; M. J. Morgan; P. J. Whitman; R. T. Wojcik, Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium, (2001), pp. 77-89). The structure of these catalysts has not been published to date. Commercial products prepared by utilizing this reaction are also undisclosed to date.

In summary it may be stated that the preparation of low-viscosity radiation-curing allophanates by ring-opening reaction of alcohols carrying activated double bonds with uretdiones at temperatures ≤130°C is not disclosed in detail in the prior art.

Surprisingly it has now been found that from the reaction of uretdiones with olefinically unsaturated alcohols, preferably containing activated double bonds, low-viscosity radiation-curing allophanates, which have a low residual monomer content and preferably have viscosities measured at 23°C of less than 100 000 mPa·s, can be obtained using specific zinc compounds as catalysts even at temperatures under 130°C.

SUMMARY OF THE INVENTION

The present invention relates to a process for preparing radiation-curing binders containing allophanate groups reacting at temperatures of ≤130°C.

A) one or more compounds containing uretdione groups with
B) one or more OH-functional compounds which contain groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation (radiation-curing groups),
C) optionally NCO-reactive compounds other than B), in the presence of
D) a catalyst containing at least one zinc compound, to form allophanate groups by opening the uretdione ring.

The present invention also relates to the binders obtained by the process of the invention.

The present invention further relates to coating compositions containing
a) one or more of the binders obtained in accordance with the invention,
b) optionally one or more polyisocyanates containing free or blocked isocyanate groups, which are free from groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation,
c) optionally compounds other than a), which contain groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, and optionally contain free or blocked NCO groups,
d) optionally one or more isocyanate-reactive compounds containing active hydrogen,
e) one or more initiators, and
f) optionally solvents.
Suitable compounds for use as component A) include all organic compounds which contain at least one ureidone group. Preferably they are compounds obtained by the catalytic dimerization of aliphatic, cycloaliphatic and/or aromatic diisocyanates or polisyocyanates by known methods (cf. J. Prakt. Chem. 1994, 336, page 196-198).

Examples of suitable diisocyanates include 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (DDI), trimethylhexane diisocyanate, 1,3- and 1,4-bis-isocyanatomethylcyclohexane, isophorone diisocyanate (IPDI), 4,4'-diisocyanatodiphenylmethane, 1,3- and 1,4-xylene diisocyanates (XDI commercial product from Takeda, Japan), diphenylmethane 4,4'-diisocyanate and diphenylmethane 2,4'-diisocyanate (MDI), 2,4- and 2,6-toluene diisocyanate (TDI), or mixtures thereof. 1,6-Diisocyanatohexane is preferred.

Examples of catalysts employed for the dimerization reaction include trialkylphosphites, dimethylamino pyridines and tris(dimethylamino)phosphine. The result of the dimerization reaction depends in known manner on the catalyst used, on the process conditions and on the diisocyanates employed. In particular it is possible for products to be formed which contain on average more than one ureidone group per molecule, the number of ureidone groups being subject to a distribution. Depending upon the catalyst used, the process conditions and the diisocyanates employed, product mixtures are also formed which in addition to ureidones also contain other structural units, such as isocyanurate and/or iminooxadiazinediones.

Particularly preferred products may be obtained by the catalytic dimerization of HDI and have a free HDI content of less than 0.5% by weight; an NCO content of 17 to 25% by weight, preferably 21 to 24% by weight; and a viscosity at 23 °C of from 20 to 500 mPas, preferably from 50 to 200 mPas.

The generally NCO-functional compounds obtained by catalytic dimerization are preferably used directly as part of component A), but they can also first be subjected to further reaction and then used as component A). Further reactions include blocking the free NCO groups or further reaction of the NCO groups with NCO-reactive compounds having a functionality of two or more to form iminooxadiazinediones, isocyanurate, urethane, allophanate, biuret urea, oxadiazinetrione, oxazolidinone, acrylates or carbodiimide groups. This results in compounds containing ureidone groups having a higher molecular weight, which, depending on the chosen proportions, may contain NCO groups or may be free from NCO groups.

Suitable blocking agents include alcohols, lactams, oximes, malonates, alkyl alkoxyacetates, triazoles, phenols, imidazoles, pyrazoles and amines, such as butanone oxime, disopropylamine, 1,2,4-triazole, dimethyl-1,2,4-triazole, imidazole, diethyl malonate, ethyl acetooxetate, aceton oxime, 3,5-dimethylpyrazole, 3-caprolactam, N-tert-butylbenzylamine, cyclopentanone carboxyethyl ester or mixtures of these blocking agents. The procedure for the blocking of NCO groups is well known and described in Progress in Organic Coatings 1990, 36, 148-172.

