

Methacrylate resins for producing of road markings

The invention relates to methacrylate resins and to their use.

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Alongside methyl methacrylate, prepolymers, polymers and multifunctional monomer units, acrylates, such as n-butyl acrylate or ethylhexyl acrylate, are also used for production of extrusion resin systems and of spray
10 resin systems, for flexible crosslinking.

Constitution has a decisive effect on feasible application temperatures.

There are therefore many different systems.

15 DE 1769792 uses from about 30 to 70% by weight of methyl methacrylate, from about 10 to 25% by weight of a copolymer of vinyl chloride with vinyl acetate, plasticizers, paraffins and esters of phosphorous acid as a composition for covering, coating and filling.

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WO 01/18102 describes resin mixtures with additives which are intended to reduce the shrinkage of the resin. Hydroxyethyl methacrylate is used alongside propylene glycol, an acid and anhydrides.

25 Most systems listed generate a strong odour. DE 19826412 discloses a reduced-odour, cold-curing reactive (meth)acrylate resin for floor coatings composed of (meth)acrylates, which also contain comonomers, vinylaromatics or vinyl esters.

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Acrylates are monomers which have high vapour pressure, their odour therefore being readily discernable. Compliance with maximum workplace concentrations is required during handling of acrylates.

35 It was an object to provide resins in which the use of acrylates is not necessary. Another intention is that hardening be rapid, and that the applications have maximum temperature latitude available.

The object has been achieved via reactive resins based on methacrylate containing
from 0.1 to 15% by weight of urethane (meth)acrylates,
5 from 30 to 50% by weight of methyl methacrylates,
from 15 to 40% by weight of (meth)acrylic polymers
and/or of comonomers,
from 0 to 10% by weight of crosslinking agents,
from 0 to 5% by weight of accelerators
10 and of other auxiliaries and additives.
It has been found that these reactive resins are an excellent basis for formulations which are usually used for road markings and floor coatings.

15 Surprisingly, it has been found that the use of acrylates is not necessary. It has been found that the use of urethane (meth)acrylates can decisively improve the property profile of the reactive resins. Reactive resins based on methacrylate with urethane (meth)-
20 acrylate exhibit markedly reduced odour, since the volatile constituents are eliminated. Furthermore, the methacrylate resins exhibit good flexibility with high mechanical stability. They moreover have excellent flow properties and excellent surface properties.

25 It has been found that the reactive resins are suitable not only for sprayable resin systems but also for extrusion resin systems. The processor can therefore easily use various processing technologies with a
30 reactive resin mixture. The viscosities are about 10-5000 mPas.

It has also been found that the resins can be processed with wide temperature latitude of from 5 to 55°C.

35 "(Meth)acrylate" here means not only methacrylate, e.g. methyl methacrylate, ethyl methacrylate, etc., but also acrylate, e.g. methyl acrylate, ethyl acrylate, etc.,

and mixtures of the two.

One particularly preferred embodiment is a reactive resin whose constitution is

- 5 from 3 to 10% by weight of urethane (meth)acrylates,
from 35 to 45% by weight of methyl methacrylates,
from 25 to 35% by weight of (meth)acrylic polymers
and/or of comonomers,
from 0 to 3% by weight of crosslinking agents,
10 from 0 to 3% by weight of accelerators
and of other auxiliaries and additives.

- Auxiliaries and additives used comprise regulators,
plasticizers, stabilizers/inhibitors, waxes, oils,
15 activators and/or antifoams. (Meth)acrylic polymers
and/or comonomers are added to improve polymerization
properties, mechanical properties, adhesion to the
substrate, and the optical properties of the resins.
The (meth)acrylate polymers and/or comonomers are
20 selected from the acrylic polymers, methacrylic
polymers, acrylic-methacrylic polymers, styrene
acrylates, urethane (meth)acrylates, these having been
prepared via bulk polymerization, emulsion
polymerization, suspension polymerization or solution
25 polymerization. Crosslinking agents used are in
particular polyfunctional methacrylates such as allyl
methacrylate, ethylene glycol dimethacrylate,
diethylene glycol dimethacrylate, triethylene glycol
dimethacrylate, tetraethylene glycol dimethacrylate,
30 polyethylene glycol dimethacrylate, 1,3-butanediol
dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-
hexanediol dimethacrylate, 1,12-dodecanediol
dimethacrylate, glycerol dimethacrylate,
trimethylolpropane trimethacrylate.

