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(54) Titre : SUSPENSION DE VERNIS CLAIR DE VISCOSE DE CONSTITUTION, SON PROCEDE D'OBTENTION ET SON UTILISATION
 (54) Title: INTRINSICALLY-VISCOUS CLEAR-LACQUER SLURRY, METHOD FOR PRODUCTION AND USE THEREOF

(57) **Abrégé/Abstract:**

Intrinsically-viscous clear-lacquer slurry, comprising solid and/or highly viscous particles which are dimensionally-stable under conditions of storage and application, containing methacrylate copolymers as binding agent, which, relative to a given methacrylate copolymer, comprises at least 90 wt. % of methacrylate comonomers, including (meth)acrylate comonomers with potentially ionic groups. The invention also relates to a method for production and use thereof.

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(54) Title: INTRINSICALLY-VISCOUS CLEAR-LACQUER SLURRY, METHOD FOR PRODUCTION AND USE THEREOF

(54) Bezeichnung: STRUKTURVISKOSE KLARLACK-SLURRY, VERFAHREN ZU IHRER HERSTELLUNG UND IHRE VERWENDUNG

(57) Abstract: Intrinsically-viscous clear-lacquer slurry, comprising solid and/or highly viscous particles which are dimensionally-stable under conditions of storage and application, containing methacrylate copolymers as binding agent, which, relative to a given methacrylate copolymer, comprises at least 90 wt. % of methacrylate comonomers, including (meth)acrylate comonomers with potentially ionic groups. The invention also relates to a method for production and use thereof.

(57) Zusammenfassung: Strukturviskose Klarlack-Slurry, enthaltend feste und/oder hochviskose, unter Lagerungs- und Anwendungsbedingungen dimensionsstabile Partikel, die als Bindemittel Methacrylatcopolymerisate enthalten, die, bezogen auf ein gegebenes Methacrylatcopolymerisat, mindestens 90 Gew.-% Methacrylatcomonomere, inklusive potentiell ionische Gruppen aufweisende (Meth)Acrylatcomonomere, einpolymerisiert enthalten; Verfahren zu ihrer Herstellung und ihre Verwendung.



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**INTRINSICALLY-VISCOUS CLEAR-LACQUER SLURRY, METHOD FOR
PRODUCTION AND USE THEREOF**

The present invention relates to a novel pseudoplastic clearcoat slurry. The present invention also relates to a novel process for preparing pseudoplastic clearcoat slurries. The present invention additionally relates to the use of the novel pseudoplastic clearcoat slurry for automotive OEM finishing, automotive refinish, the interior and exterior painting of buildings, the coating of doors, windows and furniture, and industrial coating, including coil coating, container coating, the coating of small parts, the impregnation and/or coating of electrical components, and coating of white goods. The present invention relates not least to the use of the novel pseudoplastic clearcoat slurries as adhesives and sealing compounds for producing adhesive films and seals, especially in the aforementioned fields.

10

20 U.S. patent No 5,981,653 discloses a powder clearcoat slurry preparable by means of a secondary dispersion process in which the dispersing equipment comprises pressure release homogenizing nozzles. Suitable binders include polyhydroxy polyesters, polyhydroxy polycarbonates, polyhydroxy urethanes or polyhydroxy polyacrylates. It is preferred to use polyesters/polyacrylate polyols wherein the polyacrylate fraction is prepared from methyl methacrylate, styrene, hydroxyethyl

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methacrylate, butyl methacrylate, and acrylic acid. The particles of the known clearcoat slurry preferably feature average particle size of from 0.23 to 0.43 μm . For stabilizing in addition to the ionic stabilization, 5 it is necessary to employ external emulsifiers as well, which reduce the resistance of the clearcoats concerned to water and moisture. Moreover, these known clearcoat slurries always include certain amounts of organic cosolvents or leveling agents, which cannot be removed 10 as they are essential for the leveling properties of the initially dried film. Moreover, special equipment is needed for their preparation. Prior to the application of the clearcoat slurries, they are adjusted to the application viscosity using thickeners; 15 a complex viscosity behavior, however, is not described.

A comparable clearcoat slurry is known from the European patent application EP 0 899 282 A2. The known 20 clearcoat slurry may be prepared by a direct dispersion process or by the phase inversion process. By the phase inversion process is meant the secondary dispersion process set out below. It is important that preparation is carried out using a dispersing apparatus having a 25 volume-related dispersing output of from 1×10 to $9.8 \times 10\ 000\ \text{W/cm}^3$. Suitable binders include hydroxyl-containing polyesters and polyacrylates. It is preferred to use methacrylate copolymers formed from

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methyl methacrylate, styrene, hydroxyethyl methacrylate, butyl methacrylate or butyl acrylate, and acrylic acid. For their stabilization, the known clearcoat slurries require external emulsifiers; a
5 complex viscosity behavior is not described.

In this situation, the pseudoplastic clearcoat slurry known from the German patent DE 198 41 842 C2 provided substantial advances.

10

The known pseudoplastic clearcoat slurry is free from organic solvents and external emulsifiers and comprises solid spherical particles with an average size of from 0.8 to 20 μm and a maximum size of 30 μm , the clearcoat
15 slurry having an ion-forming group content of from 0.05 to 1 meq/g, a neutralizing agent content of from 0.05 to 1 meq/g, and a viscosity of

- (i) from 50 to 1 000 mPas at a shear rate of
20 1 000 s^{-1} ,
- (ii) from 150 to 8 000 mPas at a shear rate of 10 s^{-1} ,
and
- (iii) from 180 to 12 000 mPas at a shear rate of 1 s^{-1} .

25 Binders used are methacrylate copolymers formed from tert-butyl acrylate, n-butyl methacrylate, cyclohexyl methacrylate, and hydroxypropyl methacrylate (cf. the preparation example 1, sections 1.1 and 1.2, on page 6

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of the patent, lines 30 to 63).

The known clearcoat slurries are prepared by

- 5 1) emulsifying an organic solution comprising binder
and crosslinking agent in water, to give an
emulsion of the oil-in-water type,
- 10 2) removing the organic solvent or the organic
solvents, and
- 3) replacing by water some or all of the solvent
removed, to give a clearcoat slurry comprising
solid spherical particles,

15

where

- 4) additionally, at least one ionic, especially
anionic, thickener and at least one nonionic
20 associative thickener are added to the clearcoat
slurry.

Here and below, the process in accordance with steps
(1) to (3) is referred to as the secondary dispersion
25 process.

This pseudoplastic clearcoat slurry is preparable with
a small number of processing steps; on the basis of its

typical powder slurry properties, with residual solvent contents of < 1%, and its particle sizes, it exhibits advantageous application properties. Even without the assistance of organic solvents, there is generally no popping at the required film thickness of approximately 40 to 50 μm . Moreover, the particles of the slurry, owing to mixing of their constituents in solution, are very homogeneous. The resulting clearcoats are bright, chemical-resistant, and flow out very well, without popping marks or cracking.

The pseudoplastic clearcoat slurries have very good performance properties and are highly suitable for the production of clearcoats for high-quality multicoat color and/or effect paint systems, such as are used to coat automobiles, for example. In the production of these multicoat color and/or effect paint systems, the clearcoat slurries may be used by the wet-on-wet technique in combination with any of a very wide variety of aqueous basecoat materials, without the occurrence of deleterious effects such as mudcracking.

In international patent application WO 01/51569, unpublished at the priority date of the present specification, the pseudoplastic clearcoat slurry of the German patent DE 198 41 842 C2 is subsequently subjected to wet grinding.

In international patent application WO 02/38685, a pseudoplastic clearcoat slurry free from organic solvents and external emulsifiers is described which comprises solid and/or highly viscous particles which are dimensionally stable under storage and application conditions,

1. said particles

1.1 having an average particle size of from 1.0 to 20 μm , at least 99% of the particles having a size $\leq 30 \mu\text{m}$, and

1.2 containing as binder at least one polyol with an OH number $> 110 \text{ mg KOH/g}$, containing potentially ionic groups,

and

2. said clearcoat slurry

2.1 containing from 0.01 to 1 meq of potentially ionic groups per g of solids,

2.2 containing, at a degree of neutralization of not more than 50%, an amount of ionic groups produced by neutralization of the potentially ionic groups of from 0.005 to 0.1 meq/g of solids, and

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2.3 having a viscosity of (i) from 50 to
1 000 mPas at a shear rate of 1 000 s⁻¹, (ii)
from 150 to 8 000 mPas at a shear rate of
10 s⁻¹, and (iii) from 180 to 12 000 mPas at a
5 shear rate of 1 s⁻¹.

