Coating composition based on a polyacrylate resin containing hydroxyl groups, and its use in processes for the production of coatings

The present invention relates to coating compositions comprising

(A) at least one component which contains hydroxyl groups, consisting of

(A1) from 20 to 60% by weight of at least one polyester and

(A2) from 40 to 80% by weight of at least one polyacrylate resin which contains hydroxyl groups and has been prepared, at least partially, in the presence of component (A1), and

(B) at least one crosslinking agent, characterized in that

the polyester (A1) has an OH number of from 90 to 130 mg of KOH/g, an acid number of less than 1 mg of KOH/g, a number-average molecular weight of from 1300 to 3500 and a polydispersity of from 5 to 50,

the polyacrylate resin (A2) contains as monomer component 4-hydroxy-n-butyl (meth)acrylate and/or 3-hydroxy-n-butyl (meth)acrylate and/or hydroxyethyl methacrylate, which are incorporated by polymerization, and has a hydroxyl number of from 50 to 150 and an acid number of from 0 to 10, and from 0.1 to 1% by weight, based on the weight of component (A) without solvent, of an aromatic carboxylic acid or of an anhydride is added to component (A) after its preparation or to the coating composition.
Description

BACKGROUND OF THE INVENTION

The present invention relates to a coating composition which comprises

(A) at least one component which contains hydroxyl groups, consisting of:

(A1) from 20 to 60% by weight of at least one polyester
and
(A2) from 40 to 80% by weight of at least one polyacrylate resin which contains hydroxyl groups and has been prepared, at least partially, in the presence of component (A1),

and

(B) at least one crosslinking agent.

The present invention also relates to processes for the production of a protective and/or decorative coating on a substrate surface and to the use of the coating compositions in the area of automotive refinishing.

DE-A-40 24 204 has already disclosed coating compositions which contain, as binder, a polyacrylate resin which contains hydroxyl groups and has been prepared in the presence of a polyester which contains hydroxyl groups. However, especially when these coating compositions are applied at low temperatures, from about 6 to 12°C, the masking resistance and solvent resistance of the resulting coatings is in need of improvement.

In the area of the finishing of large-size vehicles for example the finishing of goods-vehicle bodies, the masking resistance of the resulting coatings is of particular importance. This is because large-size vehicles are commonly provided with written characters, whose application requires the adjacent area to be masked off. If the masking resistance is inadequate, the marks must be removed by hand, by laborious sanding and polishing, which entails a considerable financial outlay.

Furthermore, the coating compositions must also cure as rapidly as possible, in order to avoid excessive standing times between the individual operations in the coating plant. These coating compositions must also, of course, possess good application properties and lead to coatings having good mechanical properties.

In addition, DE-A-31 33 769 discloses that the curing rate of one-component polyurethane coating compositions based on amines and on compounds containing isocyanate groups can be increased by the addition of benzoic acid. These coating compositions known from DE-A-31 33 769 differ from the coating compositions according to the invention in that no description is given of coating compositions based on polymers containing hydroxyl groups and on crosslinking agents containing isocyanate groups.

Furthermore, US-A-3, 897, 396 discloses that the curing rate of molding compositions based on polyurethaneureares can be increased by the addition of alkyl- or alkoxybenzoic acid, without thereby shortening the pot life.

These compositions known from US-A-3, 897, 396 differ from the coating compositions according to the invention in that US-A-3, 897, 396 describes molding compositions rather than coating compositions. Furthermore, these molding compositions known from US-A-3,897, 396 contain binders comprising prepolymer which contain isocyanate groups and are based on the reaction product of a polyethylenol, polyesterpolyol or hydrocarbopolyol with isocyanates and a crosslinking agent comprising polyanimes. Compositions based on acrylate copolymers containing hydroxyl groups and on compounds containing isocyanate groups, on the other hand, are not described in US-A-3, 897, 396.

Finally, German Patent Application P 44 07 409.3, which is not a prior publication, discloses coating compositions containing a polyacrylate resin, which contains hydroxyl groups and is based on hydroxy-n-butyl acrylate, and a crosslinking agent. The preparation of the polyacrylate resin in the presence of a polyester resin, however, is not described in this application.

SUMMARY OF THE INVENTION

The object of the present invention is therefore to provide coating compositions based on polyesters containing hydroxyl groups and on polyacrylate resins, which compositions exhibit rapid drying coupled with a lot pot life, i.e. which can be processed in the ready-to-use state over a long period. In particular, the coating compositions should provide a masking resistance of the resulting coatings which is improved in comparison with that of conventional coating compositions. Furthermore, the coating compositions should at least meet the requirements conventionally placed on a topcoat or clearcoat. The coating compositions should therefore, for example, exhibit good spray-mist assimilation, good...
topcoat holdout and good leveling. In addition, they should lead to coatings having good solvent resistance and a high degree of surface hardness. Furthermore, the coating compositions should cure at room temperature or at slightly elevated temperature, so that they can be employed in automotive refinishing.

The invention is surprisingly achieved by the coating compositions of the type mentioned initially, which are characterized in that

1.) the polyester (A1) has an OH number of from 90 to 130 mg of KOH/g, an acid number of less than 10 mg of KOH/g, a number-average molecular weight of from 1300 to 3500 and a polydispersity of from 5 to 50,

2.) the polyacrylate resin (A2) contains one or more monomers selected from the group consisting of 4-hydroxy-n-butyl acrylate, 4-hydroxy-n-butyl methacrylate, 3-hydroxy-n-butyl acrylate, 3-hydroxy-n-butyl methacrylate and/or hydroxyethyl methacrylate, incorporated by polymerization,

3.) the polyacrylate resin (A2) has a hydroxyl number of from 50 to 150 mg of KOH/g and an acid number of from 0 to 10 mg of KOH/g, and

4.) from 0.1 to 1% by weight, based on the weight of component (A) without solvent, of at least one aromatic mono- and/or polycarboxylic acid and/or an anhydride of an aromatic polycarboxylic acid are added to component (A) after its preparation or to the coating composition.

The invention furthermore relates to a process for the production of a protective and/or decorative coating on a substrate surface, using these coating compositions, and to the use of these coating compositions for refinishing, either as a pigmented or nonpigmented topcoat.