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Accelerators/activators that can be used comprise the
commercially available accelerators, such as aromatic-
substituted tertiary amines. Regulators can also be

used. S-Methacrylates are preferably used.

Examples of other suitable auxiliaries and additives are paraffins.

5 Preferred plasticizers used are esters, polyols, oils or phthalates. From the stabilizer/inhibitors group, it is preferable to use substituted phenols, hydroquinone derivatives, phosphines and phosphites.

10 Antifoams are preferably selected from the group of the alcohols, hydrocarbons, paraffin-based mineral oils, glycol derivatives, and derivatives of glycolic esters, of acetic esters and of polysiloxanes.

15 It has been found that reactive resins according to Claim 1 can be used in formulations which can moreover comprise dyes, glass beads, fine and coarse fillers, wetting agents, dispersing agents and flow-control agents, UV stabilizers, and rheology additives.

20 Auxiliaries and additives preferably added for the field of application of the reactive resins as road marking or surface marking comprise dyes. Particular preference is given to white, red, blue, green and yellow inorganic pigments, titanium dioxide being
25 particularly preferred.

Glass beads are preferably used in formulations for road markings and surface markings, as reflectant.

30 The diameters of the commercially available glass beads used are from 10 to 2000 μm , preferably from 50 to 800 μm . The glass beads can also be silanized to improve processing and adhesion.

Fine fillers and coarse fillers can moreover be added to the formulation. These materials also have an
35 antislip function and are therefore particularly used in floor coatings.

Fine fillers have been used from the group of the calcium carbonates, barium sulphates, quartzes, powder

quartzes, precipitated and fumed silicas, pigments and cristobalites.

Coarse fillers used comprise quartzes, cristobalites, corundums and aluminium silicates.

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Wetting agents and dispersing agents and flow-control aids are preferably selected from the group of the alcohols, hydrocarbons, glycol derivatives, polyethers, polysiloxanes, polycarboxylic acids, saturated and
10 unsaturated polycarboxylic amine amides, and derivatives of glycolic esters, of acetic esters and of polysiloxanes.

It is also possible to use conventional UV stabilizers.
15 The UV stabilizers are preferably selected from the group of the benzophenone derivatives, benzotriazole derivatives, thioxanthone derivatives, piperidinol-carboxylic ester derivatives or cinnamic ester derivatives.

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Rheology additives used preferably comprise polyhydroxycarboxamides, urea derivatives, salts of unsaturated carboxylic esters, alkylammonium salts of an acidic phosphoric acid derivative, ketoximes, amine
25 salts of p-toluenesulphonic acid, amine salts of sulphonic acid derivatives and aqueous or organic solutions or mixtures of the compounds. It has been found that rheology additives based on fumed or precipitated silicas whose BET surface area is from 10
30 to 700 nm²/g are particularly suitable. It has been found that rheology additives based on silanized fumed or precipitated silicas whose BET surface area is from 10 to 700 nm²/g can be also be used.

The inventive methacrylate resins can be used directly
35 or for production of formulations for road markings and floor coatings, for example of asphalt, concrete and earthenware, and also on old coatings and markings for renovation. The resins and formulations harden via

free-radical polymerization, which is initiated via peroxides or UV light or thermally.

The examples given below are given for better
5 illustration of the present invention but do not restrict the invention to the features disclosed herein.

Examples

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Example 1 ("sprayable cold plastic")

For production of a sprayable road-marking paint, composed of two components (resin A accelerated
15 component; resin B unaccelerated component), which is processed in a ratio of 1:1 using familiar processing machinery, a methyl methacrylate resin composed of from 0.1 to 15% by weight of urethane (meth)acrylates, from 30 to 50% by weight of methyl methacrylates,
20 from 15 to 40% by weight of (meth)acrylic polymers and/or of comonomers, from 0 to 10% by weight of crosslinking agents, from 0 to 5% by weight of accelerators and of other auxiliaries and additives is produced for
25 production of component A and a methyl methacrylate resin composed of from 0.1 to 15% by weight of urethane (meth)acrylates, from 30 to 50% by weight of methyl methacrylates, from 15 to 40% by weight of (meth)acrylic polymers and/or of comonomers,
30 from 0 to 10% by weight of crosslinking agents, and of other auxiliaries and additives for production of component B.

These are subjected to final processing as follows to
35 give finished formulations:

Component A		
Resin A	42.0	%
Disperbyk 163	0.3	%
Byk 410	0.1	%
Titanium dioxide	10.0	%
Fine filler	47.6	%

Component B		
Resin B	42.0	%
Disperbyk 163	0.3	%
Byk 410	0.1	%
Titanium dioxide	10.0	%
Fine filler	47.6	%

The viscosity of the finished paint components is about 2000 mPas, the density being 1.6 kg/l. Consumption is about 1.1 kg/m² for a layer thickness of 0.7 mm.