NCO-reactive compounds having a functionality of two or more for derivatizing the ureidones used in A) can be the preceding di- and/or polisyocyanates, and also simple alcohols with a functionality of two or more, such as ethylene glycol, propane-1,2-diol, propane-1,3-diol, diethylene glycol, dipropylene glycol, the isomeric butanediols, neopentyl glycol, hexane-1,6-diol, 2-ethylhexanediol, tripolypropylene glycol and the alkoxylated derivatives of these alcohols. Preferred dihydric alcohols are hexane-1,6-diol, dipropylene glycol and tripropylene glycol. Suitable trihydric alcohols include glycerol or trimethylolpropane or their alkoxylated derivatives. Tetrahydric alcohols include pentaerythritol or its alkoxylated derivatives.

By actinic radiation is meant electromagnetic, ionizing radiation, especially electron beams, UV radiation and also visible light (Roche Lexikon Medizin, 4th edition; Urban & Fischer Verlag, Munich 1999).

Component B) is selected from compounds having groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation (radiation-curing groups). Examples include vinyl, vinyl ether, propenyl, allyl, maleyl, fumaryl, maleimide, diacyclopentadienyl, acrylamide, acrylic and methacrylic groups, preferably vinyl ether, acrylate and/or methacrylate groups, and more preferably acrylate groups.

Examples of suitable hydroxyl-containing compounds B) include 2-hydroxyethyl (meth)acrylate, polyethylene oxide mono-(meth)acrylate (e.g. PEA66/PME6; Laporte Performance Chemicals Ltd., UK), polypropylene oxide mono-(meth)acrylate (e.g. PPEA6, PPMSS; Laporte Performance Chemicals Ltd., UK), polyallyl oxide mono-(meth)acrylate (e.g. PEMO3, Laporte Performance Chemicals Ltd., UK), poly(ε-caprolactone) mono(meth)acrylates (e.g. Tone M100®, Dow, Schwalbach, DE), 2-hydroxypropyl(meth)acrylate, 4-hydroxybutyl (meth)acrylate, hydroxybutyl vinyl ether. 3-hydroxy-2,2-dimethylpropyl (meth)acrylate, the hydroxy-functional mono-, di- or higher functional acrylates such as glyceryl di(meth)acrylate, trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate or dipentaerythritol penta(meth)acrylate, which are obtained by reacting polhydric, optionally alkoxylated, alcohols such as trimethylolpropane, glycerol, pentaerythritol or dipentaerythritol with (meth)acrylic acid.

Also suitable as component B) are alcohols obtained from the reaction of acids containing double bonds with epoxide compounds optionally containing double bonds, such as the reaction products of (meth)acrylic acid with glycidyl (meth) acrylate or bisphenol A diglycidyl ether. Additionally, it is also possible to use unsaturated alcohols which are obtained from the reaction of optionally unsaturated acid anhydrides with hydroxy compounds and epoxide compounds that optionally contain acrylate groups. Examples include the reaction products of maleic anhydride with 2-hydroxyethyl (meth)acrylate and glycidyl(meth)acrylate. Preferably, the compounds of component B) correspond to the preceding compounds that have an OH functionality of from 0.9 to 1.1.

More preferably, compounds containing primary hydroxyl groups are used in B), such as 2-hydroxyethyl acrylate and 4-hydroxybutyl acrylate.

Besides the OH-functional unsaturated compounds of component B) it is possible in the process of the invention to also use compounds C), which are different from those of B) and contain NCO-reactive groups such as OH, SH or NH. Examples include NH- or SH-functional compounds containing groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation.

Additionally it is possible to incorporate groups having a hydrophilic action, particularly if use from an aqueous medium is envisaged, such as in an aqueous coating material. Groups with a hydrophilic action include ionic groups, which may be either cationic or anionic in nature, and/or nonionic hydrophilic groups. Cationically, anionically or nonionically dispersing compounds are those which contain, for example,
sulphonium, ammonium, phosphonium, carboxylate, sulpho-
nate or phosphonate groups or the groups which can be con-
tered into these groups by forming salts (potential ionic
groups) or which contain polyether groups and can be incor-
porated by means of existing isocyanate-reactive groups. Pre-
ferred isocyanate-reactive groups are hydroxyl and amino
groups.

Examples of suitable ionic compounds or compounds con-
taining potential ionic groups are mono- and dihydroxycar-
boxylic acids, mono- and diamino carboxylic acids, mono-
and dihydroxysulphonic acids, mono- and diaminosulphonic
acids, mono- and dihydroxyphosphonic acids or mono- and
diaminophosphonic acids and their salts. Examples include
dimethyl propionic acid, diethyl-olbutyric acid, hydroxy-
pyruvic acid, N-(2-aminoethyl)-β-alanine, 2-(2-aminoethy-
lylamino)-ethanesulphonic acid, ethylenediamine-propyl-
or butyl sulphonic acid, 1,2- or 1,3-propylenediamine-β-ethyl-
sulphonic acid, maleic acid, citric acid, glycolic acid, lactic
acid, glycine, alanine, taurine, lysine, 3,5-diaminobenzoic
acid, an adduct of IPDI and acrylic acid (EP-A 0 916 647,
Example 1) and its alkali metal and/or ammonium salts, the
adduct of sodium bisulphite with but-2-ene-1,4-diol, poly-
ethersulphonate, the propoxylated adduct of 2,2-butanediol
and NaHCO₃ (described for example in DE-A 2 446 440, page
5-9, formula I-III) and also structural units which can be
converted into cationic groups, such as N-methylidethanol-
amine.

