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Radiation-curable Resins Based on Hydrogenated Ketone-aldehyde and Phenol-aldehyde resins and a Process for Preparing Them

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Radiation-curable Resins Based on Hydrogenated Ketone-aldehyde and Phenol-aldehyde Resins and a Process for Preparing Them

Abstract

5 Radiation-curable resins essentially comprising A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or B) at least one ring-hydrogenated phenol-aldehyde resin, and C) at least one compound comprising at least one ethylenically unsaturated moiety having at the same time at least one moiety which is reactive toward A) and/or B) and a process for preparing a radiation-curable resin by polymer-analogously reacting A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or B) at least one ring-hydrogenated phenol-aldehyde resin, with C) at least one compound which
10 contains at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B).

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FOR A STANDARD PATENT

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Invention Title:	Radiation-curable Resins Based on Hydrogenated Ketone- aldehyde and Phenol-aldehyde resins and a Process for Preparing Them

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

Radiation-curable Resins Based on Hydrogenated Ketone-aldehyde and Phenol-aldehyde Resins and a Process for Preparing Them

The invention relates to radiation-curable resins based on carbonyl-hydrogenated ketone-aldehyde and ring-hydrogenated phenol-aldehyde resins and to a process for preparing them.

5 Radiation-curable coating materials have increasingly gained in importance within recent years, owing not least to the low VOC (volatile organic compounds) content of these systems.

The film-forming components in the coating material are of relatively low molecular mass and hence of low viscosity, so that there is no need for high fractions of organic solvents. Durable coatings are obtained by the formation, following application of the coating material, of a high molecular mass, 10 polymeric network by means of crosslinking reactions initiated, for example, by UV light.

Ketone-aldehyde resins are used in coating materials, for example, as additive resins in order to enhance certain properties such as initial drying rate, gloss, hardness or scratch resistance. Owing to their relatively low molecular weight, customary ketone-aldehyde resins possess a low melt viscosity and solution viscosity and therefore also serve as film-forming functional fillers in coating materials.

15 Ketone-aldehyde resins normally possess hydroxy groups and can therefore be crosslinked only with, for example, polyisocyanates or amine resins. These crosslinking reactions are usually initiated and/or accelerated thermally.

For radiation-initiated crosslinking reactions, in accordance with cationic and/or free-radical reaction mechanisms, the ketone-aldehyde resins are not suitable.

20 Accordingly, the ketone-aldehyde resins are normally added to radiation-curable coating systems as, for example, a film-forming component, but not as a crosslinking component.

Owing to the uncrosslinked fractions, the resistance of such coatings to gasoline, chemicals or solvents, for example, is often low.

25 DE 23 45 624, EP 736 074, DE 2847 796, DD 240318, DE 2438 724, and JP 09143396 describe the use of ketone-aldehyde resins and ketone resins, eg., cyclohexanone formaldehyde resins, in radiation-curable systems. Radiation-induced crosslinking reactions of these resins are not described.

EP 0 902 065 describes the use of nonradiation-curable resins formed from urea (derivatives), ketone or aldehydes as an added component in a mixture with radiation-curable resins.

30 DE 24 38 712 describes radiation-curing printing inks composed of film-forming resins, ketone resins and ketone-formaldehyde resins, and polymerisable components such as polyfunctional acrylate esters of polyhydric alcohols. To the skilled worker it is obvious that a radiation-induced crosslinking reaction of the modified ketone-aldehyde resins and ketone resins can only come about through the use of unsaturated fatty acids. It is known, however, that resins having a high oil content tend toward 35 unwanted yellowing.

US 4 070 500 describes the use of nonradiation-curable ketone-formaldehyde resins as a film-forming component in radiation-curable inks.

The conversion of the carbonyl groups into secondary alcohols by hydrogenation of ketone-aldehyde resins has long been practiced (DE-C 8 70 022, DE 32 41 735). A typical and known product 40 is Kunstharz SK from Degussa AG. Likewise known are resins based on phenolic resin, whose

aromatic units have been converted into cycloaliphatic groups by hydrogenation, with some of the hydroxy groups retained. The use of carbonyl hydrogenated and ring-hydrogenated ketone-aldehyde resins based on ketones containing aromatic groups is a further possibility. A resin of this kind is described in DE 33 34 631. The OH number of said products, at more than 200mg KOH/g, is very high.