It is surprising and was not foreseeable that the coating compositions according to the invention, even on curing at low temperatures, cure rapidly while at the same time retaining long processibility (pot life). A particular advantage is the masking resistance of the resulting coatings, which is improved in comparison with that of conventional coating compositions and is of particular importance when the coating compositions are used in the area of the finishing of large-size vehicles.

An additional advantage is that the improvement of the masking resistance of the coatings can surprisingly be achieved without any impairment of the leveling, topcoat holdout and pot life. Finally, an additional advantage is that the resulting coatings possess good solvent resistance and surface hardness.

DETAILED DESCRIPTION OF THE INVENTION

The individual components of the coating composition according to the invention are now described in more detail. The coating composition according to the invention contains as binder a component (A) which contains hydroxyl groups and comprises:

(A1) from 20 to 60% by weight, preferably from 30 to 50% by weight, of at least one polyester, and

(A2) from 40 to 80% by weight, preferably from 50 to 70% by weight, of at least one polyacrylate resin which contains hydroxyl groups and has been prepared at least partially in the presence of components (A1).

The binder employed as component (A) preferably has a hydroxyl number of from 80 to 150, particularly preferably from 85 to 105, mg of KOH/g and an acid number of from 0.1 to 10, preferably from 4 to 8, mg of KOH/g.

It is essential to the invention that the polyester (A1) has an OH number of from 90 to 130, preferably from 90 to 110, mg of KOH/g, an acid number of less than 10 mg of KOH/g, preferably from 1 to 8 mg of KOH/g, a number-average molecular weight of from 1300 to 3500, preferably from 1350 to 2000, and a polydispersity of from 5 to 50, preferably from 5 to 10. The polydispersity is in this context define as the ratio of the weight-average molecular weight to the number-average molecular weight. The molecular weights are in each case determined by gel permeation chromatography against a polystyrene standard.

The polyesters (A1) are preferably obtainable by reacting

p1) polycarboxylic acids or their esterifiable derivatives, together if desired with monocarboxylic acids,

p2) polyols, together if desired with monools.

p3) if desired, other modifying components, and
Examples of polycarboxylic acids which can be employed as component (p1) are aromatic, aliphatic and cycloaliphatic polycarboxylic acids. It is preferred to employ aromatic and/or aliphatic polycarboxylic acids as component (p1).

Examples of suitable polycarboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, halophthalic acids, such as tetrachloro- or tetrabromophthalic acid, adipic acid, glutaric acid, acetic acid, sebacic acid, fumaric acid, maleic acid, trimellitic acid, pyromellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexane-dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 4-methylhexahydrophthalic acid, endomethylenedihydrophthalic acid, tricyclodecanedicarboxylic acid, endoethylenehexahydrophthalic acid, camphoric acid, cyclohexanetetracarboxylic acid, cyclobutanetetracarboxylic acid etc. The cycloaliphatic polycarboxylic acids may be employed either in their cis or in their trans form or as a mixture of the two forms. Also suitable are the esterifiable derivatives of the abovementioned polycarboxylic acids, for example their single or multiple esters with aliphatic alcohols having 1 to 4 carbon atoms or hydroxy alcohols having 1 to 4 carbon atoms. In addition, it is also possible to employ the anhydrides of the abovementioned acids, where they exist.

If desired, monocarboxylic acids can also be employed together with the polycarboxylic acids, examples being benzoic acid, tert-butylbenzoic acid, lauric acid, isononanoic acid and fatty acids of naturally occurring oils. The monocarboxylic acid preferably employed is isononanoic acid.

Alcohol components (p2) suitable for the preparation of the polyester or alkyd resin (A1) are polyhydric alcohols such as ethylene glycol, propanediols, butanediols, hexanediols, neopentylglycol, diethylene glycol, cyclohexanediol, cyclohexanecarboxylic acid, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, trishydroxyethyl isocyanate, polyethylene glycol, polypropylene glycol, together if desired with monohydric alcohols, for example butanol, octanol, lauryl alcohol, and ethoxylated and propoxylated phenols.

Suitable components (p3) for the preparation of the polyesters (A1) are in particular compounds which contain a group which is reactive with respect to the functional groups of the polyester, with the exception of the compounds cited as component (p4). As the modifying component (p3) it is preferred to use polyisocyanates and/or diepoxide compounds, and also - if desired - monoisocyanates and/or monoepoxide compounds. Examples of suitable components (p3) are described in DE-A-40 24 204 on page 4, lines 4 to 9.

Compounds which are suitable as components (p4) for the preparation of the polyesters or alkyd resins (A1) are those which also contain, in addition to a group which is reactive with respect to the functional groups of the polyester (A1), a tertiary amino group, for example monoisocyanates having at least one tertiary amino group or mercapto compounds having at least one tertiary amino group. For details reference is made to DE-A-40 24 204, page 4, lines 10 to 49.

The polyesters (A1) are prepared by the known methods of esterification (cf. various standard works, for example:

2. Dr. Johannes Scheiber, Chemie und Technologie der künstlichen Harze [Chemistry and Technology of Synthetic Resins], Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1943;

This reaction is conventionally carried out at temperatures of between 180 and 280°C, in the presence if desired of an appropriate esterification catalyst, for example lithium octanolate, dibutyltin oxide, dibutyltin dilaurate, paratoluene-sulfonic acid and the like.

The preparation of the polyesters (A1) is conventionally carried out in the presence of small quantities of a suitable solvent as entraining agent. Examples of the entraining agents employed are aromatic hydrocarbons, in particular xylene and (cyclo)aliphatic hydrocarbons, for example cyclohexane.

The polyacrylates employed as component (A2) in the coating compositions according to the invention have OH numbers of from 50 to 150 mg of KOH/g, preferably from 70 to 105 mg of KOH/g, and acid numbers of from 0 to 10 mg of KOH/g, preferably from 0 to 8 mg of KOH/g, the OH numbers and acid numbers in each case being calculated without taking into account the polyester fraction. The number-average molecular weights of the polyacrylate resins prepared
in the presence of the polyester are generally between 1500 and 5000, preferably between 2000 and 4000, in each case measured by GPC against a polystyrene standard.

It is essential to the invention that the polyacrylate resin (A2) has been prepared at least partially in the presence of the polyester resin (A1). Advantageously at least 40% by weight and, particularly advantageously, from 50 to 70% by weight of component (A2) are prepared in the presence of component (A1).