Preferred ionic or potential ionic compounds are those
having carboxyl or carboxylate, sulphonate groups and/or am-
monium groups. Particularly preferred ionic compounds are
those which contain carboxyl and/or sulphonate groups as
ionic or potential ionic groups, such as the salts of N-(2-
aminoethyl)-β-alanine, 2-(2-aminoethylylamino)ethanesul-
phonic acid, the adduct of IPDI and acrylic acid (EP-A 0 916
647, Example 1) and also dimethylpropionic acid.

Suitable nonionic hydrophilic compounds include poly-
oleylalkene ethers containing at least one hydroxyl or am-
ino group. These polyethers include a fraction of from 30% to
100% by weight of units derived from ethylene oxide. Su-
tiable compounds include linear polyethers having a func-
tionality of from 1 to 5, and also compounds of formula (I),

\[
\text{HO} \begin{array}{c}
\text{R}^1 \\
\text{R}^2
\end{array} \text{R}^3 \text{OH}
\]

wherein

R² and R³ independently of one another are each a divalent
aliphatic, cycloaliphatic or aromatic radical having 1 to 18
carbon atoms, which may be interrupted by oxygen and/or
nitrogen atoms, and

R³ is an alkoxy-terminated polyethylene oxide radical.

Nonionic hydrophilic compounds also include monohydric
polyoleylalkene oxide polymer alcohols containing on average
5 to 70, preferably 7 to 55, ethylene oxide units per molecule,
such as those obtained in known manner by alkyloxylating
suitable starter molecules (e.g. in Ullmann Encyclopedia der
technischen Chemie, 4th edition, volume 19, Verlag Chemie,
Weinheim pp. 31-38).

Examples of suitable starter molecules include saturated
monooctylcohols such as methanol, ethanol, n-propanol,
isopropanol, n-butanol, isobutanol, sec-butanol, the isomeric pen-
tanols, hexanols, octanols and nonanols, n-decanol, n-dode-
canol, n-tetradecanol, n-hexadecanol, n-octadecanol,
cyclohexanol, the isomer of methylecyclohexanols, hydroxym-
ethylecyclohexane, 3-ethyl-3-hydroxymethylexetane, tet-
hydrofurfuryl alcohol, diethylene glycol monobutyl ethers
such as diethylene glycol monobutyl ether, unsaturated al-
cohols (such as allyl alcohol, 1,1-dimethylallyl alcohol or oleyl
 alcohol), aromatic alcohols such as phenol, the isomeric cre-
sols or methoxyphenols, aliphatic alcohols (such as ben-
yl alcohol, anisyl alcohol or cinnamyl alcohol), secondary
monoamines (such as dimethylaniline, diethylaniline, dipro-
pylamine, diisopropylamine, dibutylamine, bis(2-ethyl-
 hexyl)amine, N-methyl- and N-phenylcyclohexylamine or
dicyclohexylamine) and also heterocyclic secondary amines
(such as morpholine, pyrrolidine, piperidine or 1H-pyrazole).
Preferred starter molecules are saturated monooctylcohols. Par-
ticular preference is given to using diethylene glycol
monobutyl ether as the starter molecule.

Alkylene oxides suitable for the alkylation reaction in-clude, in particular, ethylene oxide and propylene oxide,
which can be used in any order or in a mixture in the alky-
lation reaction.

The polyalkylene oxide polymer alcohols are either straight
polyethylene oxide polymers or mixed polyalkylene oxide
polyethers wherein at least 30 mole %, preferably at
least 40 mole %, of the alkylene oxide units are ethylene oxide
units. Preferred nonionic compounds are monofunctional
mixed polyalkylene oxide polyethers which contain at least
40 mole % of ethylene oxide units and not more than 60 mole
% of propylene oxide units.

Especially when using a hydrophilic agent containing ionic
groups it is necessary to investigate its effect on the action of
catalyst D. For this reason preference is given to nonionic
compounds as hydrophilic agents.

Suitable catalyst compounds D) include, in addition to the
zinc compounds for use in accordance with the invention,
the compounds known for catalysing the reaction of isocyanate
groups with isocyanate-reactive groups, individually or in
mixtures with one another.

Examples include tertiary amines such as triethylenimine,
pyridine, methylpyridine, benzylidinemethylamine, N,N-
endenylenepiperazine, N,N-diethylpiperazine, pentamethyldih-
ylenetetramine, N,N-dimethylaminocyclohexane, N,N-di-
dimethylpiperazine or 1,4-diazabicyclo[2.2.2]octane (DABCO),
or metal salts such as iron(III) chloride, tin(II) octoate, tin(II)
electrodeposate, tin(II) palmitate, dibutyltin(IV) dilaurate,
dibutyltin(IV) dioctoate and molybdenum glycolate or mix-
tures of such catalysts.