It was an object of the present invention to modify carbonyl-hydrogenated ketone-aldehyde resins and/or ring-hydrogenated phenol-aldehyde resins chemically in such a way as to give radiation-curable resins which are stable to hydrolysis, are resistant, and possess a high yellowing resistance.

Surprisingly it has been possible to achieve this object by providing carbonyl-hydrogenated ketone-aldehyde resins and/or ring-hydrogenated phenolic resins in polymer-analogous fashion with ethylenically unsaturated moieties.

It has been found that carbonyl-hydrogenated ketone-aldehyde resins and/or ring-hydrogenated phenol-aldehyde resins which possess ethylenically unsaturated moieties, in the presence of suitable compounds such as, for example, photoinitiators, and in the presence if desired of suitable photosensitisers, can, by induction with, for example, UV light, be converted into a polymeric network which depending on the fraction of ethylenically unsaturated groups possesses resistance and hardness which is high to very high.

The invention provides radiation-curable resins essentially comprising

- A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or
- B) at least one ring-hydrogenated phenol-aldehyde resin, with
- C) at least one compound comprising at least one ethylenically unsaturated moiety having at the same time at least one moiety which is reactive toward A) and/or B).

The invention also provides radiation-curable resins obtained by polymer-analogously reacting

- A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or
- B) at least one ring-hydrogenated phenol-aldehyde resin, with
- C) at least one compound comprising at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B).

Suitable ketones for preparing the carbonyl-hydrogenated ketone-aldehyde resins (component A) include all ketones, especially acetone, acetophenone, methyl ethyl ketone, heptan-2-one, pentan-3-one, methyl isobutyl ketone, cyclopentanone, cyclododecanone, mixtures of 2,2,4- and 2,4,4-trimethylcyclopentanone, cycloheptanone and cyclooctanone, cyclohexanone and all alkyl-substituted cyclohexanones having one or more alkyl radicals containing in total 1 to 8 carbon atoms, individually or in a mixture. Examples that may be mentioned of alkyl-substituted cyclohexanones include 4-tert-amylcyclohexanone, 2-sec-butylcyclohexanone, 2-tert-butylcyclohexanone, 4-tert-butylcyclohexanone, 2-methylcyclohexanone, and 3,3,5-trimethylcyclohexanone.

In general, however, any of the ketones said in the literature to be suitable for ketone resin syntheses, more generally all C-H-acidic ketones, can be used. Preference is given to carbonyl hydrogenated ketone-aldehyde resins based on the ketones acetophenone, cyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and heptanone, alone or in a mixture.

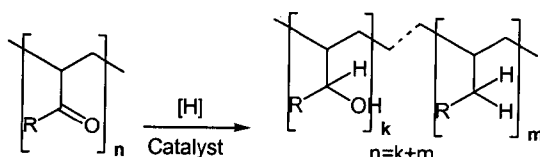
Suitable aldehyde components of the carbonyl-hydrogenated ketone-aldehyde resins (component A) include in principle linear or branched aldehydes, such as formaldehyde, acetaldehyde, n-butyraldehyde and/or isobutyraldehyde, valeraldehyde, and dodecanal. In general it is possible to use any of the aldehydes said in the literature to be suitable for ketone resin syntheses. It is preferred, however, to use formaldehyde, alone or in mixtures.

The requisite formaldehyde is normally used in the form of an aqueous or alcoholic (eg., methanol or butanol) solution with a strength of from about 20 to 40wt%. Other forms of formaldehyde, such as para-formaldehyde or trioxane, for example, are likewise possible.

Aromatic aldehydes, such as benzaldehyde, can likewise be present in a mixture with formaldehyde.

Particularly preferred starting compounds used for component A) are carbonyl-hydrogenated resins of acetophenone, cyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethyl-cyclohexanone, and heptanone, alone or in a mixture, and formaldehyde.