The possible residual quantity of component (A2) is added to the binder solution or to the coating composition subsequently. In this context it is possible for this prepolymerized resin to have the same monomer composition as the addition polymer resin built up in the presence of the condensation polymer resin. However, it is also possible for a condensation polymer resin and/or addition polymer resin containing hydroxyl groups and having a different monomer composition to be added. Furthermore, it is possible to add a mixture of different addition polymer resins and/or condensation polymer resins, it being possible for a resin to have the same monomer composition as the addition polymer resin built up in the presence of the condensation polymer resin.

It is also essential to the invention that the polyacrylate resin (A2) comprises one or more monomers selected from the group consisting of 4-hydroxy-n-butyl acrylate, 4-hydroxy-n-butyl methacrylate, 3-hydroxy-n-butyl acrylate, 3-hydroxy-n-butyl methacrylate and/or hydroxyethyl methacrylate, as monomer components which are incorporated by polymerization. The acrylate resin (A2) preferably contains one or more monomers selected from the group consisting of 4-hydroxy-n-butyl acrylate, 4-hydroxy-n-butyl methacrylate, 3-hydroxy-n-butyl acrylate and/or 3-hydroxy-n-butyl methacrylate, together if desired with hydroxyethyl methacrylate. The preparation of the polyacrylate resins which are employed in accordance with the invention can be carried out by polymerization methods which are generally well known. Polymerization methods for the preparation of polyacrylate resins are generally known and have been described in numerous references (cf. e.g.: Houben-Weyl, Methoden der organischen Chemie [Methods in organic Chemistry], 4th edition, volume 14/1, pages 24 to 255 (1961)).

The polyacrylate resins employed in accordance with the invention are preferably prepared using the solution polymerization method. In this method it is conventional to take an organic solvent or solvent mixture together with the polyester (A1) and to heat the mixture to boiling. The monomer mixture to be polymerized and one or more polymerization initiators are then added continuously to this mixture of organic solvent or solvent mixture and polyester resin (A1). Polymerization takes place at temperatures of between 100 and 150°C, preferably between 130 and 150°C.

The polymerization is preferably carried out in a high-boiling organic solvent which is inert with respect to the monomers employed. Examples of suitable solvents are relatively highly substituted aromatics, for example Solvent Naphtha, heavy benzene, various Solvesso grades, various Shellsol grades and Deasol and relatively high-boiling aliphatic and cycloaliphatic hydrocarbons, for example various white spirits, mineral terpentine oil, tetralin and decalin and various esters, for example ethylglycol acetate, butylglycol acetate, ethyldiglycol acetate and the like.

The polymerization initiators preferably employed are initiators which form free radicals. The nature and quantity of initiator are usually selected such that, at the temperature of polymerization, the supply of free radicals is substantially constant during the feed phase.

Cited examples of initiators which can be employed are di-tert-butyl peroxide, tert-butyl hydroperoxide, tert-butyl peroxybenzoate, tert-butyl peroxypropionate, tert-butyl peroxy-3,5,3,5-trimethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, dicumyl peroxide, cumyl hydroperoxide, tert-amyl peroxybenzoate, tert-amyl peroxy-2-ethylhexanoate, diacyl peroxides, for example diacetetyl peroxide, peroxysuccinates, 2,2-di(tert-amyl-peroxy)-propane, ethyl 3,3-di(tert-amyl-peroxy)butyrate and thermally labile highly substituted ethane derivatives, based for example on silyl-substituted ethane derivatives and on benzopinacol. Furthermore, it is also possible to employ aliphatic azo compounds, for example azoisovaleronitril and azobiscyclohexanenitril.

The initiators employed are primarily those containing tert-butyl groups, for example di-tert-butyl peroxide, tert-butyl hydroperoxide, 2,2-di-tert-butylperoxybutane and 1,3-bis(tert-butylperoxyisopropyl)benzene, since they promote grafting of the acrylate onto the polyester.

The quantity of initiator is in most cases from 0.1 to 8% by weight, based on the quantity of monomer to be processed, although it can be even higher if desired. The initiator, dissolved in a portion of the solvent employed for the polymerization, is metered in gradually during the polymerization reaction. The initiator feed preferably takes from about 0.5 to 2 hours longer than the monomer feed so as to achieve a good action during the after-polymerization phase as well. In another preferred preparation variant the feed of initiator is commenced about 15 minutes before the addition of the monomers, so as to ensure a good supply of free radicals at the beginning of the polymerization. If initiators are employed which only have a low rate of decomposition under the prevailing reaction conditions, then it is also possible to include the initiator in the initial charge.

The polymerization conditions (reaction temperature, feed time of the monomer mixture, nature and quantity of the organic solvents and polymerization initiators, possible use of molecular weight regulators, for example mercaptans, thioglycolic esters and chlorine-containing hydrogen compounds) are selected such that the polyacrylate resins employed in accordance with the invention have the desired molecular weight.

The acid number of the polyacrylate resins employed in accordance with the invention can be adjusted by the per-
son skilled in the art via the use of appropriate quantities of monomers which contain carboxyl groups. Similar comments apply to the adjustment of the hydroxyl number. It can be controlled via the quantity of hydroxyl group-containing monomers which are employed.

The polyacrylate resins which contain hydroxyl groups and are preferably employed as component (A2) are obtainable by polymerizing

(a) from 5 to 50% by weight, preferably from 10 to 35% by weight, of one or more monomers selected from the group consisting of 4-hydroxy-n-butyl acrylate, 4-hydroxy-n-butyl methacrylate, 3-hydroxy-n-butyl acrylate, 3-hydroxy-n-butyl methacrylate and/or hydroxyethyl methacrylate

(b) from 0 to 50% by weight, preferably from 0 to 30% by weight, of an ethylenically unsaturated, copolymerizable monomer which is different from (a) and contains hydroxyl groups, or a mixture of such monomers,

(c) from 5 to 95% by weight, preferably from 15 to 55% by weight, of an aliphatic and/or cycloaliphatic ester of methacrylic and/or acrylic acid which is different from (a) and (b), or a mixture of such monomers,

(d) from 0 to 30% by weight, preferably from 5 to 15% by weight, of a copolymerizable vinyl ester which is different from (a), (b) and (c), or a mixture of such monomers,

(e) from 0 to 85% by weight, preferably from 15 to 60% by weight, of an aromatic vinyl hydrocarbon which is different from (a), (b), (c) and (d), or a mixture of such monomers, and

(f) from 0 to 10% by weight, preferably from 0 to 8% by weight, of a further ethylenically unsaturated monomer which is different from (a), (b), (c), (d) and (e), or a mixture of such monomers,

at least partially in the presence of component (A1), to give the polyacrylate resin (A2), the sum of the proportions by weight of monomers (a) to (f) being in each case 100% by weight.