Suitable zinc compounds include any organic or inorganic
zinc compounds, such as zinc oxide, zinc sulphide, zinc car-
bonate, zinc fluoride, zinc chloride, zinc bromide, zinc iodide,
zinc phosphide, zinc borate, zinc titanate, zinc hexafluoro-
silicate, zinc sulphate, zinc sulphate, zinc nitrate, zinc tetraflu-
oro borate, zinc acetate, zinc octoate, zinc cyclohexanebui-
tyrate, zinc laurate, zinc palmitate, zinc stearate, zinc be-
herate, zinc citrate, zinc gluconate, zinc acetylatedonoate,
zinc 2,2,6,6-tetramethyl-3,5-heptadionate, zinc trifluoroac-
etate, zinc trifluoromethane-sulphonate, zinc dimethylthio-
carbonate and mixtures of these compounds. Preferred cata-
lysts D) are zinc octoate and/or zinc acetylatedonoate.

Preferably, zinc compounds are exclusively used as catalysts
D).

It is also possible to apply catalysts D) to support mate-
rials by known methods and to use them as heterogeneous cata-
lysts.

The compounds of catalyst component D) can be dissolved
advantageously in one of the components used in the process,
or in a portion thereof. In particular, the zinc compounds for
use in accordance with the invention dissolve very well in the
In order to stabilize the reaction mixture, in particular the unsaturated groups, against premature polymerization it is possible to pass an oxygen-containing gas, preferably air, into and/or over the reaction mixture. It is preferred for the gas to have a very low moisture content in order to prevent unwanted reaction in the presence of isocyanate.

In general a stabilizer is added during the preparation of the binders of the invention, and at the end, in order to achieve a long-term stability, stabilization is repeated with a phenolic stabilizer, and optionally the reaction product is saturated with air.

In the process of the invention the stabilizer component is typically used in amounts of 0.001 to 5.0% by weight, preferably 0.01 to 2.0% by weight and more preferably 0.05 to 1.0% by weight, based on solids content of the product.

The ratio of OH groups from component B) to the sum of NCO and uretdione groups from A) is preferably from 1.5:1.0 to 1.0:1.9, more preferably from 1.0:1.0 to 1.0:1.9 and most preferably from 1.0:1.0 to 1.0:1.2. The process of the invention is preferably carried out at temperatures of 20 to 130°C, more preferably of 40 to 100°C, and most preferably of 80 to 90°C.

Normally the NCO groups that may be present react more rapidly with the hydroxyl groups of component B) than do the uretdione groups of component A). Therefore, if two or more different constituents are present in B), it is possible to control the urethanization and alloanization by means of the sequence of addition of the constituents such that one constituent of B) is preferably incorporated during the urethanization reaction, while the constituent added last is preferably incorporated during the alloanization reaction.

The reaction of component A) with B) and further NCO-reactive compounds C) is over when all of the NCO groups, in accordance with the chosen stoichiometric proportions, have reacted with NCO-reactive groups from B) and C) and all uretdione groups, in accordance with the chosen stoichiometric proportions, have reacted with the hydroxyl groups from B). It is also possible to end the alloanization by adding catalyst-deactivating compounds (for example, strong acids such as acidic phosphoric esters) or adding other isocyanate-containing compounds which scavenge the remaining compounds of component B).

It is immaterial whether the process of the invention is carried out continuously, for example, in a static mixer, extruder or compounding or batchwise, for example, in a stirred reactor. Preferably, the process of the invention is carried out in a stirred reactor, the sequence of addition of components A), E) being arbitrary.

The course of the reaction can be monitored by means of suitable measuring instruments installed in the reaction vessel and/or on the basis of analyses on samples taken. Suitable techniques are known. They include viscosity measurements, measurements of the refractive index or the OH content, gas chromatography (GC), nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR) and near infrared spectroscopy (NIR). Preference is given to using IR to check for any free NCO groups present (for aliphatic NCO groups, band at approximately ν ~ 2272 cm⁻¹) and, in particular, for uretdione groups (e.g. band for uretdiones based on hexamethylene diisocyanate at ν ~ 1761 cm⁻¹) and to GC analyses for unreacted compounds from B) and C).

In one preferred embodiment of the invention there is parallel alloanization and urethanization of the compounds of component A). For that purpose A) is introduced initially, then stabilizers and, where appropriate, additives from E) are added, subsequently components B)-E) are added and the reaction mixture is brought to reaction temperature.
In another preferred embodiment initially A) is reacted with B) until the NCO groups have reacted completely. E) or parts thereof may already be present. Subsequently the reaction of the urethane groups of A) with B) is initiated by adding D) and additionally, where appropriate, by adapting the temperature.

In one particularly preferred embodiment the isocyanate groups and the urethane groups are reacted with an excess of hydroxyl groups of component B. The hydroxyl groups which remain following the reaction of A) with B), with catalysis of D), are subsequently reacted preferably with further isocyanate-containing compounds, in particular with those compounds described as component B), with urethaneization.