The resins of ketone and aldehyde are hydrogenated with hydrogen in the presence of a catalyst at pressures of up to 300 bar. In the course of the hydrogenation the carbonyl group of the ketone-aldehyde resin is converted into a secondary hydroxy group. Depending on reaction conditions, some of the hydroxy groups may be eliminated, resulting in methylene groups. This is illustrated in the following scheme:



As component B) use is made of ring-hydrogenated phenol-aldehyde resins of the novolak type using the aldehydes such as formaldehyde, butyraldehyde or benzaldehyde, for example, preferably formaldehyde. To a minor extent it is possible to use nonhydrogenated novolaks, but these then have lower light fastnesses.

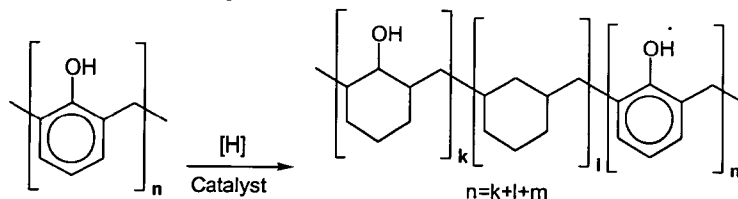
Particularly suitable are ring-hydrogenated resins based on alkyl-substituted phenols. In general it is possible to use any of the phenols said in the literature to be suitable for phenolic resin syntheses.

Examples of suitable phenols that may be mentioned include phenol, 2- and 4-tert-butylphenol, 4-amyphenol, nonylphenol, 2- and 4-tert-octylphenol, dodecylphenol, cresol, xylenols, and bisphenols. They can be used alone or in a mixture.

It is particularly preferred to use ring-hydrogenated, alkyl-substituted phenol-formaldehyde resins of the novolak type. Preferred phenolic resins are reaction products of formaldehyde and 2- and 4-tert-butylphenol, 4-amyphenol, nonylphenol, 2- and 4-tert-octylphenol, and dodecylphenol.

The novolaks are hydrogenated with hydrogen in the presence of a suitable catalyst. Through the choice of the catalyst the aromatic ring is converted into a cycloaliphatic ring. Through a suitable choice of the parameters the hydroxy group is retained.

This is illustrated by the following scheme:



Through the choice of the hydrogenation conditions it is also possible for the hydroxy groups to be hydrogenated, thereby giving rise to cycloaliphatic rings. The ring-hydrogenated resins possess OH numbers of from 50 to 450mg KOH/g, preferably from 100 to 350mg KOH/g, more preferably from 150 to 300mg KOH/g. The fraction of aromatic groups is below 50wt%, preferably below 30wt%, more preferably below 10wt%.