As a further hydroxyl group-containing monomer (component (b)) for the preparation of the acrylate resin, it is also possible, if desired, to employ other hydroxyl group-containing esters of acrylic and/or methacrylic acid. Particular examples of hydroxyl group-containing monomers which are suitable as component (b) are the reaction product of 1 mol of hydroxyethyl acrylate and/or hydroxyethyl methacrylate and on average 2 mol of e-caprolactone and/or the reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of a carboxylic acid having a tertiary carbon atom. These glycidyl esters of branched carboxylic acids having 11 to 13 carbon atoms (Versatic acid) are commercially available, for example, from Shell under the name Cardura. The reaction of the acrylic and/or saethacrylic acid with the glycidyl ester can be carried out before, during or after the polymerization.

As component (b) it is also possible to employ, however, alkyl esters of acrylic acid and/or methacrylic acid, for example hydroxyethyl acrylate, hydroxpropyl (meth)acrylate, hydroxypentyl (meth)acrylates, hydroxyhexyl (meth)acrylates, hydroxyoctyl (meth)acrylates etc., and/or the esters, different from (a) and containing hydroxyl groups, of a polymerizable, ethylenically unsaturated carboxylic acid, for example the hydroxyl group-containing esters of crotonic and isocrotonic acid.

As component (c) it is possible in principle to employ any aliphatic or cycloaliphatic esters of acrylic acid or of methacrylic acid which are different from (a) and (b), or a mixture of such monomers. Examples are aliphatic esters of acrylic acid and of metacrylic acid, for example methyl, ethyl propyl, n-butyl isobutyl, tert-butyl, n-hexyl, 2-ethylhexyl, stearyl and lauryl acrylate and methacrylates, and cycloaliphatic esters of (meth) acrylic acid, for example furfuryl, cyclohexyl, isobornyl and t-butylcyclohexyl acrylate and methacrylate.

Vinyl esters of monocarboxylic acids are employed as component (d). Preferably employed are vinyl esters of branched monocarboxylic acids having 5 to 15 carbon atoms per molecule. The branched monocarboxylic acids can be obtained by reacting formic acid or carbon monoxide and water with olefins in the presence of a liquid, strongly acidic catalyst; the olefins may be products of the cracking of paraffinic hydrocarbons, such as mineral oil fractions, and may contain both branched and straight-chain acrylic and or cycloaliphatic olefins. In the reaction of such olefins with formic acid or with carbon monoxide and water, a mixture is formed of carboxylic acids in which the arboxyl groups are located predominantly at a quaternary carbon atom. Examples of other olefinic starting materials are propylene trimer, propylene tetramer and diisobutylene. The vinyl esters may also be produced from the acids in a manner known per se, for example by reacting the acids with acetylene.

Because of their ready availability, vinyl esters of saturated aliphatic monocarboxylic acids having 9-11 carbon atoms and branched at the carbon atom are particularly preferred.

Furthermore, particular preference is given to the vinyl ester of p-tertiary-butyl benzoic acid. Examples of other suitable vinyl esters are vinyl acetate and vinyl propionate.
As component (e), aromatic vinyl hydrocarbons such as styrene, \( \alpha \)-alkyl/styrenes such as \( \alpha \)-methyl/styrenes, chlorostyrenes, \( \alpha \)-, m- and p-methylstyrene, 2,5-dimethylstyrene, p-methoxystyrene, p-tert-butyl-styrene, p-dimethylaminostyrene, p-acetamidostyrene and vinyltoluene are employed, with preference being given to the employment of vinyltoluenes and, in particular, styrene.

The monomer employed as component (f) may in principle, be any ethenically unsaturated monomer which is different from (a), (b), (c), (d) and (e), or a mixture, of such monomers. Examples of monomers which can be employed as component (f) are monomers containing carbonyl groups, such as acrylic and/or methacrylic acid; amides of acrylic acid and methacrylic acid, for example methacrylamide and acrylamide; nitriles of methacrylic acid and acrylic acid; vinyl ethers and vinyl esters.

It is essential to the invention to add to the binder component (A), after its preparation, from 0.1 to 1% by weight, preferably from 0.4 to 0.9% by weight, of at least one aromatic mono- and/or polyarboxylic acid and/or at least one anhydride of an aromatic polyarboxylic acid. The quantity of acid or anhydride added is in this context related to the weight of the hydroxyl group-containing binder, calculated as solid resin, i.e. without the solvent fraction. Preferred additions in this context are phthalic anhydride, benzoic acid and/or alkyl- and/or alkoxy-substituted benzoic acid. It is particularly preferred to add benzoic acid.

The acid is added preferably at a temperature of from 20 to 120°C, particularly preferably at a temperature of from 40 to 100°C.

The anhydride is added preferably at a temperature of from 100 to 180°C, particularly preferably at a temperature of from 130 to 170°C.

In this respect the acid can be added to the finished coating composition, i.e. after the addition of pigments, fillers, auxiliaries and crosslinking agents. Preferably, however, the acid or the anhydride is added to the acrylate resin (A2) and dispersed to give a maximum degree of homogeneity.

The polyisocyanate component (B) comprises any organic polyisocyanate which contains free isocyanate groups which are attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic structures. The polyisocyanates preferably employed are those containing 2 to 5 isocyanate groups per molecule. It is possible if desired to add to the polyisocyanates small quantities of organic solvent, preferably from 1 to 25% by weight, based on pure polyisocyanate, so as to improve the ease of incorporation of the isocyanate. Examples of solvents which are suitable as additives for the polyisocyanates are ethoxethyl propionate, butyl acetate and the like.