The unsaturated allophanates obtained by the process of the invention preferably have viscosities measured using a cone-plate viscometer at 23°C. of ≤100 000 mPas, more preferably ≤75 000 mPas; preferably have number average molecular weights Mn of from 600 to 3000 g/mol, more preferably from 750 to 1500 g/mol and preferably contain less than 0.5% by weight of free di- and/or triisocyanate monomers, more preferably less than 0.1% by weight.

The binders of the invention can be used for producing coatings and paints and also adhesives, printing inks, casting resins, dental compounds, sizes, photoresists, stereolithography systems, resins for composite materials and sealants. In the case of adhesive bonding or sealing, it is a requirement, in the case of UV radiation curing, at least one of the two substrates to be bonded or sealed to one another is permeable to UV radiation, i.e. it must be transparent. In the case of electron beams, sufficient permeability for electrons should be ensured. Preferably, the binders are used in paints and coatings.

The coating compositions according to the invention contain:

a) one or more of the binders obtained in accordance with the invention,
b) optionally one or more polycyanate containing free or blocked isocyanate groups, which are free from groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation,
c) optionally compounds other than a), which contain groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation, and

do) optionally contain free or blocked NCO groups,
ed) optionally one or more isocyanate-reactive compounds,
e) initiators, and
f) optionally solvents.

The polycyanates of component B), which are used in the coating compositions according to the invention, are known. Preferred are polycyanates which optionally contain isocyanurate, allophanate, biuret, uretdione and/or iminoazadinedione groups and are prepared from hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-diisocyanatodicyclohexylmethane and/or trimethylhexamethylene diisocyanate. The NCO groups may also block with the blocking agents previously described as suitable for blocking component A).

Compounds d) include urethane acrylates prepared from hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-diisocyanatodicyclohexylmethane and/or trimethylhexamethylene diisocyanate, which may have been modified to contain isocyanurate, allophanate, biuret, uretdione and/or iminoazadinedione groups, and which do not contain isocyanate-reactive groups. NCO-containing urethane acrylates are available commercially from Bayer MaterialScience AG, Leverkusen, DE as Roskydal® UA VP LS 2337, Roskydal® UA VP LS 2396 or Roskydal® UA XP 2510.

Also suitable as component c) are the reactive diluents already described and known in the art of radiation-curing coatings, provided that they do not contain any NCO-reactive groups.

Compounds d) can be saturated or unsaturated and contain isocyanate-reactive groups, such as hydroxyl, amine or thiol. Preferred are saturated polyhydroxy compounds, such as polyether polyls, polyester polyls, polycarbonate polyls, poly(meth)acrylate polyls and/or polyurethane polyls, which are known from the technology of coating, adhesive bonding, printing inks or sealants and which contain no groups which react, with polymerization, with ethylenically unsaturated compounds on exposure to actinic radiation.

Unsaturated hydroxy-functional compounds include the epoxy acrylates, polyester acrylates, polyether acrylates and acrylated polyacrylates which are known in the art of radiation-curing coatings and have an OH number of from 30 to 300 mg KOH/g. It is also possible to use the reactive diluents, previously described and known in the art of radiation-curing coatings as a constituent of d), provided that they contain NCO-reactive groups.

Suitable initiators for free-radical polymerization, which can be used as component e), are those which can be activated thermally and/or by radiation. Photoinitiators, which are activated by UV or visible light, are preferred in this context. The photoinitiators are known compounds. A distinction is made between unimolecular (type I) and bimolecular (type II) initiators. Suitable (type I) systems include aromatic ketone compounds, e.g. benzophenones in combination with tertiary amines, alkybenzophenones, 4,4'-bis(dimethylamino)benzophenone (Michler's ketone), anthranil and halogenated benzophenones or mixtures thereof. Suitable (type II) initiators include benzoin and its derivatives, benzil ketals, acrylophine oxides, 2,4,6-trimethylbenzyldiphenyl phosphine oxide, bis(acryloxypropyl) phosphine oxide, bis(acryloxyethyl) phosphine oxide, phenylglyoxylic esters, camphorquinone, α-aminooctylphosphines, α,α-di-alkoxyacetophenones and α-hydroxyalkylphosphines.

The initiators are used in amounts of 0.1% to 10% by weight, preferably 0.1% to 5% by weight, based on the weight of the film-forming binder. The initiators can be used individually or, to obtain advantageous synergistic effects, in combination with one another.

When electron beams are used instead of UV irradiation there is no need for a photoinitiator. Electron beams are generated by means of thermal emission and accelerated by way of a potential difference. The high-energy electrons then pass through a titanium foil and are guided onto the binders to be cured. The general principles of electron beam curing are described in detail in "Chemistry & Technology of UV & EB Formulations for Coatings, Inks & Paints", Vol. 1, P. K. T Oldring (Ed.), SITA Technology, London, England, pp. 101-157, 1991.