The radiation-curable resins on which the invention is based are obtained by polymer-analogous reaction of the carbonyl-hydrogenated ketone-resins and/or of the ring-hydrogenated phenolic resins, in the melt or in a suitable solvent solution, with component C). Suitability is possessed by maleic anhydride, (meth)acrylic acid derivatives such as (meth)acryloyl chloride, glycidyl (meth)acrylate, (meth)acrylic acid and/or the low molecular mass alkyl esters and/or anhydrides thereof alone or in a mixture. It is also possible to obtain radiation-curable resins by reacting the carbonyl-hydrogenated ketone-aldehyde resins and ring-hydrogenated phenolic urea-aldehyde resins with isocyanates possessing an ethylenically unsaturated moiety, such as (meth)acryloyl isocyanate, α,α -dimethyl-3-isopropenylbenzyl isocyanate, (meth)acryloylalkyl isocyanate with alkyl spacers possessing from 1 to 12, preferably from 2 to 8, more preferably from 2 to 6 carbon atoms, such as methacryloylethyl isocyanate and methacryloylbutyl isocyanate, for example. Further reaction products which have proven suitable are those of hydroxyalkyl (meth)acrylates whose alkyl spacers have from 1 to 12, preferably from 2 to 8, more preferably from 2 to 6 carbon atoms and diisocyanates such as, for example, cyclohexane diisocyanate, methylcyclohexane diisocyanate, ethylcyclohexane diisocyanate, propylcyclohexane diisocyanate, methyldiethylcyclohexane diisocyanate, phenylene diisocyanate, tolylene diisocyanate, bis(isocyanatophenyl)methane, propane diisocyanate, butane diisocyanate, pentane diisocyanate, hexane diisocyanate, such as hexamethylene diisocyanate (HDI) or 1,5-diisocyanato-2-methylpentane (MPDI), heptane diisocyanate, octane diisocyanate, nonane diisocyanate, such as 1,6-diisocyanato-2,4,4-trimethylhexane or 1,6-diisocyanato-2,2,4-trimethylhexane (TMDI), nonane triisocyanate, such as 4-isocyanatomethyloctane 1,8-diisocyanate (TIN), decane di- and triisocyanate, undecane di- and triisocyanate, dodecane di- and triisocyanates, isophorone diisocyanate (IPDI), bis(isocyanatomethylcyclohexyl)methane (H_{12} MDI) isocyanatomethylmethylcyclohexyl isocyanate, 2,5(2,6)-bis(isocyanatomethyl)bicyclo[2.2.1]heptane (NBDI), 1,3-bis(isocyanatomethyl)-cyclohexane (1,3- H_6 -XDI) or 1,4-bis(isocyanatomethyl)cyclohexane (1,4- H_6 -XDI) alone or in a mixture. Examples that may be mentioned include the reaction products in a 1:1 molar ratio of hydroxyethyl acrylate and/or hydroxyethyl methacrylate with isophorone diisocyanate and/or H_{12} MDI and/or HDI.

Another preferred class of polyisocyanates are the compounds having more than two isocyanate groups per molecule which are prepared by trimerising, allophanatising, biuretising and/or urethanising the simple diisocyanates, examples being the reaction products of these simple diisocyanates, such as IPDI, HDI and/or HMDI, for example, with polyhydric alcohols (eg., glycerol, trimethylolpropane, pentaerythritol) and/or polyfunctional polyamines or else the triisocyanates obtainable by trimerising the simple diisocyanates, such as IPDI, HDI, and HMDI, for example.

If desired it is possible to use a suitable catalyst for preparing the resins of the invention. Suitable compounds are all those known in the literature which accelerate an OH-NCO reaction, such as diazabicyclooctane (DABCO) or dibutyltin dilaurate (DBTL), for example.

The functionality of the resins obtained ranges from low to high in accordance with the ratio of the reactants to one another. Through the choice of reactants it is also possible to set the subsequent hardness of the crosslinked film. If, for example, a hard resin such as hydrogenated acetophenone-formaldehyde resin is reacted with α,α -dimethyl-3-isopropenylbenzyl isocyanate, the resulting products are harder than those obtained through the use of (meth)acryloylethyl isocyanate and/or hydroxyethyl acrylate-isophorone diisocyanate adducts; the flexibility, however, is then lower. It has also been found that the reactivity of ethylenically unsaturated compounds with little steric hindrance - such as hydroxyethyl acrylate, for example - is higher than in the case of those which are sterically hindered, such as α,α -dimethyl-3-isopropenylbenzyl isocyanate, for example.

It is also possible to replace some of the carbonyl-hydrogenated ketone-aldehyde resins A) and/or ring-hydrogenated phenol-aldehyde resins B) by further hydroxy-functional polymers such as hydroxy-functional polyethers, polyesters and/or polyacrylates, for example. In this case, mixtures of these polymers with components A) and/or B) can be reacted polymer-analogously with component C) directly. It has been found that first of all it is also possible to prepare adducts of A) and/or B) with, for example, hydroxy-functional polyethers, polyesters and/or polyacrylates, using the abovementioned diisocyanates and/or triisocyanates, and only then are these adducts reacted polymer-analogously with component C). In contrast to the "plain" carbonyl-hydrogenated ketone-aldehyde resins A) and/or ring-hydrogenated phenol aldehyde resin B) it is possible by this means better to set properties such as flexibility and hardness, for example. The further hydroxy-functional polymers generally possess molecular weights M_n of between 200 and 10 000g/mol, preferably between 300 and 5000g/mol.