- 5 The formulations are suitable for applying paint with a layer thickness of from 0.3 to 0.8 mm.

First, 4.0% of hardener powder (50% strength dibenzoyl peroxide phlegmatized in phthalate) are stirred into
10 the unaccelerated paint mixture (component B). The two components A and B are then placed in separate tanks of the spray machinery, which mixes the components in the ratio 1:1 and sprays them. Component B is storage-stable for a plurality of days at room temperature with
15 hardener, but only for 1-2 hours at 55°C.

The pot lives and curing times at various temperatures are:

Temperature (°C)	Pot life (min)	Curing time (min)
+5	5	20
+20	3	8
+45	3	9

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The formulation was applied using "ECOZET" processing machinery (600 µm layer thickness), and then 450 g/m² of "Megalux 600-800 MKT 18" glass beads (comprising corundum) were scattered on the material (type I). The
25 marking has the following properties:

Total residual monomers %	Shore D hardness	TABER H 22 abrasion 500 g-1000 rpm	Slump (2% BPO powder) (2% BPO S.)		Tensile bond strength on asphalt	HUNTERLAB Y whiteness
0.15	56	0.12	9.0 cm	9.0 cm	> 2 N/mm ²	90.54

Susceptibility to wear and traffic-engineering properties were tested by the Bundesanstalt für Strassenwesen [Federal Highway Research Institute]

5 (test number: 2005 1DY 10.11).

Properties	Number of wheel traverses (millions)							
	0	0.1	0.2	0.5	1.0	2.0	3.0	4.0
Wear resistance (%)	100	100	100	100	100	100	100	100
Grip (SRT units)	54	41	41	40	40	40	39	36
Night visibility, dry ($\text{mcd}\cdot\text{m}^{-2}\cdot\text{lx}^{-1}$)	255	551	522	537	618	591	434	363
Luminance coefficient Qd ($\text{mcd}\cdot\text{m}^{-2}\cdot\text{lx}^{-1}$)	250	226	219	222	245	236	229	223
Standard colour coordinates	x = 0.324				y = 0.344			

Example 2 ("cold plastic")

- 5 For production of an extrudable road-marking paint, composed of two components (resin A accelerated component; resin B unaccelerated component), which is processed in a ratio of 1:1 using familiar processing machinery, a methyl methacrylate resin composed of
- 10 from 0.1 to 15% by weight of urethane (meth)acrylates, from 30 to 50% by weight of methyl methacrylates, from 15 to 40% by weight of (meth)acrylic polymers and/or of comonomers,
- 15 from 0 to 10% by weight of crosslinking agents, from 0 to 5% by weight of accelerators and of other auxiliaries and additives is produced for production of component A and a methyl methacrylate resin composed of
- 20 from 0.1 to 15% by weight of urethane (meth)acrylates, from 30 to 50% by weight of methyl methacrylates, from 15 to 40% by weight of (meth)acrylic polymers and/or of comonomers,
- 25 from 0 to 10% by weight of crosslinking agents, and of other auxiliaries and additives for production of component B.

These are subjected to final processing as follows to give finished formulations:

Component A		
Resin A	20.00	%
Byk 410	0.10	%
Bentone 27	0.10	%
Titanium dioxide	10.00	%
Fine filler	20.00	%
Coarse filler	25.00	%
Reflective beads	25.00	%

Component B		
Resin B	20.00	%
Byk 410	0.10	%
Bentone 27	0.10	%
Titanium dioxide	10.00	%
Fine filler	17.50	%
Coarse filler	25.00	%
Reflective beads	25.00	%

- 5 The viscosity of the finished paint components is about 15 000 mPas, the density being 1.85 kg/l. Consumption is about 3.7 kg/m² for a layer thickness of 2 mm. The formulations are suitable for applying paint with a layer thickness of from 1.5 to 3 mm.

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- First, 4.0% of hardener powder (50% strength dibenzoyl peroxide phlegmatized in phthalate) are stirred into component B. The two components A and B are then placed in separate tanks of the extrusion machinery, which mixes the components in the ratio 1:1 and extrudes them. Component B is storage-stable for a plurality of days at room temperature with hardener, but only for 1-2 hours at 55°C.