Thermal curing of the activated double bonds can take place with the addition of thermally decomposing free-radical initiators. Suitable initiators include peroxo compounds such as dialkxy dicarbonates, for example, bis(tert-butyl cyclohexyl) peroxycarbonate; dialkyl peroxides such as dialkyl peroxide; peresters of aromatic or aliphatic acids such as tert-butyl perbenzoate or tert-arly peroxy 2-ethyl hexanoate; inorganic peroxides such as ammonium peroxydisulfate or potassium peroxydisulfate; organic peroxides such as 2,2-bis(tert-butylperoxy)butane, dicumyl peroxide or tert-butyl hydroperoxide; and azo compounds such as 2,2'-azobis[N-(2-propenyl)-2-methylpropanimides], 1-[cyano-1-methylthyl]azoformamides, 2,2'-azobis[N-(butyl-2-methylthyl)]peroxide, and 2,2'-azobis(N-cyanoethyl-2,2-dimethylpropanimides).
Methyl(2-methylimidazol-1-yl)propylamines), 2,2'-azobis[N-cyclohexyl-2-methylpropionamides], 2,2'-azobis[N-(1-phenylethyl)-2-methyl-N-(1-phenylethyl)propionamides]. Also suitable are highly substituted 1,2-diphenylethanes (benzpinacols) such as 3,4-dimethyl-3,4-diphenylhexane, 1,2,3,4-tetraphenylethane, 1,2-diol or the silylated derivatives thereof.

It is also possible to use a combination of initiators active by UV light and thermally. Additives e) include solvents of the type specified above under E). Additionally, it is possible for e), in order to increase the weather stability of the cured coating film, to contain UV absorbers and/or HALS stabilizers. Preferred is a combination of these stabilizers. The UV absorbers should have an absorption range of not more than 390 nm, such as the triphenyltriazine types (e.g. Tinuvin® 400 (Ciba Spezialitatenchemie GmbH, Lampertheim, DE)), benzotriazoles such as Tinuvin® 622 (Ciba Spezialitatenchemie GmbH, Lampertheim, DE) or oxalic diamides (e.g. Sanduruvor® 3206 (Clariant, Mutтенz, CH)). They are added at 0.5% to 3.2% by weight, based on resin solids. Suitable HALS stabilizers are also available commercially and include (Tinuvin® 292 or Tinuvin® 123 (Ciba Spezialitatenchemie GmbH, Lampertheim, DE) or Sanduruvor® 3258 (Clariant, Muttenz, CH)). They are preferably added in amounts of 0.5% to 2.5% by weight based on resin solids.

It is also possible for component e) to contain pigments, dyes, fillers, levelling additives and devolatilizing additives. Additionally it is possible, if necessary, for the catalysts known from polyurethane chemistry for accelerating the NCO/OH reaction to be present in e). They include tin salts, zinc salts, organotin compounds, tin soaps and/or zinc soaps such as tin octoate, dibutyltin dilaurate, dibutyltin oxide or tertiary amines such as dicyclohexyl[2,2,2]octane (DABCO).

The application of the coating compositions of the invention to the material to be coated takes place using the methods known in coatings technology, such as spraying, knife coating, rolling, pouring, dipping, spin coating, brushing or spraying or by means of printing techniques such as screen, gravure, flexographic or offset printing and also by means of transfer methods.

Suitable substrates include wood, metal, including in particular metal as used in the applications of wire enamelling, coil coating, can coating or container coating, and also plastic, including plastic in the form of films, especially ABS, AMMA, ASA, CA, CABA, EP, UF, CF, ME, MPE, PF, PAN, PA, PE, HDPE, LDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM, and UP (abbreviations according to DIN 772811), paper, leather, textiles, felt, glass, wood, wood materials, cork, inorganically bonded substrates such as wooden boards and fiber cement slabs, electronic assemblies or mineral substrates. It is also possible to coat substrates containing a variety of the preceding materials, or to coat already coated substrates such as vehicles, aircraft or boats and also parts thereof, especially vehicle bodies or parts for exterior mounting. It is also possible to apply the coating compositions to a substrate temporarily, then to cure them partly or fully and optionally to detach them again, in order to produce films.

For curing it is possible to remove solvents present entirely or partly by flushing off. Subsequently or simultaneously it is possible for the optional thermal and the photochemical curing operation or operations to be carried out in succession or simultaneously.

If necessary the thermal curing can take place at room temperature or at elevated temperature, preferably at 40 to 160°C, preferably at 60 to 150°C, and more preferably at 80 to 110°C.

Where photoinitiators are used in d) the radiation cure takes place preferably by exposure to high-energy radiation, in other words UV radiation or daylight, such as light having a wavelength 200 to 700 nm or by bombardment with high-energy electrons (electron beams, 150 to 300 keV). Radiation sources of light or UV light include high-pressure or medium-pressure mercury vapor lamps. It is possible for the mercury vapor to have been modified by doping with other elements such as gallium or iron. Lasers, pulsed lamps (known under the designation of UV flashlamps), halogen lamps or excimer emitters may also be used. As an inherent part of their design or through the use of special filters and/or reflectors, the emitters may be equipped so that part of the UV spectrum is prevented from being emitted. By way of example, for reasons of occupational hygiene, for example, the radiation assigned to UV-C or to UV-V and UV-B may be filtered out. The emitters may be installed in stationary fashion, so that the material for irradiation is conveyed past the radiation source by means of a mechanical device, or the emitters may be mobile and the material for irradiation may remain stationary during curing. The radiation dose which is normally sufficient for crosslinking in the case of UV curing is from 80 to 5000 mJ/cm².