Hereagain, the binders used are methacrylate copolymers
formed from tert-butyl acrylate, n-butyl methacrylate,
cyclohexyl methacrylate, and hydroxypropoy methacrylate.

10 The pseudoplastic clearcoat slurry may again be
prepared by the secondary dispersion process.

The known clearcoat slurries have the disadvantage that
they sometimes give clearcoats having microdefects.

15 These microdefects are manifested in particular on
black basecoats by way of optical effects which are
reminiscent of metallic effects. These optical effects
are also referred to as "starry sky".

20 It is an object of the present invention to provide a
novel pseudoplastic clearcoat slurry which no longer
has the disadvantages of the prior art but which
instead retain all of the advantages of the known
pseudoplastic clearcoat slurries while giving
25 clearcoats which no longer have any microdefects,
especially no disruptive optical effects, such as
"starry sky".

The invention accordingly provides a pseudo-plastic clearcoat slurry comprising solid and/or highly viscous particles which are dimensionally stable under storage and application conditions and comprising as binders methacrylate copolymers containing in copolymerized form, based on a given methacrylate copolymer, at least 90% by weight of methacrylate comonomers, including (meth)acrylate comonomers containing potentially ionic groups.

- 10 The invention as claimed is however more specifically directed to a pseudoplastic clearcoat slurry comprising water and particles that are at least one of solid and viscous and are dimensionally stable under storage and application conditions and which comprise binders comprising at least one methacrylate copolymers containing in copolymerized form, based on a given methacrylate copolymer, at least 99% by weight of at least one methacrylate comonomer, and wherein at least one methacrylate comonomer for the copolymer comprises at least one methacrylate comonomers having potentially ionic groups and at least one methacrylate comonomer free from
- 20 reactive functional groups and from potentially ionic groups.

In the text below, the novel, pseudoplastic clearcoat slurry is referred to as the "slurry of the invention".

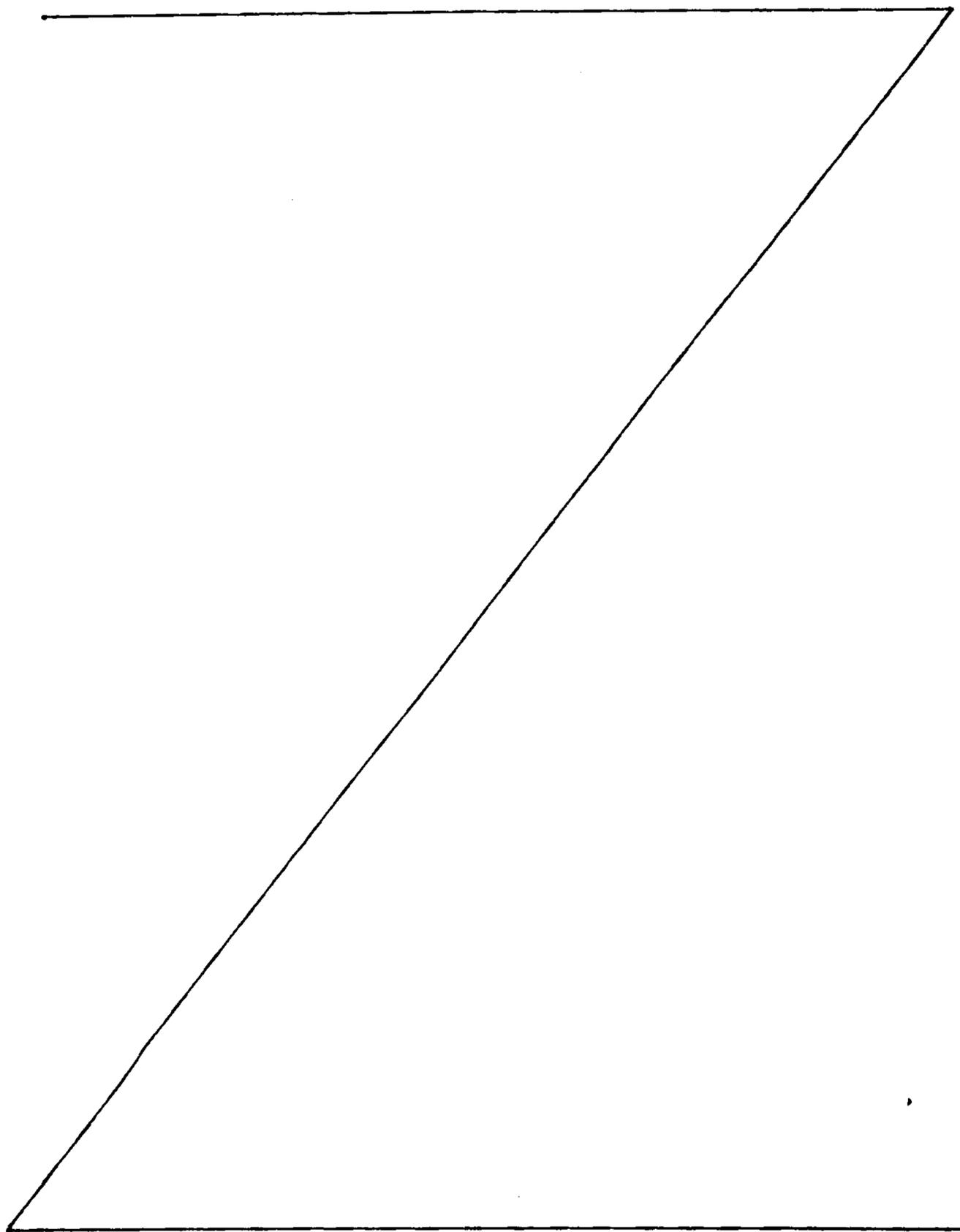
Further subject matter of the invention will emerge from the description.

- In the light of the prior art it was surprising for the skilled worker, and, unforeseeable, that the object on which the present invention is based could be achieved
- 30 by using the specific methacrylate copolymers as binders in the slurries of the invention. A particular surprise was that the slurries of the invention and the

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clearcoats produced from them had the same advantageous profile of properties as the prior art clearcoat slurries and clearcoats but no longer formed any microdefects.

The slurries of the invention may be curable



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physically, thermally, with actinic radiation, or thermally and with actinic radiation (dual cure). The thermally curable slurries of the invention may in turn be self-crosslinking or externally crosslinking.

5

In the context of the present invention, the term "physical curing" denotes the curing of a layer of a coating material by filming as a result of loss of solvent from the coating material, with linking within
10 the coating taking place by looping of the polymer molecules of the binders (regarding the term, cf. Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, "binders", pages 73 and 74). Or else filming takes place by the coalescence of
15 binder particles (cf. Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, "curing", pages 274 and 275). Normally, no crosslinking agents are required for this purpose. Where appropriate, physical curing may be assisted by
20 atmospheric oxygen, by heat, or by exposure to actinic radiation.

In the context of the present invention, the term "self-crosslinking" refers to the capacity of a binder
25 to enter into crosslinking reactions with itself. A prerequisite for this is that the binders already contain both kinds of complementary reactive functional groups which are necessary for crosslinking. Externally

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crosslinking slurries, on the other hand, are those slurries of the invention in which one kind of the complementary reactive functional groups is present in the binder and the other kind is present in a curing or
5 crosslinking agent. For further details, refer to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, "curing", pages 274 to 276, especially bottom of page 275.

10 In the context of the present invention, actinic radiation means electromagnetic radiation, such as near infrared (NIR), visible light, UV radiation or x-rays, especially UV radiation, and corpuscular radiation such as electron beams.

15

Where thermal curing and curing with actinic light are employed together, the terms "dual cure" and "dual-cure powder slurry clearcoat" are also used.

20 Preferably, the slurry of the invention is curable thermally, or thermally and with actinic radiation.

The slurry of the invention comprises dimensionally stable particles. In the context of the present
25 invention, "dimensionally stable" means that, under the customary known conditions of storage and application of clearcoat slurries, the particles undergo little if any agglomeration and/or breakdown into smaller

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particles, but instead substantially retain their original form even under the influence of shear forces. The particles may be highly viscous and/or solid. Preferably, the dimensionally stable particles are
5 solid.