- 20 The pot lives and curing times at various temperatures are:

Temperature (°C)	Pot life (min)	Curing time (min)
+5	7	17
+20	3	8
+45	4	12

- The formulation was applied at 2 mm layer thickness using a Plastomarker, and then 400 g/m² of "SWARCO 600-

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800 MKT 18 3:1" glass beads were scattered on the material (type I). The marking has the following properties:

Total residual monomers %	Shore D hardness	TABER H 22 abrasion 500 g-1000 rpm	Slump (2% BPO powder) (2% BPO S.)		Tensile bond strength on asphalt	HUNTERLAB Y whiteness
0.03	48	0.15	7.2 cm	7.2 cm	> 2 N/mm ²	87.21

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Susceptibility to wear and traffic-engineering properties were tested by the Bundesanstalt für Strassenwesen [Federal Highway Research Institute] (test number: 2005 1DY 10.12).

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Properties	Number of wheel traverses (millions)							
	0	0.1	0.2	0.5	1.0	2.0	3.0	4.0
Wear resistance (%)	100	100	100	100	100	100	100	100
Grip (SRT units)	62	44	44	41	40	40	37	36
Night visibility, dry (mcd*m-2 *lx-1)	267	523	567	569	554	544	446	372
Luminance coefficient Qd (mcd*m-2 *lx-1)	251	230	244	245	243	235	235	240
Standard colour coordinates	x = 0.326				y = 0.345			

Example 3 ("agglomerate structure", PATHFINDER®)

For production of an extrudable road-marking paint of PATHFINDER® type, composed of two components (resin A accelerated component; resin B unaccelerated component), which is processed in a ratio of 1:1 using familiar processing machinery, a methyl methacrylate

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resin composed of
from 0.1 to 15% by weight of urethane (meth)acrylates,
from 30 to 50% by weight of methyl methacrylates,
from 15 to 40% by weight of (meth)acrylic polymers
5 and/or of comonomers,
from 0 to 10% by weight of crosslinking agents,
from 0 to 5% by weight of accelerators
and of other auxiliaries and additives is produced for
production of component A and a methyl methacrylate
10 resin composed of
from 0.1 to 15% by weight of urethane (meth)acrylates,
from 30 to 50% by weight of methyl methacrylates,
from 15 to 40% by weight of (meth)acrylic polymers
and/or of comonomers,
15 from 0 to 10% by weight of crosslinking agents,
and of other auxiliaries and additives for production
of component B.

These are subjected to final processing as follows to
give finished formulations:

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Component A		
Resin A	20.00	%
Byk 410	0.30	%
Bentone 27	0.30	%
Titanium dioxide	10.00	%
Fine filler	24.40	%
Reflective beads	45.00	%

Component B		
Resin B	20.00	%
Byk 410	0.30	%
Bentone 27	0.30	%
Titanium dioxide	10.00	%
Fine filler	24.40	%
Reflective beads	45.00	%

The viscosity of the finished paint components is about
9 cm by the DANIEL slump method. Consumption is about
1.6-3 kg/m².

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First, 4.0% of hardener powder (50% strength dibenzoyl
peroxide phlegmatized in phthalate) are stirred into
component B. The two components A and B are then placed
in separate tanks of the extrusion machinery, which
30 mixes the components in the ratio 1:1 and extrudes them

over a toothed roll. Component B is storage-stable for a plurality of days at room temperature with hardener, but only for 1-2 hours at 55°C.

- 5 The pot lives and curing times at various temperatures are:

Temperature (°C)	Pot life (min)	Curing time (min)
+5	8	18
+20	3	8
+45	3	11

- 10 The formulation was applied in the form of "agglomerate" using "Plastomarker Junior" machinery, consumption of material being about 3 kg/m² - the material then for scattering being Potters 3D-AC-05 (type I).

- 15 Susceptibility to wear and traffic-engineering properties were tested by the Bundesanstalt für Strassenwesen [Federal Highway Research Institute] (test number: 2005 1DY 10.13).