Suitable examples are 1,2-ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, diisocyanatodipropyl ether, cyclobutane 1,3-diisocyanate, cyclohexane 1,3- and 1,4-diisocyanate, 2,2- and 2,6-diisocyanatodipropyl-cyclohexane, 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (Oxiphorene diisocyanate), 2,5- and 3,5-bis(isocyanatomethyl)-8-methyl-1,4-methano-decaphydra-naphthalene, 1,5-, 2,5-, 1,6- and 2,6-bis(isocyanatomethyl)4,7-methanohexahydroindane, 1,5-, 2,5-, 1,6- and 2,6-bis(isocyanato)4,7-methano-hexahydroindane, ciclohexyl 2,4,1- and 4,4'-diisocyanate, 2,4- and 2,6-hexahydrizable diisocyanate, perhydro-2,4'- and 4,4'-diaryl methane diisocyanate, diisocyanato-1,4-diethylenebenzene, 1,3- and 1,4-phenylene diisocyanate, 4,4'-diisocyano-bisphenyl, 4,4'-diisocyanato-3,3'-dichloro-biphenyl, 4,4'-diisocyanato-3,3'-dimethoxy-biphenyl, 4,4'-diisocyanato, 3,3'-diethyl-biphenyl, 4,4'-diisocyanato-3,3'-diphenyl-biphenyl, 2,4'- and 4,4'-diisocyanato diphenylmethane, naphthylene 1,5-diisocyanate, tolylene diisocyanates, such as 2,4- or 2,6-tolylene diisocyanate, N,N'-4,4'-dimethyl-3,3'-diisocyanato-diphenylurea, 1,2-xylylene diisocyanate, dicyclohexylmethane diisocyanate, tetramethylylenediisocyanate, and also triisocyanates, such as 2,4,4'-triisocyanatodiphenyl ether, and 4,4',4'-trisocyanatotriphenylmethane. The polyisocyanates preferably employed, in combination if desired with the abovementioned polyisocyanates, are those containing isocyanurate groups and/or biuret groups and/or allophanate groups and/or urethane groups and/or urea groups. Polyisocyanates containing urethane groups are obtained, for example, by reacting some of the isocyanate groups with polyols, for example trimethylolpropane and glycerol.

It is preferred to employ aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, dicyclohexylmethane 2,4'-diisocyanate or dicyclohexylmethane 4,4'-diisocyanate, or mixtures of these polyisocyanates. Very particular preference is given to employing mixtures of polyisocyanates which contain uretdione and/or isocyanurate groups and/or allophanate groups and which are based on hexamethylene diisocyanate, as are formed by the catalytic oligomerization of hexamethylene diisocyanate using appropriate catalysts. Otherwise, the polyisocyanate component (B) can also consist of any desired mixtures of the polyisocyanates mentioned by way of example.
0 to 30% by weight of the other binder component and from 7 to 50% by weight of the crosslinking agent (B), based in each case on the overall weight of the coating composition and on the solids content of the binder and crosslinking components.

The coating compositions according to the invention also contain one or more organic solvents. These solvents are usually employed in quantities of from 20 to 70% by weight, preferably from 30 to 60% by weight, based on each case on the overall weight of the coating composition.

Examples of suitable solvents are relatively highly substituted aromatic compounds, for example solvent naphtha, heavy benzene, various Solvesso grades, various Shell sol grades and Deasol, and relatively high-boiling aliphatic and cycloaliphatic hydrocarbons, for example various white spirits, mineral terpentine oil, tetralin and decalin, and various esters, for example ethylglycol acetate, butylglycol acetate, ethyldiglycol acetate and the like.

The coating compositions according to the invention may furthermore contain conventional auxiliaries and additives in conventional quantities, preferably from 0.01 to 10% by weight based on the overall weight of the coating composition. Examples of suitable auxiliaries and additives are leveling agents such as silicone oils, plasticizers such as phosphoric esters and phthalic esters, viscosity-controlling additives, latent agents, UV absorbers, light stabilizers, exturing agents and, if desired, fillers.

The coating compositions according to the invention may also contain conventional pigments in conventional quantities, preferably from 0 to 40% by weight based on the overall weight of the coating composition. Examples of suitable pigments are organic and inorganic color pigments and metallic and/or special-effect pigments.

The coating compositions are prepared in a known manner, by mixing and - if desired - dispersing the individual components.

These coating compositions may be applied to a substrate, by spraying, flow coating, dipping, rolling, knife coating or brushing, in the form of a film, the film subsequently being cured to give a firmly adhering coating.

The curing of these coating compositions is carried out conventionally at room temperature or at slightly elevated temperature, preferably at slightly elevated temperature, advantageously at temperatures below 120°C and preferably at temperatures of between 80°C and 60°C. The coating compositions can, however, also be cured under baking conditions, i.e. at temperatures of at least 120°C.

Particularly suitable substrates are metals and also wood or plastic.

Because of the short curing times and low curing temperatures, the coating compositions according to the invention are preferably employed for automotive refinishing, and for the finishing of large-size vehicles and goods-vehicle bodies. However, depending on the crosslinking agent employed, they may also be used for the production-line finishing of motor vehicles. Furthermore, they are particularly suitable as solid-color topcoat. However, they can, of course also be employed as clearcoat, in particular over a metallic basecoat or a solid-color basecoat.

The present invention therefore also relates to processes for the production of a protective and/or decorative coating on a substrate surface, which process is characterized in that the coating composition according to the invention is applied.

PREFERRED EMBODIMENTS OF THE INVENTION

The invention is now illustrated in more detail with reference to exemplary embodiments. All parts and percentages in these examples are by weight, unless expressly stated otherwise.

I. 1. Preparation of a polyester resin A1:

796 parts of trimethylolpropane, 540 parts of isononanoic acid, 821 parts of phthalic anhydride and 83 parts of xylene are placed in a 4 liter condensation polymerization vessel fitted with stirrer, steam-heated column and water separator and are heated slowly. Condensation is carried out at a temperature of max. 190°C up to an acid number of 5 mg of KOH/g and a viscosity of 8.0 dPas (60% in xylene). The batch is then cooled, diluted at 130°C with 910 parts of Shell sol A, and cooled further to room temperature. The resulting polyester has a solids content of 66.5%, an acid number of 5 mg of KOH/g, a (theoretical) OH number of 97.2 mg of KOH/g and a viscosity of 70 dPas (original). The number-average molecular weight Mn is 1493, the weight-average molecular weight Mw is 13,243 and the polydispersity Mw/Mn is 8.87 (each determined by gel permeation chromatography against a polystyrene standard).