Irradiation can also be carried out in the absence of oxygen, such as under an inert gas atmosphere or an oxygen-reduced atmosphere. Suitable inert gases are preferably nitrogen, carbon dioxide, noble gases or combustion gases. Irradiation may additionally take place by covering the coating with media transparent to the radiation. Examples include polymeric films, glass or liquids such as water.

Depending on the radiation dose and curing conditions it is possible to vary the type and concentration of any initiator used in known manner.

Particular preference is given to carrying out curing using high-pressure mercury lamps in stationary installations. Photoinitiators are then employed at concentrations of from 0.1% to 10% by weight, more preferably from 0.2% to 3.0% by weight, based on the solids content of the coating composition. For curing these coatings it is preferred to use a dose of from 200 to 3000 mJ/cm², measured in the wavelength range from 200 to 600 nm.

When thermally activatable initiators are used in d), curing is carried out by increasing the temperature. The thermal energy may be introduced into the coating by means of radiation, thermal conduction and/or convection using ovens, near-infrared lamps and/or infrared lamps that are known in coatings technology.

The applied film thicknesses (prior to curing) are typically between 0.5 and 5000 μm, preferably between 5 and 1000 μm and more preferably between 15 and 200 μm. Where solvents are used, they are removed after application and before curing by known methods.

EXAMPLES

All percentages are by weight unless indicated otherwise. The determination of the NCO contents in % was determined by back-titration with 0.1 mol/l hydrochloric acid following reaction with butyamine in accordance with DIN EN ISO 11909.
The viscosity measurements were carried out with a cone-plate viscosimeter (SM-KP), Viskolab L.C3/ISO from Paar Physica, Ostfildern, DE in accordance with ISO/DIS 3219: 1990.

Infrared spectroscopy was on liquid films applied between sodium chloride plates on a model 157 instrument from Perkin Elmer, Überlingen, DE.

The amount of residue monomers and amount of volatile synthesis components were analyzed by means of GC (method using tetradecane as internal standard, oven temperature 110°C, injector temperature 150°C, carrier gas helium, instrument: 6890 N, Agilent, Waldbronn, DE, column: Restek RT 50, 30 m, 0.32 mm internal diameter, film thickness 0.25 μm).

The solids content was determined in accordance with DIN 55216/1 draft 4/89, ISO 3251.

An ambient temperature of 23°C, which prevailed at the time when the experiments were conducted is referred to as RT.

Desmodur® N 3400—HDI polyisocyanate predominantly containing uretdione groups, viscosity 185 mPa*s/23°C, NCO content 21.4%, commercial product of Bayer MaterialScience AG, Leverkusen, DE

Desmorapid® Z—dibutyltin dilaurate (DBTL), commercial product of Bayer MaterialScience AG, Leverkusen, DE

Durum® 1173—photoinitiator, commercial product of Ciba Spezialitätenchemie GmbH, Lampereim, DE

Example 1

Inventive Allophanate-Containing Binder

A three-necked flask with reflux condenser, stirrer and dropping funnel, and through which air was passed (0.5 l/h), was charged at RT with 253.13 g of Desmodur® N 3400, 0.50 g of 2,6-di-tet-butyl-4-methylphenol and 0.07 g of Desmorapid® Z and this initial charge was then heated to 60°C. 219.25 g of 2-hydroxyethyl acrylate were slowly added dropwise, during which a maximum temperature of 70°C was attained. Thereafter the reaction mixture was held at 65°C until the NCO content was <0.1%. Subsequently a mixture of 14.41 g of 2-hydroxyethyl acrylate and 2.14 g of zinc(II) ethylhexanate was added dropwise. The reaction mixture was heated up again and held at 80°C until after 3.5 h only a very weak signal for uretdione groups was detected in the IR spectrum at ν=1768 cm⁻¹. 0.50 g of isophthalic dichloride was added and the mixture was cooled rapidly to RT.

The hydroxystyryl acrylate content of a sample taken was found by gas chromatography to be 4.96%. 41.33 g of Desmodur N 3400 and 0.07 g of Desmorapid® Z were then added. The mixture was stirred at 60°C until in the IR spectrum at ν=2272 cm⁻¹ there was no longer any signal present for isocyanate groups. The hydroxystyryl acrylate content of a sample taken was found by gas chromatography to be 0.14%. A product was obtained with a viscosity of 62,800 mPa*s/23°C, an APHA color number of 8 and an NCO content of less than 0.1%.

Example 2

Inventive Allophanate-Containing Binder

Example 1 was repeated with the difference that, instead of zinc(II) ethylhexanate, 1.59 g of zinc(II) acetylacetonate were used. The reaction time following addition of the cate...