For the slurry of the invention it is advantageous if the average size of the particles is from 0.8 to 20 μm and with particular preference from 3 to 15 μm . By
10 average particle size is meant the 50% median value as determined by the laser diffraction method, i.e., 50% of the particles have a diameter \leq the median value and 50% of the particles have a diameter \geq the median value. Preferably, at least 99% of the particles have a
15 size $<$ 30 μm .

Slurries having average particle sizes of this kind and a solvent content of $<$ 1% exhibit better application properties and, at the applied film thicknesses of
20 $>$ 30 μm as presently practiced in the automobile industry for the finishing of automobiles, exhibit much less of a tendency toward popping marks and mudcracking than conventional clearcoat slurries.

25 The upper limit on particle size is reached when the size of the particles means that they are no longer able to flow out fully on baking, and thus film leveling is adversely affected. In cases where

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requirements regarding the appearance are not very stringent, however, the limit may also be higher. 30 μm is considered a sensible upper limit, since above this particle size the spray nozzles and rinsing ducts of the highly sensitive application apparatus are likely to become blocked.

The slurry of the invention is, preferably, substantially or entirely free from organic solvents. In the context of the present invention this means that it has a residual volatile solvent content of < 3% by weight, preferably < 2% by weight, and with particular preference < 1% by weight.

Preferably, the slurry of the invention is substantially free or entirely free, in the sense mentioned above, from external emulsifiers (regarding "emulsifiers", cf. Johan Bieleman, "Lackadditive" [Additives for coatings], pages 160 to 100, "Grenzflächenaktive Verbindungen" ["interface-active compounds"]). Excluded from this are the alkoxyated C_{16} - C_{18} fatty alcohols, which are preferably added to the slurries of the invention in the course of their preparation by the secondary dispersion process, by way of the organic solution or by way of the water of the constituents.

The preferred particle sizes as described above may

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also be obtained even without the aid of additional, external emulsifiers, if the slurry of the invention contains from 0.05 to 1, preferably from 0.05 to 0.9, more preferably from 0.05 to 0.8, with particular
5 preference from 0.05 to 0.7, and in particular from 0.05 to 0.6 meq of potentially ionic groups per g of solids. The amount of neutralizing agents is preferably chosen such that the degree of neutralization is 100%, preferably below 80%, with particular preference below
10 60%, and in particular below 50%.

The chemical nature of the binder is generally not restricting in this respect, provided it contains ion-forming groups which can be converted into salt groups
15 by neutralization and which, as a result, are able to take over the function of ionic stabilization of the particles in water.

Suitable anion-forming groups include acid groups such
20 as carboxylic acid, sulfonic acid or phosphonic acid groups, especially carboxylic acid groups. Accordingly, bases, such as alkali metal hydroxides, ammonia or amines, are used as neutralizing agents. Alkali metal hydroxides can be used only to a limited extent, since
25 the alkali metal ions are not volatile on baking and, owing to their incompatibility with organic substances, may cause the film to become cloudy and may lead to loss of gloss. Therefore, ammonia or amines are

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preferred. In the case of amines, tertiary amines are preferred. By way of example, mention may be made of N,N-dimethylethanolamine or aminomethylpropanolamine (AMP).

5

Suitable cation-forming groups include primary, secondary and tertiary amines. Accordingly, neutralizing agents used are, in particular, low molecular mass organic acids such as formic acid, acetic acid, dimethylolpropionic acid or lactic acid.

10

For the preferred use of the slurry of the invention in automobile finishing as an unpigmented clearcoat material, preference is given to polymers or oligomers containing acid groups as ion-forming groups, since these so-called anionic binders generally exhibit better resistance to yellowing than the class of the cationic binders.

15

However, cationic binders containing groups which can be converted into cations, such as amino groups, are likewise suitable for use in principle, provided the field of use tolerates their typical secondary properties such as their tendency toward yellowing.

20

It is essential for the slurries of the invention that the dimensionally stable particles comprise as binder(s) at least one methacrylate copolymer which

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contain in copolymerized form, based on a given methacrylate copolymer, at least 90% by weight, preferably at least 95% by weight, and in particular at least 99% by weight of methacrylate comonomers, including methacrylate comonomers containing potentially ionic groups.

Preferably, the (meth)acrylate comonomers containing potentially ionic groups comprise acrylic acid, beta-carboxyethyl acrylate and/or methacrylic acid, especially methacrylic acid. The (meth)acrylate comonomers containing potentially ionic groups are preferably copolymerized into the methacrylate copolymers in an amount such that the above-described amount of potentially ionic groups in the particles can be set without problems. They are copolymerized into the methacrylate copolymers preferably in an amount of from 0.1 to 3%, more preferably from 0.2 to 2.8%, with particular preference from 0.3 to 2.6%, with very particular preference from 0.4 to 2.4%, and in particular from 0.5 to 2.2% by weight, based in each case on a given methacrylate copolymer.

The methacrylate copolymers preferably have a glass transition temperature, T_g , of not more than 50°C; at the same time the glass transition temperature T_g should not go below preferably 0°C, more preferably 10°C, and in particular 20°C.

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The glass transition temperature, T_g , of the methacrylate copolymers is preferably set by way of at least one methacrylate comonomer which is free from reactive functional groups and from potentially ionic groups. More preferably, the glass transition temperature, T_g , is set by way of at least two, in particular two, methacrylate comonomers which are free from reactive functional groups and from potentially ionic groups. Preferably, the glass transition temperatures, T_g , of the respective homopolymers of the methacrylate comonomers that are free from reactive functional groups and from potentially ionic groups differ from one another by not more than 40°C.

Examples of suitable methacrylate comonomers free from reactive functional groups and from potentially ionic groups are methyl, ethyl, n-propyl, n-butyl, i-butyl, tert-butyl, n-pentyl, isoamyl, cyclopentyl, n-hexyl and cyclohexyl methacrylate. Of these, i-butyl methacrylate (glass transition temperature, T_g , of the homopolymer: 326°C) and n-butyl methacrylate (glass transition temperature, T_g , of the homopolymer: 293°C) are of advantage and are therefore used with particular preference.

25

The amount of the copolymerized methacrylate comonomers, free from reactive functional groups and from potentially ionic groups, that is copolymerized

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into the methacrylate copolymers for use in accordance with the invention may vary widely. It is essential that the amount is chosen such that the resulting methacrylate copolymers have the glass transition
5 temperatures, T_g , described above. The amount is preferably at least 50%, more preferably at least 55%, with particular preference at least 60%, with very particular preference at least 65%, and in particular at least 70% by weight, based in each case on a given
10 methacrylate copolymer.

The weight ratio of the methacrylate comonomers used with particular preference, n-butyl methacrylate and i-butyl methacrylate, may vary widely. The n:i weight
15 ratio is preferably from 10:1 to 1:6, more preferably from 8:1 to 1:4, with particular preference from 6:1 to 1:2, with very particular preference from 5:1 to 1:1.5, and in particular from 4:1 to 1:1.

20 Where the slurries of the invention are physically curable slurries, the methacrylate copolymers contain reactive functional groups, if at all, only in a number which is insubstantial as far as crosslinking is concerned.

25

Where the slurries of the invention are thermally self-crosslinking, the methacrylate copolymers contain the complementary reactive functional groups for thermal

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crosslinking, described below, and/or reactive functional groups which are able to crosslink "with themselves", i.e., with groups of their own kind.

5 Where the slurries of the invention are curable with actinic radiation, the methacrylate copolymers may contain reactive functional groups having at least one bond which can be activated with actinic radiation. These reactive functional groups are mandatorily
10 present in the methacrylate copolymers of the slurries of the invention that are curable with actinic radiation if the slurries contain no other radiation-curable constituents.

15 Where the slurries of the invention are dual-cure slurries, the methacrylate copolymers contain reactive functional groups for thermal crosslinking and/or reactive functional groups containing at least one bond which can be activated with actinic radiation. The
20 reactive functional groups containing at least one bond which can be activated with actinic radiation are mandatorily present in the methacrylate copolymers of the dual-cure slurries of the invention if the dual-cure slurries contain no other radiation-curable
25 constituents.

Examples of suitable complementary reactive functional groups for use in accordance with the invention are

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placed together in the following overview. In the
overview, the variable R stands for an acyclic or
cyclic aliphatic radical, an aromatic radical and/or an
aromatic-aliphatic (araliphatic) radical; the variables
5 R' and R" stand for identical or different aliphatic
radicals or are linked with one another to form an
aliphatic or heteroaliphatic ring.