Properties	Number of wheel traverses (millions)							
	0	0.1	0.2	0.5	1.0	2.0	3.0	4.0
Wear resistance (%)	100	100	100	100	100	100	100	100
Grip (SRT units)	56	51	48	48	46	45	43	42
Night visibility, dry (mcd*m-2 *lx-1)	282	355	335	316	335	356	298	299
Night visibility, wet, 2% inclination	295	120	221	70	66	81	122	114
Luminance coefficient Qd (mcd*m-2 *lx-1)	244	244	240	223	233	253	248	249

Standard colour
coordinates

$x = 0.332$

$y = 0.349$

Patent claims

1. Methacrylate resins, containing
from 0.1 to 15% by weight of urethane
5 (meth)acrylates,
from 30 to 50% by weight of methyl methacrylates,
from 15 to 40% by weight of (meth)acrylic polymers
and/or of comonomers,
from 0 to 10% by weight of crosslinking agents,
10 from 0 to 5% by weight of accelerators
and of other auxiliaries and additives.
2. Methacrylate resins according to Claim 1, contain-
ing
15 from 3 to 10% by weight of urethane
(meth)acrylates,
from 35 to 45% by weight of methyl methacrylates,
from 25 to 35% by weight of (meth)acrylic polymers
and/or of comonomers,
20 from 0 to 3% by weight of crosslinking agents,
from 0 to 3% by weight of accelerators
and of other auxiliaries and additives.
3. Methacrylate resins according to Claim 1 or 2,
25 characterized in that the auxiliaries and addi-
tives used comprise regulators, plasticizers,
stabilizers/inhibitors, waxes, oils, activators
and/or antifoams.
- 30 4. Methacrylate resins according to Claim 1 or 2,
characterized in that the crosslinking agents used
are polyfunctional methacrylates such as allyl
methacrylate, ethylene glycol dimethacrylate,
diethylene glycol dimethacrylate, triethylene
35 dimethacrylate, tetraethylene glycol
dimethacrylate, polyethylene glycol
dimethacrylate, 1,3-butanediol dimethacrylate,
1,4-butanediol dimethacrylate, 1,6-hexanediol

dimethacrylate, 1,12-dodecanediol dimethacrylate, glycerol dimethacrylate, trimethylolpropane trimethacrylate.

- 5 5. Methacrylate resins according to Claim 1 or 2, characterized in that the accelerators used are aromatic-substituted tertiary amines.
- 10 6. Formulation based on methacrylate resins according to any of Claims 1 to 5 comprising dyes, glass beads, fine and coarse fillers, wetting agents, dispersing agents and flow-control agents, UV stabilizers, and rheology additives.
- 15 7. Formulation according to Claim 6, characterized in that inorganic pigments are used, preferably titanium dioxide.
- 20 8. Formulation according to Claim 6, characterized in that glass beads or silanized glass beads with diameters of from 10 to 2000 μm are used.
- 25 9. Formulation according to Claim 8, characterized in that glass beads or silanized glass beads with diameters of from 50 to 800 μm are used.
- 30 10. Formulation according to Claim 6, characterized in that fine fillers are used from the group of the calcium carbonates, barium sulphates, quartzes, powder quartzes, precipitated and fumed silicas, pigments and cristobalites.
- 35 11. Formulation according to Claim 6, characterized in that the coarse fillers used comprise quartzes, cristobalites, corundums and aluminium silicates.
12. Formulation according to Claim 6, characterized in that the wetting agents, dispersing agents and

5 flow-control agents used are preferably selected from the group of the alcohols, hydrocarbons, glycol derivatives, polyethers, polysiloxanes, polycarboxylic acids, saturated and unsaturated polycarboxylic amine amides, and derivatives of glycolic esters, of acetic esters and of polysiloxanes.

10 13. Formulation according to Claim 6, characterized in that the UV stabilizers used are selected from the group of the benzophenone derivatives, benzotriazole derivatives, thioxanthone derivatives, piperidinolcarboxylic ester derivatives or cinnamic ester derivatives.

15 14. Formulation according to Claim 6, characterized in that rheology additives used have been selected from the group of the polyhydroxycarboxamides, urea derivatives, salts of unsaturated carboxylic esters, alkylammonium salts of an acidic phosphoric acid derivative, ketoximes, amine salts of p-toluenesulphonic acid, amine salts of sulphonic acid derivatives and aqueous or organic solutions or mixtures of the compounds.

25 15. Formulation according to Claim 6, characterized in that rheology additives based on fumed or precipitated silicas whose BET surface area is from 10 to 700 nm²/g are used.

30 16. Formulation according to Claim 6, characterized in that rheology additives based on silanized fumed or precipitated silicas whose BET surface area is from 10 to 700 nm²/g are used.

35 17. Use of methacrylate resins according to any of Claims 1 to 5 for preparation of formulations for road markings and floor coatings.

18. Use of formulations according to any of Claims 6 to 16 for floor coatings and road markings on asphalt, concrete and earthenware.

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19. Use of formulations according to any of Claims 6 to 16 for renovation of old coatings and markings.