The present invention comprises a novel formulation for marking trafficways, for example roads, which when compared with the prior art have improved mechanical properties and improved heat resistance during curing. The invention also relates to improved reactive resins for other applications than roadmarkings. The present invention in particular relates to reactive resins which comprise core-shell particles.
IMPACT-MODIFIED REACTION RESIN

FIELD OF THE INVENTION

[0001] The present invention comprises a novel formulation for marking or coating floor surfaces or trafficways, for example roads, which when compared with the prior art have improved mechanical properties and improved resistance during curing. The invention also relates to improved reactive resins for other applications than roadmarkings. The present invention in particular relates to reactive resins which comprise core-shell particles.

[0002] Modern trafficway markings are subject to a large number of requirements. Firstly, these systems are expected to be easy to apply on the road surface and at the same time to provide long shelf life, and also to provide a marking with long lifetime. Other important factors are capability for rapid operations and in particular capability for operations over the widest possible temperature range. Many reactive roadmarking and flooring systems of the prior art cure in an excessively uncontrolled manner at temperatures above 100°C. Results can be blistering, tacky surfaces, and regions where curing is incomplete. This leads in turn to reduced adhesion values and shortened lifetimes. In contrast, at temperatures below 10°C hardening is very slow, and newly marked road sections have to be removed from use for a prolonged period, or an artificial method has to be used to adjust the temperature of the markings. Marking operations using systems of the prior art are often completely impossible at temperatures below freezing point.

PRIOR ART

[0003] For quite some time now, an aim of development work has been to improve temperature dependency during the hardening of reactive resins, and also to improve their mechanical properties. Examples of systems currently used for trafficway marking materials are solvent-based paints, aqueous paints, thermoplastic paints, paints based on reactive resins, and also prefabricated adhesive tapes. A disadvantage of the latter is that they are complicated to produce and to apply. There are also restrictions on the freedom available in respect of the design of the marking for desirable long life, e.g., use of glass beads.

[0004] Thermoplastic coatings which are applied in the molten state to the trafficway surface can per se also be optimized for high hardening rate. Their use has the great disadvantage of an additional step in that the product first has to be melted, for example at 200°C., before it can be applied. Firstly, this is potentially dangerous because of the high temperature, and secondly thermoplastic systems per se have relatively high susceptibility to abrasion, and relatively low thermal stability. Thermoplastic systems often have markedly shorter life than systems which are based by way of example on reactive resins and which react with crosslinking.

[0005] Reactive-resin systems of the prior art are typically flexibilized by adding, to the monomer-polymer mixture, (meth)acrylic comonomers or plasticizers which lower the glass transition temperature of the hardened composition, an example being n-butyl acrylate, 2-ethylhexyl acrylate, or other long-chain or branched monomers that can be cured by a free-radical route, where the homopolymer of these has a glass transition temperature below 0°C. However, these monomers generate another known problem, since when monomers of this type are added for flexibilization the typically incomplete hardening of these in the application increases VOC content and long-term odor problems due to slow evaporation of the monomers, and also slows hardening.

OBJECT

[0006] It is an object of the present invention to provide a novel reactive resin which, irrespective of the application, has a longer lifetime when compared with the prior art.

[0007] In particular, an object of the present invention is to provide a novel reactive resin, by way of example for formulations for the marking of trafficway surfaces, which has improved mechanical properties, in particular with regard to the combination of hardness and flexibility, in comparison with the prior art. The improvements to be made in mechanical properties in particular relate to reduction of crack propagation, to flexibilization, to greater mechanical strength, and to improved capability to withstand point load.

[0008] Another object of the present invention is to provide a novel formulation for the marking of trafficway surfaces which, in comparison with the prior art, has longer lifetime.

[0009] The formulation for the marking of trafficway surfaces is moreover intended to be capable of application without blistering irrespective of ambient temperature in the range from 5°C. to 50°C.

[0010] A particular object consists in providing a reactive resin which, in comparison with the prior art, can give trafficway markings with longer life, with good substrate adhesion, with good retroreflective properties, with good day- and night-visibility, with high, stable whiteness, and with good grip capability, even when the trafficway is wet.

[0011] Other objects not explicitly mentioned are apparent from the entire context of the description, claims, and examples below.

ACHIEVEMENT OF OBJECT

[0012] The objects are achieved via a novel reactive resin which comprises at least one crosslinking agent, monomers, polymers, and at least one impact modifier.