10 Overview: Examples of complementary reactive functional
groups

Binder and crosslinking agent

or

Crosslinking agent and binder

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-SH

-C(O)-OH

-NH₂

-C(O)-O-C(O)-

-OH

-NCO

-O-(CO)-NH-(CO)-NH₂

-NH-C(O)-OR

-O-(CO)-NH₂

-CH₂-OH

>NH

-CH₂-O-R

-NH-CH₂-O-R

-NH-CH₂-OH

-N(-CH₂-O-R)₂

-NH-C(O)-CH(-C(O)OR)₂

-NH-C(O)-CH(-C(O)OR)(-C(O)-R)

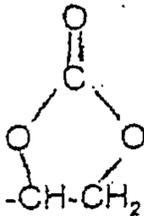
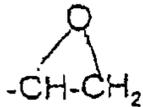
-NH-C(O)-NR'R''

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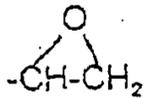
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> Si(OR)₂



-C(O)-OH



-C(O)-N(CH₂-CH₂-OH)₂

The selection of the respective complementary reactive functional groups is guided on the one hand by the consideration that they should not enter into any unwanted reactions during the preparation of the binders and during the preparation, storage, application, and melting of the slurries of the invention, and in particular should not form any polyelectrolyte complexes or undergo premature cross-linking, and/or must not disrupt or inhibit curing with actinic radiation, and secondly by the temperature range within which crosslinking is to take place.

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For the slurries of the invention it is preferred to employ crosslinking temperatures of from 60 to 180°C. Use is therefore made preferably of binders containing thio, hydroxyl, N-methylolamino, N-alkoxymethylamino, imino, carbamate, and/or allophanate groups, preferably 5 hydroxyl groups, on the one hand and, preferably, crosslinking agents containing anhydride, epoxy, blocked and unblocked, especially blocked, isocyanate, urethane, methylol, methylol ether, siloxane, 10 carbonate, amino, hydroxyl and/or beta-hydroxyalkylamide groups, preferably blocked isocyanate, carbamate and/or N-alkoxymethylamino groups, on the other.

15 In the case of self-crosslinking slurries of the invention, the binders contain, in particular, methylol, methylol ether and/or N-alkoxymethylamino groups.

20 Complementary reactive functional groups which are especially suitable for use in the thermally externally crosslinking slurries of the invention and the dual-cure slurries of the invention are hydroxyl groups on the one hand and blocked isocyanate groups on the 25 other.

The functionality of the binders in respect of the reactive functional groups described above may vary

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very widely and is guided in particular by the desired crosslinking density and/or by the functionality of the crosslinking agents that are employed in each case. In the case of hydroxyl-containing binders, for example,
5 the OH number is preferably from 20 to 300, more preferably from 40 to 250, with particular preference from 60 to 200, with very particular preference from 80 to 190, and in particular from 100 to 180 mg KOH/g.

10 The above-described complementary reactive functional groups may be incorporated into the binders in accordance with the customary and known methods of polymer chemistry. This can be done, for example, through the incorporation of methacrylate comonomers
15 which carry the corresponding reactive functional groups, and/or with the aid of polymer-analogous reactions.

Examples of suitable methacrylate comonomers containing
20 reactive functional groups are methacrylate comonomers which carry at least one hydroxyl, amino, alkoxymethyl-amino, carbamate, allophanate or imino group per molecule, such as

25 - hydroxyalkyl esters of methacrylic acid, which are derived from an alkylene glycol which is esterified with the acid, or which are obtainable by reaction of the methacrylic acid with an

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alkylene oxide such as ethylene oxide or propylene
oxide, especially hydroxyalkyl esters of
methacrylic acid in which the hydroxyalkyl group
contains up to 20 carbon atoms, such as 2-hydroxy-
5 ethyl, 2-hydroxypropyl, 3-hydroxypropyl,
3-hydroxybutyl or 4-hydroxybutyl methacrylate; or
hydroxycycloalkyl esters such as 1,4-bis(hydroxy-
methyl)cyclohexane, octahydro-4,7-methano-1H-
indenedimethanol or methylpropanediol monometh-
10 acrylate; or reaction products of cyclic esters,
such as epsilon-caprolactone, and these hydroxy-
alkyl methacrylates;

- reaction products of methacrylic acid of the
15 glycidyl ester of an alpha-branched monocarboxylic
acid having from 5 to 18 carbon atoms per
molecule, particularly a Versatic® acid, or
instead of the reaction product an equivalent
amount of methacrylic acid, which is then reacted,
20 during or after the polymerization reaction, with
the glycidyl ester of an alpha-branched
monocarboxylic acid having from 5 to 18 carbon
atoms per molecule, particularly a Versatic® acid;

25 - aminoethyl methacrylate or N-methylaminoethyl
methacrylate, which may also be used to introduce
potentially ionic groups;

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- N,N-di(methoxymethyl)aminoethyl methacrylate or
N,N-di(butoxymethyl)aminopropyl methacrylate;
- methacrylamides such as methacrylamide, N-methyl-,
5 N-methylol-, N,N-dimethylol-, N-methoxymethyl-,
N,N-di(methoxymethyl)-, N-ethoxymethyl- and/or
N,N-di(ethoxyethyl)-methacrylamide;
- methacryloyloxyethyl, -propyl or -butyl carbamate
10 or allophanate; further examples of suitable
methacrylate comonomers containing carbamate
groups are described in the patents
US 3,479,328 A, US 3,674,838 A, US 4,126,747 A, US
4,279,833 A or US 4,340,497 A.

15

In minor amounts, the reactive functional groups for
thermal crosslinking may be introduced by way of other
olefinically unsaturated monomers, such as the
corresponding acrylates, allylamine, allyl alcohol or
20 polyols, such as trimethylolpropane monoallyl or
diallyl ether or pentaerythritol monoallyl, diallyl or
triallyl ether.

The binders of the dual-cure slurries may contain on
25 average per molecule at least one, preferably at least
two, group(s) containing at least one bond which can be
activated with actinic radiation.

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In the context of the present invention, a bond which can be activated with actinic radiation means a bond which, on exposure to actinic radiation, becomes reactive and, together with other activated bonds of
5 its kind, enters into polymerization reactions and/or crosslinking reactions which proceed in accordance with free-radical and/or ionic mechanisms. Examples of suitable bonds are carbon-hydrogen single bonds or carbon-carbon, carbon-oxygen, carbon-nitrogen, carbon-
10 phosphorus or carbon-silicon single bonds or double bonds. Of these, the carbon-carbon double bonds are particularly advantageous and are therefore used with very particular preference in accordance with the invention. For the sake of brevity, they are referred
15 to below as "double bonds".

Accordingly, the group that is preferred in accordance with the invention contains one double bond or two, three or four double bonds. Where more than one double
20 bond is used, the double bonds may be conjugated. In accordance with the invention, however, it is of advantage if the double bonds are present in isolation, in particular each terminally, within the group in question. It is of particular advantage in accordance
25 with the invention to use two double bonds, especially one double bond.

The dual-cure binder contains on average at least one

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of the above-described groups which can be activated with actinic radiation. This means that the functionality of the binder in this respect is integral, i.e., for example, is two, three, four, five
5 or more, or is nonintegral, i.e., for example, is from 2.1 to 10.5 or more. The decision as to which functionality is chosen is guided by the requirements which are imposed on the respective dual-cure slurries.

10 Where on average per molecule more than one group which can be activated with actinic radiation is used, the groups are structurally different from one another or of the same structure.

15 Where they are structurally different from one another, this means in the context of the present invention that two, three, four or more, but especially two, groups which can be activated with actinic radiation are used which derive from two, three, four or more, but
20 especially two, monomer classes.

Examples of suitable groups are (meth)acrylate, ethacrylate, crotonate, cinnamate, vinyl ether, vinyl ester, dicyclopentadienyl, norbornenyl, isoprenyl,
25 isopropenyl, allyl or butenyl groups; dicyclopentadienyl ether, norbornenyl ether, isoprenyl ether, isopropenyl ether, allyl ether or butenyl ether groups; dicyclopentadienyl ester, norbornenyl ester, isoprenyl

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ester, isopropenyl ester, allyl ester or butenyl ester groups, but especially acrylate groups.