The catalysts described in US-A 2003/0153713 for the crosslinking of powder coating compositions containing uretdione group-containing curing agents and polymeric hydroxyl compounds without activated double bonds were examined for suitability:

Example 1 was repeated with the difference that, instead of the catalyst from Example 3, 0.51 g of tetrabutylammonium hydroxide was used as catalyst. The reaction mixture was heated to and held at 80°C until after 2 h only a very weak signal for uretdione groups was detected in the IR spectrum at ν=1768 cm⁻¹. 0.10 g of benzoyl chloride was added and the mixture was cooled rapidly to RT.

During this cooling the reaction mixture turned cloudy. The hydroxystyryl acrylate content of a sample taken was found by gas chromatography to be 2.4%. 5.20 g of Desmodur® N 3400 were added to the reaction mixture, which was stirred at 70°C until in the IR spectrum at ν=2272 cm⁻¹ there was no longer any signal for isocyanate groups. The hydroxystyryl acrylate content of a sample taken was found by gas chromatography to be 0.17%. A cloudy product was obtained with a viscosity of 84,000 mPa*s/23°C and an NCO content of 0%.

Comparative Example 4

Attempt to prepare an allophanate-containing binder. The catalysts described in US-A 2003/0153713 for the crosslinking of powder coating compositions containing uretdione group-containing curing agents and polymeric hydroxyl compounds without activated double bonds were examined for suitability:

Example 1 was repeated with the difference that, instead of the catalyst from Example 3, 0.67 g of tetrabutylammonium fluorode was used as catalyst. The reaction mixture was heated to and held at 80°C until after 3 h only a very weak signal for uretdione groups was detected in the IR spectrum at ν=1768 cm⁻¹. 0.10 g of benzoyl chloride was added and the mixture was cooled rapidly to RT. During this cooling the reaction mixture turned cloudy, and a colorless precipitate formed.

The hydroxystyryl acrylate content of a sample taken was found by gas chromatography to be 1.7%. 4.30 g of Desmodur® N 3400 were added to the reaction mixture, which was stirred at 70°C until in the IR spectrum at ν=2272 cm⁻¹ there...
was no longer any signal for isocyanate groups. The hydroxyethyl acrylate content of a sample taken was found by gas chromatography to be 0.15%. A cloudy product was obtained with a viscosity of 92,000 mPas/23°C and an NCO content of 0%.

Comparison Examples 3 and 4 show that the catalysts which are suitable for crosslinking powder coating compositions containing uretdione group-containing curing agents and polymeric hydroxyl compounds are not suitable for the targeted synthesis of aliphonates from uretdiones and alcohols. The resulting products are cloudy and have a relatively high viscosity making them unsuitable for producing coatings.

Example 5

Coating Formulation and Coating Material

In each case a portion of the products from Examples 1 and 2 was mixed thoroughly with 3.0% of the photoinitiator Darocur® 1173. Using a bone doctor blade with a gap of 90 μm the mixture was drawn down in the form of a thin film onto a glass plate. UV irradiation (medium pressure mercury lamp, IST Metz GmbH, Nürtingen, DE, 750 mJ/cm²) gave a hard, transparent coating which was solvent-resistant. Had a pendulum hardness of 153 s or 154 s, could hardly be damaged by scratching using steel wool (grade 0/0/0) in ten back-and-forth strokes with a force of 500 g directed onto the film and was not visibly altered after 100 back-and-forth strokes with a wad of cotton wool soaked in butyl acetate.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

What is claimed is:
1. A process for preparing a radiation-curing binder containing aliphonate groups which comprises reacting at temperatures of ≤130°C.
   A) one or more compounds containing uretdione groups with
   B) one or more OH-functional compounds which contain at least one group selected from vinyl ethers, acrylates and methacrylates which polymerize with ethylenically unsaturated compounds on exposure to actinic radiation,
   C) optionally NCO-reactive compounds other than B), in the presence of
   D) a catalyst comprising at least one zinc compound, to form aliphonate groups by opening the uretdione ring.
2. The process of claim 1 wherein said compounds containing uretdione groups are prepared from hexamethylene diisocyanate.
3. The process of claim 1 wherein component B) comprises 2-hydroxyethyl acrylate and/or 4-hydroxybutyl acrylate.
4. The process of claim 2 wherein component B) comprises 2-hydroxyethyl acrylate and/or 4-hydroxybutyl acrylate.
5. The process of claim 1 wherein component D) consists essentially of zinc compounds.
6. The process of claim 1 wherein component D) comprises zinc acrylatecetone and/or zinc ethylhexanoate.
7. The process of claim 2 wherein component D) comprises zinc acrylatecetone and/or zinc ethylhexanoate.
8. The process of claim 3 wherein component D) comprises zinc acrylatecetone and/or zinc ethylhexanoate.
9. The process of claim 4 wherein component D) comprises zinc acrylatecetone and/or zinc ethylhexanoate.
10. The process of claim 1 wherein the reaction is carried out at a temperature of 40 to 100°C.