I. 2. Preparation of a Polyester resin A2:

796 parts of trimethylolpropane, 540 parts of isononanoic acid, 821 parts of phthalic anhydride and 83 parts of xylene are placed in a 4 liter condensation polymerization vessel fitted with stirrer, steam-heated column and water separator and are heated slowly. Condensation is carried out at a temperature of max. 1901°C up to an acid number of 10
mg of KOH/g and a viscosity of 7.2 dPas (60% in xylene). The batch is then cooled, diluted at 130°C with 910 parts of Shellsol A, and cooled further to room temperature.

The resulting polyester has a solids content of 65.4%, an acid number of 8.9 mg of KOH/g, a (theoretical) OH number of 101 mg of KOH/g and a viscosity of 50 dPas (original). The number-average molecular weight Mn is 1350, the weight-average molecular weight Mw is 7830 and the polydispersity Mw/Mn is 5.8 (each determined by gel permeation chromatography against a polystyrene standard).

I. 3. Preparation of a polyester resin A3:

796 parts of trimethylolpropane, 540 parts of isononanoic acid, 821 parts of phthalic anhydride and 83 parts of xylene are placed in a 4 liter condensation polymerization vessel fitted with stirrer, steam-heated column and water separator and are heated slowly.

Condensation is carried out at a temperature of max. 190°C up to an acid number of 15 mg of KOH/g and a viscosity of 5.3 dPas (60% in xylene). The batch is then cooled, diluted at 130°C with 910 parts of Shellsol A, and cooled further to room temperature.

The resulting polyester has a solids content of 66.5%, an acid number of 13 mg of KOH/g, a (theoretical) OH number of 104 mg of KOH/g and a viscosity of 22 dPas (original). The number-average molecular weight Mn is 1241, the weight-average molecular weight Mw is 5843 and the polydispersity Mw/Mn is 4.71 (each determined by gel permeation chromatography against a polystyrene standard).

I. 4. Preparation of a polyester resin A4:

848 parts of trimethylolpropane, 444 parts of isononanoic acid, 876 parts of phthalic anhydride and 83 parts of xylene are placed in a 4 liter condensation polymerization vessel fitted with stirrer, steam-heated column and water separator and are heated slowly. Condensation is carried out at a temperature of max. 190°C up to an acid number of 18 mg of KOH/g and a viscosity of 80 dPas (60% in xylene). The batch is then cooled, diluted at 130°C with 1200 parts of Shellsol A, and cooled further to room temperature.

The resulting polyester has a solids content of 66.5%, an acid number of 16 mg of KOH/g, a theoretical OH number of 114 mg of KOH/g and a viscosity of >90 dPas (original). Because of the high viscosity of the resulting polyester, no further reactions were carried out.

II. 1. Preparation of the hydroxyl group-containing acrylate resins E1 to E5 and C1 to C6

The preparation of the acrylate copolymers was in each case carried out in a 4 liter stainless steel polymerization vessel fitted with stirrer, reflux condenser, a monomer feed and an initiator feed. The components, specified in each case in Table 1, are weighed in and then the initial charge is heated to 165°C.

All of the additions are commenced at the same time: the monomer feed is metered in at a uniform rate over the course of 4 h, and the initiator feed is metered in at a uniform rate over the course of 5 h. During the polymerization the temperature in the vessel is held at 160-165°C.

After this, polymerization is continued for a further 2 h. The resulting acrylate resin solution has a solids content of 80%. The temperature is then lowered to 120°C and the acrylate resin is diluted with butyl acetate to a solids content of 65%, and the quantity of benzoic acid indicated in Table 1, or the quantity of tert-butyl benzoic acid or hydroxystearic acid indicated in Table 1, is added.

The polyester resin A1 or A2 or A3 and the commercially available vinyl ester of Versatic acid (commercial product VeoVa 10 from Shell Chemie), in each case in the quantities specified in Table 1, are weighed into the initial charge.

The quantities of styrene, OH monomer and methyl methacrylate indicated in each case in Table 1 are weighed into the monomer feed.

14 parts of di-tert-butyl peroxide,

44 parts of Shellsol A (commercially available aromatic solvent mixture having a boiling range of 165 to 185°C) and

25 parts of xylene

are weighed into the initiator feed. This composition of the initiator feed is employed in the preparation of all of the acrylate resins.
II. 2. Preparation of the hydroxyl group-containing acrylate resin E6

The preparation of the acrylate copolymer according to the invention was carried out in each case in a 4 liter stainless steel polymerization vessel fitted with stirrer, reflux condenser, a monomer feed and an initiator feed. The components, indicated in Table 1, of the initial charge, of the monomer feed and of the initiator feed are weighed in, and the initial charge is then heated to 165°C.

The additions are all commenced at the same time; the monomer feed is metered in uniformly over the course of 4 h, and the initiator feed is metered in uniformly over the course of 5 h. During the polymerization the temperature in the vessel is held at 160-165°C. After this, polymerization is continued for a further 2 h. The resulting acrylate resin solution has a solids content of 80%. 7.5 parts of phthalic anhydride are added at 165°C, and the temperature is held at 165°C for about a further 2 hours. The temperature is then lowered to 120°C and the acrylate resin is diluted with butyl acetate to a solids content of 65%.

The polyacrylate resin obtained in this way has a solids content of 64.4%, an acid number of 4.4 mg of KOH/g, a viscosity of 3.0 dPas (55% in butyl acetate) and a hydroxyl number of about 90.

11.3. Preparation of the hydroxyl group-containing acrylate resin C7

The preparation of the hydroxyl group-containing acrylate resin C7 was carried out analogously to the preparation of the acrylate resin E6, but adding 7.8 parts of hexahydrophthalic anhydride instead of phthalic anhydride.

II. 4. Preparation of the hydroxyl group-containing acrylate resin C8

The preparation of the hydroxyl group-containing acrylate resin C8 is carried out analogously to the preparation of the acrylate resin C1, the acrylic acid likewise being weighed into the monomer feed and added with the other monomers.

II. 5. Preparation of the hydroxyl group-containing acrylate resin C9

177 parts of Shellsol A and 113 parts of VeoVa 10 are weighed into the initial charge.

565 parts of styrene

250 parts of hydroxy-n-butyl acrylate and

201 parts of methyl methacrylate

are weighed into the monomer feed.

22.6 parts of di-tert-butyl peroxide,

71 parts of Shellsol A (commercially available aromatic solvent mixture having a boiling range of 165 to 185°C) and

40 parts of xylene

are weighed into the initiator feed.