The groups are attached to the respective parent
5 structures of the binders preferably by way of urethane, urea, allophanate, ester, ether and/or amide groups, but in particular by way of ester groups. This is normally done by means of customary and known continuous polymer-analogous reactions such as, for
10 instance, the reaction of pendant glycidyl groups with olefinically unsaturated comonomers containing an acid group, of pendant hydroxyl groups with the halides of these comonomers, of hydroxyl groups with isocyanates containing double bonds, such as vinyl isocyanate,
15 methacryloyl isocyanate and/or 1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene (TMI® from CYTEC), or of pendant isocyanate groups with the hydroxyl-containing comonomers described above.

20 In the particles it is, however, also possible to employ mixtures of binders that are curable by means of heat alone and of binders that are curable by means of actinic radiation alone.

25 Processes for preparing the methacrylate copolymers are described, for example, in the European patent application EP 0 767 185 A1, in the German patents DE 22 14 650 B1 or DE 27 49 576 B1 and in the American

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patents US 4,091,048 A, US 3,781,379 A, US 5,480,493 A,
US 5,475,073 A or US 5,534,598 A or in the standard
work Houben-Weyl, Methoden der organischen Chemie,
4th edition, volume 14/1, pages 24 to 255, 1961.

5 Suitable reactors for the copolymerization include the
customary and known stirred tanks, stirred tank
cascades, tube reactors, loop reactors or Taylor
reactors, such as are described, for example, in the
patent applications DE 1 071 241 B1, EP 0 498 583 A1 or
10 DE 198 28 742 A1 or in the article by K. Kataoka in
Chemical Engineering Science, volume 50, number 9,
1995, pages 1409 to 1416. With particular preference,
the methacrylate copolymers are prepared under
pressure.

15

The amount of the binders described above in the
dimensionally stable particles of the slurry of the
invention may vary widely. Said amount is preferably
from 5 to 80%, more preferably from 6 to 75%, with
20 particular preference from 7 to 70%, with very
particular preference from 8 to 65% and in particular
from 9 to 60% by weight, based in each case on the
solids of the slurries of the invention. In the case of
the slurries of the invention that are curable
25 physically and those that are curable with actinic
radiation, but especially those that are curable
physically, the amount may be up to 100% by weight.

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The dimensionally stable particles of the slurries of the invention that are curable thermally, or thermally and with actinic radiation, may comprise crosslinking agents which contain complementary reactive functional groups for thermal crosslinking and/or reactive functional groups containing at least one bond which can be activated with actinic radiation.

Suitable crosslinking agents are all crosslinking agents that are customary in the field of light-stable clearcoats. Examples of suitable crosslinking agents are

- amino resins, as described for example in Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, 1998, page 29, "amino resins", in the textbook "Lackadditive" [Additives for coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998, pages 242 ff., in the book "Paints, Coatings and Solvents", second, completely revised edition, edited by D. Stoye and W. Freitag, Wiley-VCH, Weinheim, New York, 1998, pages 80 ff., in the patents US 4 710 542 A1 or EP 0 245 700 A1, and in the article by B. Singh and coworkers, "Carbamylmethylated Melamines, Novel Crosslinkers for the Coatings Industry", in Advanced Organic Coatings Science and Technology Series, 1991, volume 13, pages 193 to 207;

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- 5
- carboxyl-containing compounds or resins, as described for example in the patent DE 196 52 813 A1 or 198 41 408 A1, especially 1,12-dodecanedioic acid,
- 10
- resins or compounds containing epoxide groups, as described for example in the patents EP 0 299 420 A1, DE 22 14 650 B1, DE 27 49 576 B1, US 4,091,048 A or US 3,781,379 A;
- 15
- tris(alkoxycarbonylamino)triazines, as described in the patents US 4 939 213 A, US 5 084 541 A, US 5 288 865 A or in the patent application EP 0 604 922 A;
- 20
- blocked polyisocyanates, as described for example in the patents US 4,444,954 A1, DE 196 17 086 A1, DE 196 31 269 A1, EP 0 004 571 A1 or EP 0 582 051 A1; or
 - beta-hydroxyalkylamides such as N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide or N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide.

The crosslinking agents described above may be used
25 individually or as a mixture of at least two crosslinking agents. In accordance with the invention, the blocked polyisocyanates and/or tris(alkoxycarbonylamino)triazines, especially the blocked poly-

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isocyanates, afford particular advantages and are therefore used with particular preference.

The amount of crosslinking agent(s) in the dimensionally stable particles of the slurry of the invention may likewise vary widely and is guided primarily by the functionality and amount of the binders on the one hand and by the functionality of the crosslinking agents on the other. The amount is preferably from 10 to 95%, more preferably from 12 to 94%, with particular preference from 14 to 93%, with very particular preference from 16 to 92%, and in particular from 18 to 90% by weight, based in each case on the solids of the slurry of the invention.

15

In addition to the essential constituents described above, the dimensionally stable particles of the slurry of the invention may comprise additives such as are commonly used in clearcoat materials. It is essential that these additives do not substantially lower the glass transition temperature, T_g , of the binders.

20

Examples of suitable additives are polymers (other than the above-described methacrylate copolymers and crosslinking agents), crosslinking catalysts, defoamers, adhesion promoters, additives for improving substrate wetting, additives for improving surface smoothness, flattening agents, light stabilizers,

25

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corrosion inhibitors, biocides, flame retardants, and polymerization inhibitors, especially photoinhibitors, as described in the book "Lackadditive" by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

5

Moreover, the dual-cure slurry of the invention and the slurry of the invention which is curable with actinic radiation may also comprise constituents curable with actinic radiation, different than the methacrylate copolymers described above, as additives. Examples of such constituents include

- the binders envisaged for use in UV-curable clearcoat materials and powder clearcoat materials and described in the European patent applications EP 0 928 800 A1, EP 0 636 669 A1, EP 0 410 242 A1, EP 0 783 534 A1, EP 0 650 978 A1, EP 0 650 979 A1, EP 0 650 985 A1, EP 0 540 884 A1, EP 0 568 967 A1, EP 0 054 505 A1 or EP 0 002 866 A1, the German patent applications DE 197 09 467 A1, DE 42 03 278 A1, DE 33 16 593 A1, DE 38 36 370 A1, DE 24 36 186 A1 or DE 20 03 579 B1, the international patent applications WO 97/46549 or WO 99/14254 or the American patents US 5,824,373 A, US 4,675,234 A, US 4,634,602 A, US 4,424,252 A, US 4,208,313 A, US 4,163,810 A, US 4,129,488 A, US 4,064,161 A or US 3,974,303 A;

15

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- reactive diluents curable with actinic radiation, such as those described in Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, on page 491 under the headword
5 "reactive diluents"; or

- photoinitiators as described in Römpp Chemie Lexikon, 9th, expanded and revised edition, Georg Thieme Verlag, Stuttgart, vol. 4, 1991, or in
10 Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, 1998, pages 444 to 446.

The slurry of the invention may likewise comprise additives in the aqueous phase.

15

Preferably, the additives in question are nonionic and/or ionic thickeners. This effectively counters the tendency of the comparatively large solid particles toward sedimentation.

20

Examples of nonionic thickeners are hydroxyethyl-cellulose and polyvinyl alcohols. So-called nonionic associative thickeners are likewise available on the market in a diverse selection. They generally comprise
25 water-dilutable polyurethanes which are reaction products of water-soluble polyetherdiols, aliphatic diisocyanates, and monofunctional hydroxyl compounds with an organophilic radical.

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Likewise available commercially are ionic thickeners. These normally contain anionic groups and are based in particular on special polyacrylate resins with acid groups, some or all of which may have been neutralized.

5

Examples of suitable thickeners for use in accordance with the invention are known from the text book "Lackadditive" by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998, pages 31 to 65, or from the German
10 patent application DE 199 08 018 A1, page 13, line 18 to page 14, line 48.

For the slurry of the invention it may be advantageous if both of the above-described types of thickener are
15 present therein. In by far the majority of cases, however, one thickener is sufficient, particularly a nonionic thickener, to provide the desired pseudo-plasticity.

20 The amount of thickeners to be added, and, where two different thickeners are employed, the ratio of ionic to nonionic thickener, are guided by the desired viscosity of the slurry of the invention, which in turn is determined by the required sedimentation stability
25 and the specific requirements of spray application. The skilled worker is therefore able to determine the amount of the thickeners and, where appropriate, the ratio of the thickener types to one another on the

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basis of simple considerations, possibly with the aid of preliminary tests.