The invention also provides a process for preparing radiation-curable resins obtained by polymer-analogously reacting

A) carbonyl-hydrogenated ketone-aldehyde resins, and/or

B) ring-hydrogenated phenol-aldehyde resins, with

C) compounds which contain at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B), with the use if desired of further hydroxy-functionalised polymers.

The resins on which the invention is based are prepared in the melt or in a suitable, organic solvent solution of the carbonyl-hydrogenated ketone-aldehyde resin and/or ring-hydrogenated phenol-aldehyde resin.

For this purpose, in one preferred embodiment I, the compound which contains firstly at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B), in the presence if desired of a suitable catalyst, is added to the solution or melt of the carbonyl-hydrogenated ketone aldehyde resin A) and/or ring-hydrogenated phenol-aldehyde resin B).

The temperature of the reaction is selected in accordance with the reactivity of component C). Where isocyanates are used as component C), suitable temperatures have been found to be between 30 and 150°C, preferably between 50 and 140°C.

The solvent that may be present can be separated off if desired after the end of the reaction, in which case a powder of the product of the invention is then generally obtained.

It has proven advantageous to react 1 mol of the carbonyl-hydrogenated ketone-aldehyde resin and/or ring-hydrogenated-aldehyde resin phenol - based on M_n - with from 0.5 to 15mol, preferably from 1 to 10mol, in particular from 2 to 8mol of the unsaturated compound (component C).

In a preferred embodiment II, the compound which contains at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B) and the additional polymer, in the presence if desired of a suitable catalyst, is added to the solution or melt of the carbonyl hydrogenated ketone-aldehyde resin A) and/or ring-hydrogenated phenol-aldehyde resin B) and the hydroxy-functional polymer, such as polyether, polyester and/or polyacrylate, for example.

The temperature of the reaction is selected in accordance with the reactivity of component C). Where isocyanates are used as component C), suitable temperatures have been found to be between 30 and 150°C, preferably between 50 and 140°C.

The solvent that may be present can be separated off if desired after the end of the reaction, in which case a powder of the product of the invention is then generally obtained.

It has proven advantageous to react 1mol of component A) and/or component B) and/or additional polymers - based on M_n - with from 0.5 to 15mol, preferably from 1 to 10mol in particular from 2 to 8mol of the unsaturated compound (component C).

In a preferred embodiment III a di- and/or trifunctional isocyanate is added to the solution or melt of the carbonyl hydrogenated ketone-aldehyde resin A) and/or ring-hydrogenated phenol-aldehyde resin B) and the hydroxy-functional polymer, such as polyether, polyester and/or polyacrylate, for example, and a hydroxy-functional preadduct is prepared. Only then is the compound which contains at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B) and the additional polymer, in the presence if desired of a suitable catalyst, added.

The temperature of the reaction is selected in accordance with the reactivity of component C). Where isocyanates are used as component C), suitable temperatures have been found to be between 30 and 150°C, preferably between 50 and 140°C.

The solvent that may be present can be separated off if desired after the end of the reaction, in which case a powder of the product of the invention is then generally obtained.

It has proven advantageous to react 1mol of component A) and/or component B) and/or additional polymers - based on M_n - with from 0.5 to 15mol, preferably from 1 to 10mol, in particular from 2 to 8mol of the unsaturated compound (component C).

In the presence of suitable photoinitiators, and in the presence if desired of suitable photosensitisers, these resins can be converted by irradiation into polymeric, insoluble networks which, depending on the level of ethylenically unsaturated groups present, produce elastomers to thermosets.

The examples which follow are intended to illustrate the invention but not to restrict its scope of application:

Example 1

Synthesis takes place by reaction of 1mol of Kunstharz SK (Degussa AG; hydrogenated acetophenone-formaldehyde resin, OHN = 240mg KOH/g (acetic anhydride method), $M_n \sim 1000$ g/mol) with 1.5mol of a reaction product of IPDI and hydroxyethyl acrylate in a ratio of 1:1 in the presence of 0.2% (on resin) of 2,6-bis(tert-butyl)-4-methylphenol (Ralox BHT, Degussa AG) and 0.1% (on resin) of dibutyltin dilaurate, 65% strength in methoxypropyl acetate, at 80°C under nitrogen in a three-necked flask with stirrer, reflux condenser, and temperature sensor until an NCO number of less than 0.1 is reached. The pale, clear solution obtained possesses a dynamic viscosity of 51.56Pa.s.