The polymerization is carried out analogously to the preparation of the polyacrylate resin C1, by heating the initial charge at 165°C. All of the additions are commenced at the same time; the monomer feed is metered in uniformly over the course of 4 h, and the initiator feed is metered in uniformly over the course of 5 h. During the polymerization the temperature in the vessel is held at 160-165°C. After this, polymerization is continued for a further 2 h. The resulting acrylate resin solution has a solids content of 80%. The temperature is then lowered to 120°C and the acrylate resin is diluted with butyl acetate to a solids content of 65%. 3.94 parts of benzoic acid are then added. After this, 1133 parts of polyester resin AI are added to the polyacrylate resin solution.

The polyacrylate resin/polyester mixture obtained in this way has a solids content of 64.5%, an acid number of 4.0 mg of KOH/g, a viscosity of 7.2 dPas (55% in butyl acetate) and a hydroxyl number of about 90. Because of the high viscosity of the polyacrylate resin/polyester mixture, no coating composition was prepared using this mixture.
III. Preparation of the coating compositions E1 to E6 and C1 to C8 (Comparative Examples)

III. 1. Preparation of the curing agent solution

The curing agent solutions are prepared by mixing the components specified below:

- 4 parts of catalyst solution\(^1\)
- 50.6 parts of Desmodur N 3390\(^2\)
- 10.0 parts of Solvent naphtha
- 7.5 parts of xylene
- 1.5 parts of n-butyl acetate 98/100
- 0.6 part of Baysilon coating additive OL443\(^3\)
- 14.0 parts of 1-methoxypropyl 2-acetate
- 11.0 parts of butylglycol acetate

III. 2. Preparation of an adjustment additive

An adjustment additive is prepared by mixing the components specified below:

- Xylene 15.0 parts
- Solvent naphtha 13.0 parts
- Petroleum spirit 1351180 10.0 parts
- Butylglycol acetate 3.0 parts
- n-Butyl acetate 98/100 50.0 parts
- 1-Methoxypropyl 2-acetate 5.0 parts
- Butoxyl 2.0 parts
- Dipentenes 2.0 parts

III. 3. Preparation of a catalyst solution

1.0 part of dibutyltin dilaurate is mixed with 50 parts of butyl acetate 98/100 and 49 parts of xylene.

III. 4. Preparation of topcoats E1 to E6 and C1 to C8

The topcoats are prepared by adding 5.5 parts of a commercially available organic red pigment (commercial product Novopermrot F2RK 70 from Hoechst) to 38.8 parts of the respective acrylate resin solution together with 3.2 parts of butyl acetate 98/100. The batch is first placed in a dissolver at 2000 revolutions/min for 10 min and then, with cooling, is ground to a Hegmann particle fineness of < 10 \(\mu\)m. After this a mixture of 3.4 parts of butyl acetate 98/100, 20 parts of a commercially available acrylate resin containing hydroxyl groups and having an OH number of 150 mg of KOH/g (commercial product Macrynal SM 510 N from Hoechst AG) 0.5 parts of a commercially available light stabilizer based on sterically hindered amine (commercial product Tinuvin 292 from Ciba Geigy), 0.2 part of the catalyst solution described above and 28.4 parts of the respective acrylate resin solution is added, and the mixture is homogenized using a stirre (1000 revolutions/min).

In order to prepare the topcoats, in each case 4 parts by volume of the resulting mixture are mixed with 1 part by volume of the curing agent solution described above and 1 part by volume of the adjustment additive described above.

\(^1\) the catalyst solution described in section III.3.
\(^2\) commercially available polyisocyanate from Bayer AG, a 90% strength solution in butyl acetate/solvent naphtha, 1:1, of a trimer based on hexamethylene diisocyanate and having a number-average molecular weight of about 700, an average functionality of between 3 and 4 and a content of uretdione groups of not more than 5%;
\(^3\) commercially available leveling agent based on a polyether-modified methylpolysiloxane from Bayer AG
III. 5. Application of the topcoats

The resulting topcoat is then applied to phosphatized steel panels which have been treated with filler. The phosphatized steel panels are for this purpose coated with a commercially available, conventional filler (commercial product Glasurit Grundfüller [primer surfacer] 283-1874 from Glasurit GmbH, Münster) based on a binder containing epoxide groups and on an aminofunctional curing agent, and are subjected to intermediate drying at room temperature for 1 h. Then the topcoat is applied in 2 spray passes, with a flash off time of 15 min in between, and dried at 20°C for 16 h. The dry film thickness is from 50 to 60 μm.

The panels coated in this way are then subjected to various tests. The test results are shown in Table 3.

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**Explanations for Table 1**

- A1, A2, A3 = polyester resin A1, A2 and A3 respectively
- VeoVa = commercially available mixture of vinyl esters of saturated aliphatic monocarboxylic acids having predominantly 10 carbon atoms and being branched at the carbon atom
- HBA = 4-hydroxy-n-butyl methacrylate
- HEMA = hydroxyethyl methacrylate
- HPMA = hydroxypropyl methacrylate
- HEA = hydroxyethyl acrylate
- MMA = methyl methacrylate
- AA = acrylic acid
Table 2

Characteristics of the acrylate resins and acrylate resin/polyester mixture

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Table 3

Test results of the resulting coatings of Examples 1 to 6 and of Comparative Examples C1 to C8

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</tbody>
</table>

Summary of the test results:

The spray mist assimilation is equally good across all the examples. A rating of > 3 or above for the leveling is no
The solvent resistance of the resulting coatings is only acceptable at a rating of 2 or better. Coatings with a rating > 2 exhibit dulling phenomena and are no longer acceptable. Therefore, the coatings of Comparative Examples C2, C3, C4 and C8 are not suitable with respect to solvent resistance. All the coating compositions show an adequate pot life of at least 3-4h.

For the most important criterion of the coatings, the masking tape test, the rating for acceptable coatings must be at least 2-3 or better. Therefore, the coatings of Comparative Examples C2, C3, C4, C8 and C8 exhibit a masking resistance which is completely inadequate. The best masking resistance is shown by the coating of Example 1.