The viscosity is preferably set to within a range from
5 50 to 1 500 mPas at a shear rate of 1 000 s⁻¹ and from
150 to 8 000 mPas at a shear rate of 10 s⁻¹, and also
from 180 to 12 000 mPas at a shear rate of 1 s⁻¹.

This viscosity behavior, known as "pseudoplasticity",
10 describes a state which does justice both to the
requirements of spray application, on the one hand, and
to the requirements in terms of storage and
sedimentation stability, on the other: in the state of
motion, such as when pumping the slurry of the
15 invention in circulation in the ring circuit of the
coating plant and when spraying, for example, the
slurry of the invention adopts a state of low viscosity
which ensures easy processability. In the absence of
shear stress, on the other hand, the viscosity rises
20 and thus ensures that the coating material already
present on the substrate to be coated has a reduced
tendency to form runs on vertical surfaces. In the same
way, a result of the higher viscosity in the stationary
state, such as during storage, for instance, is that
25 sedimentation of the solid particles is very largely
prevented or that any slight degree of settling of the
slurry of the invention during the storage period can
be removed again by agitation.

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The aqueous phase of the slurry of the invention may further comprise leveling assistants which can be incorporated in the film by crosslinking. Examples of suitable constituents of this kind are thermally curable reactive diluents such as positionally isomeric diethyloctanediols or hydroxyl-containing hyperbranched compounds or dendrimers such as are described in the German patent applications DE 198 05 421 A1, DE 198 09 643 A1 or DE 198 40 405 A1.

10

Furthermore, the aqueous phase of the slurry of the invention may additionally comprise alkoxyated, especially ethoxyated, C₁₆-C₁₈ fatty alcohols containing more than 20 oxaalkanediy1 groups in the molecule, such as are sold, for example, by BASF Aktiengesellschaft under the brandname Lutensol® AT 50.

15

In its aqueous phase the slurry of the invention may further comprise at least one, especially one, water-soluble salt, preferably in an amount of from 0.1 to 50 mmol per 1 000 g of water in the slurry of the invention. The salt is decomposable without residue or substantially without residue. This means that its decomposition is not accompanied by the formation of any residues at all, or is accompanied only by the formation of residues in an amount which induces no deleterious technical effects in the clearcoats of the

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invention.

The salt may be decomposable by means of heat and/or actinic radiation. Preferably, it is thermally decomposable. It is preferably decomposable under the conditions of the curing of the clearcoat films of the invention produced from the slurries of the invention. It is of advantage in accordance with the invention if the salt is decomposable at temperatures above 100°C. The decomposition of the salt is preferably at an end at 250°C, more preferably 200°C, with particular preference 190°C, and in particular 180°C.

The decomposition of the salt may be accompanied by formation of any of a very wide variety of organic, inorganic and organometallic decomposition products. The decomposition products, accordingly, may comprise volatile elements, neutral organic or inorganic hydrogen compounds, organic and inorganic bases, organic and inorganic acids, or oxides.

Examples of volatile elements are phosphorus, sulfur, nitrogen and oxygen, especially nitrogen.

Examples of neutral organic and inorganic hydrogen compounds are water and hydrocarbons, especially water.

Examples of organic and inorganic bases are ammonia,

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methylamine, dimethylamine and trimethylamine, especially ammonia.

Examples of organic and inorganic acids are formic
5 acid, acetic acid, propionic acid, oxalic acid, citric
acid, tartaric acid, hydrochloric acid, hydrogen
bromide, phosphoric acid, phosphorous acid,
amidosulfonic acid, sulfuric acid, sulfurous acid,
thiosulfuric acid, HSCN and hydrogen sulfide,
10 especially acetic acid.

Examples of oxides are carbon dioxide, sulfur dioxide,
sulfur trioxide and phosphorus oxide, especially carbon
dioxide.

15

It is preferred to select a salt whose decomposition
products are of little or no toxicity and/or of little
or no corrosiveness. Preference is given to selecting a
salt which forms, as its decomposition products, water,
20 nitrogen, carbon dioxide, ammonia and organic acids.

With particular preference, the salt is selected from
the group of ammonium salts, with very particular
preference from the group consisting of salts of
25 ammonia and of organic amines with organic and
inorganic acids.

The ammonium salt is selected in particular from the

group consisting of ammonium carbonate, ammonium thiocyanate, ammonium sulfamate, ammonium sulfite monohydrate, ammonium formate, ammonium acetate, ammonium hydrogen oxalate monohydrate, diammonium oxalate monohydrate, ammonium citrate, and ammonium tartrate. Of these, in turn, ammonium carbonate and ammonium acetate are very particularly advantageous and are therefore used with very particular preference in accordance with the invention.

10

The slurry of the invention is preferably prepared by the secondary dispersion processes from U.S. patent 5,981,653, from German patent DE 198 41 842 C2 or from international patent application WO 02/38685.

For this process, the ionically stabilizable binders and the crosslinking agents and also, where appropriate, the additives are mixed in organic solution and dispersed together in water with the aid of neutralizing agents. The dispersion is then diluted with water, while stirring. To start with a water-in-oil emulsion is formed, which on further dilution is transformed into an oil-in-water emulsion. This point is generally reached at solids contents of < 50% by weight, based on the emulsion, and is evident externally from a relatively sharp fall in viscosity in

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the course of the dilution.

The oil-in-water emulsion may also be prepared directly by the melt emulsification of the binders and of the
5 crosslinking agents and also, where appropriate, of the additives in water.

The resulting emulsion, which still contains solvents, is subsequently freed from its solvents by azeotropic
10 distillation.

In accordance with the invention it is of advantage if the solvents to be removed are distilled off at a distillation temperature below 70°C, preferably below
15 50°C, and in particular below 40°C. If desired, the distillation pressure is chosen so that this temperature range is observed in the case of relatively higher-boiling solvents.

20 At its most simple, the azeotropic distillation may be effected by stirring the emulsion at room temperature in an open vessel for several days. Preferably, the solvent-containing emulsion is freed from its solvents by vacuum distillation.

25

In order to avoid high viscosities, the amount of water and solvents removed by evaporation or distillation is replaced by water. The water may be added before,

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during, or after the evaporation or distillation, by addition in portions.

Following the loss of solvents, the glass transition
5 temperature, T_g , of the dispersed particles rises and a solid-in-liquid dispersion, i.e. the slurry of the invention, forms instead of the previous solvent-containing emulsion (liquid-in-liquid dispersion).

10 The salts for use in accordance with the invention may be introduced into the slurries of the invention, or their precursors, in a variety of ways. For example, the salts may be added to customary and known clearcoat slurries to give the slurries of the invention. They
15 may also be added to the organic solution of constituents of the powder slurry of the invention. Preferably, they are dissolved in the water prior to the emulsification of the organic solution.

20 If desired, the particles of the slurry of the invention are mechanically comminuted in the wet state, a procedure also referred to as wet grinding. In the course of this treatment it is preferred to employ conditions such that the temperature of the material
25 being ground does not exceed 70°C , more preferably 60°C , and in particular 50°C . The specific energy input during the grinding process is preferably from 10 to 1 000, more preferably from 15 to 750, and in

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particular from 20 to 500 Wh/g.

For wet grinding it is possible to employ a very wide
variety of equipment which produces high or low shear
5 fields.

Examples of suitable equipment producing low shear
fields are customary and known stirred tanks, slot
homogenizers, microfluidizers, and dissolvers.

10

Examples of suitable equipment producing high shear
fields are customary and known stirred mills and inline
dissolvers.

15

Particular preference is given to employing the
equipment which produces high shear fields. Of this
equipment, the stirred mills are particularly
advantageous in accordance with the invention and are
therefore used with very particular preference.

20

During wet grinding, generally, the slurry of the
invention is supplied to the above-described equipment,
and circulated therein, by means of appropriate
devices, such as pumps, until the desired particle size
25 has been reached.

The slurry of the invention advantageously has a solids
content of from 10 to 60% by weight, in particular from

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20 to 50% by weight.

The slurry of the invention is preferably filtered prior to its use. This is done using the customary and
5 known filtration equipment and filters, such as are also suitable for filtering the known clearcoat slurries. The mesh size of the filters may vary widely and is guided primarily by the size and size distribution of the particles of the slurry of the
10 invention. The skilled worker is therefore easily able to determine the appropriate filters on the basis of this physical parameter. Examples of suitable filters are bag filters. These are available on the market under the brand names Pong® or Cuno®. It is preferred
15 to use bag filters having mesh sizes of from 25 to 50 μm , examples being Pong® 25 to Pong® 50.