Example 2

The reaction is carried out of 1mol of Kunstharz SK (Degussa AG; OHN = 240mg KOH/g (acetic anhydride method), $M_n \sim 1000$ g/mol) and 4 mol of a reaction product of IPDI and hydroxyethyl acrylate in a ratio of 1:1 in the presence of 0.2% (on resin) of 2,6-bis(tert-butyl)-4-methylphenol (Degussa AG) and 0.1% (on resin) of dibutyltin dilaurate, 65% strength in methoxypropyl acetate, at 80°C under nitrogen in a three-necked flask with stirrer, reflux condenser, and temperature sensor until an NCO number of less than 0.1 is reached. The pale, clear solution obtained possesses a dynamic viscosity of 26.2Pa.s.

The resin solutions from examples 1 and 2 were admixed with Darocur 1173 (Ciba Specialty Chemicals, 1.5% based on resin solids) and applied to a glass plate and the solvent was evaporated at elevated temperature (30 min, 80°C). The films were then cured by means of UV light (medium-pressure mercury lamp, 70W/optical filter 350nm) for about 12 seconds. The films, previously soluble, are no longer soluble in methyl ethyl ketone.

The claims defining the invention are as follows:

1. A radiation-curable resin essentially comprising
A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or
B) at least one ring-hydrogenated phenol-aldehyde resin, and
C) at least one compound comprising at least one ethylenically unsaturated moiety having at the same time at least one moiety which is reactive toward A) and/or B).

2. A radiation-curable resin obtained by polymer-analogously reacting
A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or
B) at least one ring-hydrogenated phenol-aldehyde resin, with
C) at least one compound comprising at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B).

3. A radiation-curable resin as claimed in claim 1 or claim 2, obtained by polymer-analogously reacting
A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or
B) at least one ring-hydrogenated phenol-aldehyde resin, with
C) at least one compound comprising at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B) and at least one further hydroxy-functionalised polymer.

4. A radiation-curable resin as claimed in claim 3, wherein polyethers, polyesters and/or polyacrylate are used.

5. A radiation-curable resin as claimed in claim 3 or claim 4, wherein mixtures of the further polymers with the ketone-aldehyde resins A) and/or phenol-aldehyde resins B) are reacted polymer-analogously with component C).

6. A radiation-curable resin as claimed in any one of claims 3 to 5, wherein first of all adducts of the ketone-aldehyde resins A) and/or phenol-aldehyde resins B) with the further polymers, using suitable di- and/or triisocyanates, are prepared, and only then are these adducts reacted polymer-analogously with component C).

7. A radiation-curable resin as claimed in any one of the preceding claims, wherein C-H-acidic ketones are used in component A).

8. A radiation-curable resin as claimed in any one of the preceding claims, wherein ketones selected from acetone, acetophenone, methyl ethyl ketone, heptan-2-one, pentan-3-one, methyl isobutyl ketone, cyclopentanone, cyclododecanone, mixtures of 2,2,4- and 2,4,4-trimethylcyclopentanone, cycloheptanone, cyclooctanone, and cyclohexanone are used as starting compounds, alone or in mixtures, in the carbonyl-hydrogenated ketone aldehyde resins of component A).

9. A radiation-curable resin as claimed in any one of the preceding claims, wherein alkyl-substituted cyclohexanones having one or more alkyl radicals containing in total 1 to 8 carbon atoms, individually or in a mixture, are used in the carbonyl-hydrogenated ketone-aldehyde resins of component A).

10. A radiation-curable resin as claimed in claim 9, wherein 4-tert-amylcyclohexanone, 2-sec-butylcyclohexanone, 2-tert-butylcyclohexanone, 4-tert-butylcyclohexanone, 2-methylcyclohexanone, and 3,3,5-trimethylcyclohexanone are used.