Claims

1. Coating composition comprising

   (A) at least one component which contains hydroxyl groups, consisting of

   (A1) from 20 to 60% by weight of at least one polyester

   and

   (A2) from 40 to 80% by weight of at least one polyacrylate resin which contains hydroxyl groups and has been prepared, at least partially, in the presence of component (A1),

   and

   (B) at least one crosslinking agent,

   characterized in that

   1.) the polyester (A1) has an OH number of from 90 to 130 mg of KOH/g, an acid number of less than 10 mg of KOH/g, a number-average molecular weight of from 1300 to 3500 and a polydispersity of from 5 to 50

   2.) the polyacrylate resin (A2) contains one or more monomers selected from the group consisting of 4-hydroxy-n-butyl acrylate, 4-hydroxy-n-butyl methacrylate, 3-hydroxy-n-butyl-acrylate, 3-hydroxy-n-butyl methacrylate and/or hydroxyethyl methacrylate, incorporated by polymerization,

   3.) the polyacrylate resin (A2) has a hydroxyl number of from 50 to 150 mg of KOH/g and an acid number of from 0 to 10 mg of KOH/g, and

   4.) from 0.1 to 1% by weight, based on the weight of component (A) without solvent, of at least one aromatic mono- and/or polycarboxylic acid and/or an anhydride of an aromatic polycarboxylic acid are added to component (A) after its preparation or to the coating composition.

2. Coating composition according to claim 1, characterized in that component (A) comprises

   (A1) from 30 to 50% by weight of at least one polyester (A1) and

   (A2) from 50 to 70% by weight of at least one polyacrylate resin (A2).

3. Coating composition according to claim 1 or 2, characterized in that the polyester (A1) has an OH number of from 90 to 110 mg of KOH/g, an acid number of from 1 to 8 mg of KOH/g, a number-average molecular weight of from 1350 to 2000 and a polydispersity of from 5 to 10 and/or the acrylate resin (A2) has an OH number from 70 to 105 mg of KOH/g and an acid number of from 0 to 8 mg of KOH/g and/or component (A) has an OH number of from 80 to 150, preferably from 85 to 105 mg of KOH/g and an acid number of from 0.1 to 10, preferably from 4 to 8, mg of KOH/g.

4. Coating composition according to one of claims 1 to 3, characterized in that from 0.4 to 0.9% by weight, based on the weight of component (A) without solvent, of at least one aromatic mono- and/or polycarboxylic acid and/or one anhydride of an aromatic polycarboxylic acid is added to component (A) after its preparation or to the coating com-
position.

5. Coating composition according to one of claims 1 to 4, characterized in that benzoic acid, alkyl- and/or alkoxy-substituted benzoic acid and/or phthalic anhydride, preferably benzoic acid, is added to component (A) after its preparation.

6. Coating composition according to one of claims 1 to 5, characterized in that the polyacrylate resin (A2) is obtainable by polymerizing

(a) from 5 to 50% by weight, preferably from 10 to 35% by weight, of one or more monomers selected from the group consisting of 4-hydroxy-n-butyl acrylate, 4-hydroxy-n-butyl methacrylate, 3-hydroxy-n-butyl acrylate, 3-hydroxy-n-butyl methacrylate and/or hydroxyethyl methacrylate,

(b) from 0 to 50% by weight, preferably from 0 to 30% by weight, of an ethylenically unsaturated, copolymerizable monomer which is different from (a) and contains hydroxyl groups, or a mixture of such monomers,

(c) from 5 to 95% by weight, preferably from 15 to 55% by weight, of an aliphatic and/or cycloaliphatic ester of methacrylic and/or acrylic acid which is different from (a) and (b), or a mixture of such monomers,

(d) from 0 to 30% by weight, preferably from 5 to 15% by weight, of a copolymerizable vinyl ester which is different from (a), (b) and (c), or a mixture of such monomers,

(e) from 0 to 85% by weight, preferably from 15 to 60% by weight, of an aromatic vinyl hydrocarbon which is different from (a), (b), (c) and (d), or a mixture of such monomers, and

(f) from 0 to 10% by weight, preferably from 0 to 8% by weight, of a further ethylenically unsaturated monomer which is different from (a), (b), (c), (d) and (e), or a mixture of such monomers,

at least partially in the presence of component (A1), to give the polyacrylate resin (M), the sum of the proportions by weight of monomers (a) to (f) being in each case 100% by weight.

7. Coating composition according to one of claims 1 to 6, characterized in that at least 40% by weight of component (A2) have been prepared in the presence of component (A1).

8. Coating composition according to one of claims 1 to 7, characterized in that it contains as component (B) at least one di- and/or polyisocyanate, preferably at least one di- and/or polyisocyanate which contains isocyanurate groups.

9. Process for the production of a protective and/or decorative coating on a substrate surface, characterized in that a coating composition according to one of claims 1 to 8 is applied.

10. Use of the coating compositions according to one of claims 1 to 8 as topcoat, especially as solidcolor topcoat.

11. Use of the coating compositions according to one of claims 1 to 8 for refinishing, especially for the area of automotive refinishing.
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (INT.CI.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>DE 195 35 603 A (BASF LACKE &amp; FARBEN) 27 March 1997 * page 3, line 12 - page 12, line 67 * * examples II.1,2,IV.3; tables 1,2,4 * * claims 1,4-12 *</td>
<td>1-11</td>
<td>C08G18/40  C08G18/63  C08G18/65  C09D151/08  C09D175/04</td>
</tr>
<tr>
<td>A</td>
<td>DATABASE WPI Section Ch. Week 8003 Derwent Publications Ltd., London, GB; Class A25, AN 80-04353C XP002075268 &amp; JP 54 153 900 A (ASAHI CHEM IND CO LTD) 4 December 1979 * abstract *</td>
<td>1,5,8</td>
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<td>D,A</td>
<td>WO 92 02590 A (BASF LACKE &amp; FARBEN) 20 February 1992 * page 3, line 14 - page 21, line 24 * * claims 1,15 * * page 25, line 3 - page 35, line 35; examples 1-8; table 2 *</td>
<td>1,10,11</td>
<td>C08G  C09D</td>
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The present search report has been drawn up for all claims

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**Place of search**: THE HAGUE  **Date of completion of the search**: 24 August 1998  **Examiner**: Neugebauer, U

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**CATEGORY OF CITED DOCUMENTS**

X: particularly relevant if taken alone  Y: particularly relevant if combined with another document of the same category  A: technological background  O: non-written disclosure  P: intermediate document  T: theory or principle underlying the invention  E: earlier patent document, but published on, or after the filing date  D: document cited in the application  L: document cited for other reasons  S: member of the same patent family, corresponding document