To produce the clearcoats of the invention, the slurry of the invention is applied to the substrate that is to
20 be coated. No special measures need be taken here; instead, the application may take place in accordance with the customary and known processes, which is another particular advantage of the slurry of the invention.

25

Following its application, the slurry of the invention dries without problems and does not film at the processing temperature, generally at room temperature.

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In other words, the slurry of the invention, applied as a wet film, loses water when flashed off at room temperature or slightly elevated temperatures, with the particles present therein changing their original form.

5 As a result, the tendency toward mudcracking is extremely low.

In the subsequent baking step, the now substantially water-free powder layer is melted and caused to
10 crosslink. In some cases it may be of advantage to carry out the leveling process and the crosslinking reaction with a chronological offset, by operating a staged heating program or a so-called heating ramp. The crosslinking temperature that is appropriate for the
15 present examples is situated between 120 and 160°C. The corresponding baking time is between 20 and 60 minutes.

In the case of the dual-cure slurry of the invention, thermal curing is supplemented by curing with actinic
20 radiation, which may be carried out using the customary and known radiation sources and processes, such as are described, for example, in the German patent application DE 198 18 735 A1, column 10, line 31 to column 11, line 22. These processes and equipment may
25 also be used to cure the slurry of the invention that is curable with actinic radiation.

The resultant clearcoat has outstanding performance

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properties. For instance, it adheres firmly to all
customary and known basecoats or to substrates such as
metal, glass, wood, ceramic, stone, concrete or
plastic. It is of high gloss, smooth, scratch-
5 resistant, stable to weathering and chemicals, and even
at high coat thicknesses is free from defects, such as
stress cracks or popping marks. It no longer exhibits
any blushing on exposure to moisture. Furthermore, it
is free from microdefects and displays no disruptive
10 optical effects, such as a starry sky that is similar
to the metallic effect.

On the basis of this advantageous profile of
properties, the slurry of the invention is
15 outstandingly suitable for automotive OEM finishing,
automotive refinish, the interior and exterior painting
of buildings, the coating of doors, windows and
furniture, and industrial coating, including coil
coating, container coating, the coating of small parts,
20 the impregnation and/or coating of electrical
components, or the coating of white goods. It is used
in particular to produce clearcoats as part of
multicoat color and/or effect paint systems, which are
produced from basecoat materials and the slurry of the
25 invention by the customary and known wet-on-wet
techniques.

For the wet-on-wet technique, the slurry of the

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invention may readily be combined with numerous
basecoat materials, especially aqueous basecoat
materials, without the occurrence of problems, such as
cracking, lack of wettability, or poor intercoat
5 adhesion.

The slurry of the invention may surprisingly also be
used as an adhesive for producing adhesive films and as
a sealing compound for producing seals, especially in
10 the technical fields referred to above.

Inventive and comparative examples

Preparation example 1 (comparative)

15

The preparation of a solution polyacrylate similar to
preparation example 1 of DE 198 41 842 C2

43.53 parts by weight of methyl ethyl ketone were
20 charged to a reaction vessel equipped with stirrer,
reflux condenser, oil heating, nitrogen inlet pipe and
two feed vessels, and heated to 78°C. To this initial
charge there were added the initiator solution,
consisting of 4.76 parts by weight of TBPEH (tert-butyl
25 perethylhexanoate) and 2.856 parts by weight of methyl
ethyl ketone, metered in from a feed vessel at a
uniform rate over 4.75 h at 80°C. 15 minutes after the
beginning of the initiator feed, the monomer mixture,

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consisting of 18.326 parts by weight of tert-butyl acrylate, 7.14 parts by weight of n-butyl methacrylate, 9.52 parts by weight of cyclohexyl methacrylate, 12.138 parts by weight of hydroxyethyl methacrylate and 0.476
5 part by weight of acrylic acid, was metered in from a further feed vessel at a uniform rate over 4 h. The feed lines and feed vessels were additionally rinsed with 1.25 parts by weight of MEK. Thereafter the reaction mixture was held at 78°C until it had a
10 viscosity of from 3.0 to 5.5 dPas (resin solids, 55 percent strength, xylene at 23°C). After this, the volatile fractions were removed by vacuum distillation until a solids content of 70% by weight (1 h at 130°C) had been established, after which the resin solution
15 was discharged. The resin solution had an acid number of from 7.0 to 10.0 mg KOH/g resin solids.

Preparation example 2

20 The preparation of a blocked polyisocyanate based on isophorone diisocyanate

837 parts by weight of isophorone diisocyanate were charged to a suitable reaction vessel, and 0.1 part by
25 weight of dibutyl tin dilaurate was added. Then a solution of 168 parts by weight of trimethylolpropane and 431 parts by weight of methyl ethyl ketone was run in slowly. As a result of the exothermic reaction, the

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temperature rose. After 80°C had been reached, the temperature was kept constant by external cooling and the feed was throttled slightly if appropriate. After the end of the feed, this temperature was maintained
5 for about 1 hour more until the isocyanate content of the solids had reached 15.7% (based on NCO groups). Thereafter the reaction mixture was cooled to 40°C and a solution of 362 parts by weight of 3,5-dimethylpyrazole in 155 parts by weight of methyl
10 ethyl ketone was added over the course of 30 minutes. After the reaction mixture had warmed to 80°C as a result of the exothermicity, the temperature was kept constant for 30 minutes until the NCO content had dropped to less than 0.1%. Then 47 parts by weight of
15 n-butanol were added to the reaction mixture, which was held at 80°C for 30 minutes more and, after brief cooling, discharged.

The reaction product had a solids content of 69.3% (1 h
20 at 130°C).

Preparation example 3

The preparation of a blocked polyisocyanate based on
25 diisocyanate

534 parts by weight of Desmodur® N 3300 (commercial isocyanurate of hexamethylene diisocyanate from Bayer

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AG) and 200 parts by weight of methyl ethyl ketone were charged to a reaction vessel and this initial charge was heated to 40°C. 100 parts by weight of 2,5-dimethylpyrazole were added to the solution, with
5 cooling, and the subsidence of the exothermic reaction was awaited. Thereafter, with continued cooling, a further 100 parts by weight of 2,5-dimethylpyrazole were added. After the exothermic reaction had again subsided, a further 66 parts by weight of 2,5-dimethyl-
10 pyrazole were added. Cooling was then switched off, as a result of which the reaction mixture slowly warmed up to 80°C. It was held at this temperature until its isocyanate content had fallen to below 0.1%. The reaction mixture was then cooled and discharged.

15

The resulting solution of the blocked polyisocyanate had a solids content of 81% by weight (1 h at 130°C) and a viscosity of 3.4 dPas (70% in methyl ethyl ketone; cone and plate viscometer at 23°C).

20

Preparation example 4 (inventive)

**The preparation of a methacrylate copolymer (binder)
for inventive use**

25

39.75 parts by weight of methyl ethyl ketone were charged to a reaction vessel equipped with stirrer, reflux condenser, oil heating, nitrogen inlet pipe and

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two feed vessels, and this initial charge was heated to 78°C.

Thereafter, an initiator solution of 4 parts by weight
5 of methyl ethyl ketone and 5 parts by weight of TBPEH
was metered in at a uniform rate from the first feed
vessel over the course of 6.75 h.

15 minutes after the beginning of the initiator feed, a
10 monomer mixture of 27.5 parts by weight of n-butyl
methacrylate, 9.15 parts by weight of i-butyl
methacrylate, 12.75 parts by weight of hydroxyethyl
methacrylate and 0.6 part by weight of methacrylic acid
was metered in at a uniform rate from the second feed
15 vessel over the course of 6 h. The monomer line was
then flushed with 0.25 part by weight of methyl ethyl
ketone and the feed vessel with 0.5 part by weight of
methyl ethyl ketone. After the end of the initiator
feed, the feed vessel in question was likewise flushed
20 with 0.5 part by weight of methyl ethyl ketone.

The reaction mixture was left to react at 78°C for a
further 3 h. The volatile fractions were then removed
by vacuum distillation until the solids content was 70%
25 by weight. The resin solution was then discharged. It
had a viscosity of from 7.0 to 10.0 dPas (resin solids,
60 percent, xylene, at 23°C). The acid number was from
9.0 to 11.0 and the hydroxyl number was 110 mg KOH/g

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resin solids.