11. A radiation-curable resin as claimed in any one of the preceding claims, wherein cyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and heptanone, alone or in a mixture, are used in component A).

12. A radiation-curable resin as claimed in any one of the preceding claims, wherein formaldehyde, acetaldehyde, n-butyraldehyde and/or isobutyraldehyde, valeraldehyde, and dodecanal, alone or in mixtures, are used as aldehyde component of the carbonyl hydrogenated ketone-aldehyde resins in component A).

13. A radiation-curable resin as claimed in claim 12, wherein formaldehyde and/or paraformaldehyde and/or trioxane are used.

14. A radiation-curable resin as claimed in claim 1, 2 or 3, wherein hydrogenation products of the resins formed from acetophenone, cyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and heptanone, alone or in a mixture, and formaldehyde are used as component A.

15. A radiation-curable resin as claimed in any one of the preceding claims, wherein the aldehydes, formaldehyde, butyraldehyde and/or benzaldehyde are used in the ring-hydrogenated phenol-aldehyde resins (component B).

16. A radiation-curable resin as claimed in any one of the preceding claims, wherein nonhydrogenated phenol-aldehyde resins are used to a minor extent.

17. A radiation-curable resin as claimed in any one of the preceding claims, wherein ring-hydrogenated resins based on alkyl-substituted phenols are used in component B).

18. A radiation-curable resin as claimed in claim 17, wherein 4-tert-butylphenol, 4-amylphenol, nonylphenol, tert-octylphenol, dodecylphenol, cresol, xylenols, and bisphenols, alone or in mixtures, are used.

19. A radiation-curable resin as claimed in any one of the preceding claims, wherein maleic acid is used as component C).

20. A radiation-curable resin as claimed in any one of the preceding claims, wherein (meth)acrylic acid and/or derivatives are used as component C).

21. A radiation-curable resin as claimed in claim 20, wherein (meth)acryloyl chloride, glycidyl (meth)acrylate, (meth)acrylic acid and/or the low molecular mass alkyl esters and/or anhydrides thereof, alone or in a mixture, are used as component C).

22. A radiation-curable resin as claimed in any one of the preceding claims, wherein isocyanates which possess an ethylenically unsaturated moiety are used as component C).

23. A radiation-curable resin as claimed in claim 22, wherein the isocyanates are (meth)acryloyl isocyanate, α,α -dimethyl-3-isopropenylbenzyl isocyanate and/or (meth)acryloylalkyl isocyanate with alkyl spacers possessing 1 to 12 carbon atoms.

24. A radiation-curable resin as claimed in claim 23, wherein the alkyl spacers possess 2 to 8 carbon atoms.

25. A radiation-curable resin as claimed in claim 23, wherein the alkyl spacers possess 2 to 6 carbon atoms.

26. A radiation-curable resin as claimed in claim 22, wherein the isocyanates are methacryloylethyl isocyanate and/or methacryloylbutyl isocyanate.

27. A radiation-curable resin as claimed in any one of the preceding claims, wherein reaction products of hydroxyalkyl (meth)acrylates whose alkyl spacers possess 1 to 12 carbon atoms with diisocyanates are used as component C).

28. A radiation-curable resin as claimed in claim 27, wherein the alkyl spacers possess 2 to 8 carbon atoms.

29. A radiation-curable resin as claimed in claim 27, wherein the alkyl spacers possess 2 to 6 carbon atoms.

30. A radiation-curable resin as claimed in any one of claims 27 to 29, wherein diisocyanates selected from cyclohexane diisocyanate, methylcyclohexane diisocyanate, ethylcyclohexane diisocyanate, propylcyclohexane diisocyanate, methyl-diethylcyclohexane diisocyanate, phenylene diisocyanate, tolylene diisocyanate, bis(isocyanatophenyl)methane, propane diisocyanate, butane diisocyanate, pentane diisocyanate alone or in mixtures, are used.