Inventive example 1

5 The preparation of an inventive slurry

27.1 parts by weight of the methacrylate copolymer
solution from preparation example 4, 13.6 parts by
weight of the blocked polyisocyanate from preparation
10 example 3, 0.7 part by weight of Tinuvin® 400 and
0.3 part by weight of Tinuvin® 123 (commercial light
stabilizers from Ciba Specialty Chemicals, Inc.) were
charged to an appropriate mixing vessel and were
stirred at room temperature for 30 minutes. Then
15 0.024 part by weight of dibutyltin dilaurate and
0.128 part by weight of dimethylethanolamine were
added.

Then 22.6 parts by weight of deionized water in which a
20 small amount of ammonium acetate (about 0.9% by weight)
had been dissolved were metered in over the course of
30 minutes, with cooling, after which the resulting
mixture was homogenized. Thereafter, a further
21.614 parts by weight of deionized water were metered
25 in over 45 minutes and 10.8 parts by weight of
deionized water were metered in over 45 minutes.
Following both additions, the resulting mixtures were
emulsified for 30 minutes.

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Following emulsification, the volatile fractions of the emulsion were distilled off under reduced pressure at 32°C until a methyl ethyl ketone content < 0.2% by weight and a solids content (15 minutes at 180°C) of 5 from 35 to 37% by weight had been reached.

The resulting slurry was then admixed with 3.0 parts by weight of Acrysol® RM-8W (commercial nonionic associative thickener from Rohm & Haas).

10

Comparative example C1

The preparation of a noninventive slurry

15 22.1 parts by weight of the solution polyacrylate from preparation example 1, 11.2 parts by weight of the blocked polyisocyanate from preparation example 2, 0.211 part by weight of dimethylethanolamine, 0.165 part by weight of Tinuvin® 123 (commercial light 20 stabilizer from Ciba Specialty Chemicals, Inc.), 0.49 part by weight of Cyasorb® 1164L (commercial light stabilizer) and 0.14 part by weight of benzoin were charged to an appropriate mixing vessel and homogenized. The mixture was then emulsified in 60.7 25 parts by weight of deionized water at not more than 30°C.

Following emulsification, the volatile fractions of the

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emulsion were distilled off under reduced pressure at not more than 35°C until a methyl ethyl ketone content < 0.2% by weight and a solids content (15 minutes at 180°C) of from 35 to 37% by weight had been reached.

5

Thereafter, the resulting slurry was also admixed with 1.52 parts by weight of Acrysol® RM 8-W (commercial nonionic associative thickener from Rohm & Haas), 0.437 part by weight of Viscalex® HV 30 (anionic thickener based on polyacrylate resin, from Allied Colloids) and 3.05 parts by weight of deionized water.

Inventive example 2

15 The production of a multicoat paint system with an inventive clearcoat

For application of the inventive slurry 1 of inventive example 1, a so-called integrated system with a black basecoat was prepared.

For this purpose, steel panels coated cathodically with commercially customary electrocoat materials were coated, using a gravity-feed cup gun, first with a functional coat (Ecoprime®; BASF Coatings AG). After 5 minutes' flashing off at room temperature, this coat was overcoated in the same way with a black aqueous basecoat material (Ecostar®; BASF Coatings AG) and then

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applied initially at 80°C for 5 minutes.

After the panels had cooled, the inventive slurry 1 was applied in the same way. The panels were then left to flash off initially for 5 minutes and were then
5 subjected to initial drying at 40°C for 15 minutes. They were then baked at 145°C for 30 minutes.

The wet films applied were chosen so that, after baking, the dry film thicknesses of the functional coat
10 and the aqueous basecoat were each 15 µm. The inventive clearcoat 1 had a film thickness of from 40 to 45 µm.

The inventive clearcoat 1 was hard, scratch-resistant, clear, bright, resistant to chemicals, weathering, and
15 condensation, and free from microdefects which induce an optical effect similar to the metallic effect (starry sky).

Comparative example C2

20

The production of a multicoat paint system with a noninventive clearcoat

Example 1 was repeated except that the noninventive
25 slurry of comparative example C1 was used.

The resulting, noninventive clearcoat was hard, scratch-resistant, clear, bright, and resistant to

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chemicals, weathering and condensation. However, it was not free from microdefects. These defects induced an optical effect which was similar to the metallic effect (starry sky).

CLAIMS

1. A pseudoplastic clearcoat slurry comprising water and particles that are at least one of solid and viscous and are dimensionally stable under storage and application conditions and which comprise binders comprising at least one methacrylate copolymers containing in copolymerized form, based on a given methacrylate copolymer, at least 99% by weight of at least one methacrylate comonomer, and wherein at least one methacrylate comonomer for the copolymer comprises at least one methacrylate comonomers having potentially ionic groups and at least one methacrylate comonomer free from reactive functional groups and from potentially ionic groups.
10
2. The pseudoplastic clearcoat slurry as claimed in claim 1, wherein the at least one methacrylate comonomer containing potentially ionic groups is selected from the group consisting of acrylic acid, beta-carboxyethyl acrylate, methacrylic acid, and combinations thereof.
3. The pseudoplastic clearcoat slurry as claimed in claim 1 or 2, wherein the at least one methacrylate copolymer has a glass transition temperature T_g of not more than 50°C.
4. The pseudoplastic clearcoat slurry as claimed in claim 3, wherein the glass transition temperature T_g is set by way of at least one methacrylate comonomer which is free from reactive functional groups and from potentially ionic groups.
20
5. The pseudoplastic clearcoat slurry as claimed in claim 3 or 4, wherein the glass transition temperature T_g is set by way of at least two methacrylate comonomers which are free from reactive functional groups and from potentially ionic groups.
6. The pseudoplastic clearcoat slurry as claimed in claim 5, wherein the glass transition temperatures T_g of the respective homopolymers of the at least two

methacrylate comonomers which are free from reactive functional groups and from potentially ionic groups differ from one another by not more than 40°C.

7. The pseudoplastic clearcoat slurry as claimed in any one of claims 3 to 6, wherein the at least one methacrylate copolymer, based on a given methacrylate copolymer, contain the at least one methacrylate comonomer which is free from reactive functional groups and from potentially ionic groups in an amount of at least 50% by weight.

8. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 7, which is substantially or entirely free from organic solvents.

10 9. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 8, which is substantially or entirely free from external emulsifiers content, except for alkoxyated C16-C18 fatty alcohols.

10. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 9, wherein the slurry containings from 0.1 to 50 mmol per 1 000 g of water, of at least one water-soluble salt, which optionally wherein the salt can be decomposed without residue or substantially without residue.

11. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 10, further comprising at least one thickener selected from the group consisting of ionic thickeners, and nonionic associative thickeners.

20 12. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 11, wherein the particles have an average size of from 0.8 to 20 µm and a maximum size of 30 µm.

13. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 12, having an ion-forming group content of from 0.05 to 1 meq/g and a neutralizing agent content of from 0.05 to 1 meq/g of solids.

14. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 13, which has a viscosity of

- (i) from 50 to 1 000 mPas at a shear rate of 1 000 s⁻¹,
- (ii) from 150 to 8 000 mPas at a shear rate of 10 s⁻¹, and
- (iii) from 180 to 12 000 mPas at a shear rate of 1 s⁻¹.

15. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 14, wherein the slurry is curable thermally or thermally and with actinic radiation.

16. The pseudoplastic clearcoat slurry as claimed in any one of claims 1 to 15, prepared by

- 10
- 1) emulsifying an organic solvent solution of constituents of the clearcoat slurry in water to give an emulsion of the oil-in-water type,
 - 2) removing the organic solvent or the organic solvents, and
 - 3) replacing by water some or all of the volume of solvent removed.

17. The use of the clearcoat slurry as claimed in any one of claims 1 to 16 for automotive OEM finishing, an automotive refinish, the interior and exterior painting of buildings, the coating of doors, windows and furniture, and industrial coating, including coil coating, container coating, the coating of small parts, the impregnation and/or coating of electrical components coating, and the coating of white goods.

20 18. The use as claimed in claim 17, wherein the clearcoat slurry is used to produce clearcoats as a part of multicoat color and/or effect paint systems.

19. The use of the clearcoat slurry as claimed in any one of claims 1 to 16 as an adhesive or sealing compound adhesive films and seals.