31. A radiation-curable resin as claimed in claim 30, wherein diisocyanates selected from hexamethylene diisocyanate (HDI), 1,5-diisocyanato-2-methylpentane (MPDI), heptane diisocyanate, octane diisocyanate, 1,6-diisocyanato-2,4,4-trimethylhexane, 1,6-diisocyanato-2,2,4-trimethylhexane (TMDI), 4-isocyanatomethyloctane 1,8-diisocyanate (TIN), decane di- and triisocyanate, undecane di- and triisocyanate, dodecane di- and triisocyanates, isophorone diisocyanate (IPDI), bis(isocyanatomethylcyclohexyl)methane (H₁₂MDI) isocyanatomethylmethylcyclohexyl isocyanate, 2,5(2,6)-bis(isocyanato-methyl)bicyclo[2.2.1]heptane (NBDI), 1,3-bis(isocyanatomethyl)cyclohexane (1,3-H₆-XDI), 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H₆-XDI) alone or in mixtures, are used.

32. A radiation-curable resin as claimed in claim 30 or claim 31, wherein polyisocyanates prepared by trimerising, allophanatising, biuretising and/or urethanising simple diisocyanates are used.

33. A radiation-curable resin as claimed in any one of the preceding claims, wherein the reaction products in a molar ratio of 1:1 of hydroxyethyl acrylate and/or hydroxyethyl methacrylate with isophorone diisocyanate and/or H₁₂MDI and/or HDI are used as component C).

34. A radiation-curable resin as claimed in any one of the preceding claims, wherein 1mol of the carbonyl-hydrogenated ketone-aldehyde resin and/or ring-hydrogenated phenol-aldehyde resin - based on M_n - and from 0.5 to 15mol of the unsaturated compound are used.

35. A radiation-curable resin as claimed in claim 34, wherein from 1 to 10mol of the unsaturated compound is used.

36. A radiation-curable resin as claimed in claim 34, wherein from 2 to 8mol of the unsaturated compound is used.

37. A radiation-curable resin, substantially as hereinbefore described with reference to any one of the examples.

38. A process for preparing a radiation-curable resin by polymer-analogously reacting A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or

B) at least one ring-hydrogenated phenol-aldehyde resin, with
C) at least one compound which contains at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B).

39. A process for preparing a radiation-curable resin by polymer-analogously reacting

5 A) at least one carbonyl-hydrogenated ketone-aldehyde resin, and/or
B) at least one ring-hydrogenated phenol-aldehyde resin, with
C) at least one compound which contains at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and B) and at least one further hydroxy-functionalised polymer.

10 40. A process as claimed in claim 38 or claim 39, wherein a catalyst is used.

41. A process as claimed in any one of claims 38 to 40, wherein reaction is conducted in the melt or in a solvent.

42. A process as claimed in any one of claims 38 to 41, wherein compounds according to any one of claims 3 to 37 are used.

15 43. A process as claimed in any one of claims 38 to 42, wherein the compound C), in the presence if desired of a suitable catalyst, is added to the solution or melt of the ketone aldehyde resins A) and/or phenol-aldehyde resins B).

44. A process as claimed in any one of claims 38 to 42, wherein the compound C), in the presence if desired of a suitable catalyst, is added to the solution or melt of the ketone aldehyde resins A) and/or phenol-aldehyde resins B) and the hydroxy-functional polymer.

20 45. A process as claimed in any one of claims 38 to 42, wherein a di- and/or trifunctional isocyanate is added to the solution or melt of the ketone-aldehyde resins A) and/or phenol-aldehyde resins B) and the hydroxy-functional polymer and a hydroxy-functional preadduct is prepared and subsequently the compound C), in the presence if desired of a suitable catalyst, is added.

25 46. A process as claimed in any one of claims 38 to 45, wherein reaction is conducted at temperatures between 30 and 150°C.

47. A process as claimed in claim 46, wherein reaction is conducted at temperatures between 50 and 140°C.

30 48. A process as claimed in any one of claims 38 to 47, wherein polyethers, polyesters and/or polyacrylate are used as hydroxy-functionalised polymer.

49. A process for preparing a radiation-curable resin, said process being substantially as hereinbefore described with reference to any one of the examples.

50. A radiation-curable resin prepared by a process as claimed in any one of claims 38 to 49.

35 **Dated 20 August, 2004**
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