[0013] It is preferable that the objects are achieved via a novel reactive resin which comprises at least one crosslinking agent, monomers, polymers, and at least one core-shell polymer.

[0014] In particular, the objects are achieved via a novel reactive resin which has at least the following ingredients:

[0015] from 0.5% by weight to 30% by weight of crosslinking agent, preferably dimethacrylates,

[0016] from 20% by weight to 85% by weight of monomers, preferably (meth)acrylates and/or components copolymerizable with (meth)acrylates,

[0017] from 0% by weight to 20% by weight of urethane (meth)acrylates,

[0018] from 3% by weight to 40% by weight of prepolymers, preferably poly(meth)acrylates,

[0019] from 0% by weight to 5% by weight of accelerator, preferably amines,

[0020] from 1% by weight to 25% by weight of core-shell polymer, preferably comprising poly(meth)acrylates, and

[0021] optionally other auxiliaries.

[0022] The other auxiliaries can by way of example involve stabilizers, inhibitors, chain-transfer agents, or waxes.

[0023] The expression poly(meth)acrylates comprises not only polymethacrylates but also polyacrylates, and also...
copolymers and mixtures of the two. The expression (meth)acrylates correspondingly comprises methacrylates, acrylates, and mixtures of the two.

[0024] The present invention also comprises sprayable and other cold plastics comprising the reactive resin of the invention. These cold plastics have the following components:

[0025] from 5 to 60% by weight of the reactive resin described above,

[0026] from 1 to 5% by weight of a mixture comprising one or more initiators, preferably peroxides,

[0027] from 7 to 15% by weight of an inorganic pigment, preferably titanium dioxide, and

[0028] from 50 to 60% by weight of mineral fillers.

[0029] In the use for the marking of traffiway surfaces, the components of the cold plastic are mixed before or during application on the traffiway surface. In the case of other uses, the use determines whether the components are appropriately mixed shortly before or during the casting process, coating process, or charging process.

[0030] It is preferable that the peroxide involves dilauroyl peroxide and/or dibenzyol peroxide. It is preferable that the amine involves a tertiary, aromatically substituted amine.

[0031] In an alternative embodiment, the peroxide is a constituent of the reactive resin, and the accelerator is not a constituent of the reactive resin, but instead is a separate component of the cold plastic.

[0032] The dispersion of the core-shell particles in the monomer-polymer mixture of the reactive resin has to be good in order to avoid causing any haze or clumping. This can easily be ensured through appropriate stirring or by means of any other known dispersion technique.

[0033] Surprisingly, the addition of core-shell particles, in particular known as impact modifiers for by way of example PMMA molding compositions or PVC achieved a decisive improvement in significant properties of reactive acrylic resins.

[0034] Mention should especially be made here of high flexibility of structures which are nevertheless hard, and also of improved resistance to temperature change during the curing process, with avoidance of blistering. The content of the core-shell particles introduced into the reactive resins is from 1 to 25% by weight, preferably from 1 to 15%, by weight, particularly preferably from 2 to 12% by weight.

[0035] Said properties lead to greater mechanical strength and moreover to reduced crack propagation and to greater capability to withstand point load.

[0036] Overall, the reactive resins of the invention, the cold plastics produced therefrom, and the traffiway markings produced by way of example in turn therefrom, have a longer lifetime than systems of the prior art. They also exhibit improved adhesion through avoidance of breakaway from the substrate, since the material is capable of compensating, or bridging, any shrinkage stresses that may arise. Other properties that can be observed, in comparison with the prior art, are improved adhesion to the substrate, and also markedly improved shrinkage behavior.

[0037] Surprisingly, it has been found that said properties are obtained irrespective of temperature in the temperature range relevant to the application of from −30° C. to 70° C., preferably from −10° C. to 50° C.

[0038] Surprisingly, it has also been found that the mechanical properties of the traffiway marking of the invention are independent of the application thickness in a typical range from 200 μm to 7000 μm. The application thickness of the sprayable or other cold plastic of the invention is preferably from 400 μm to 1000 μm, and particularly preferably from 600 μm to 800 μm. Thinner and thicker layers are of course possible in appropriate applications.

[0039] Surprisingly, it has also been found that a traffiway marking obtainable through application of a cold plastic of the invention, comprising a reactive resin of the invention that comprises core-shell particles can be formulated in such a way that it hardens rapidly and after as little as 10 min, or if formulated appropriately after as little as 5 min, has sufficient strength, substrate adhesion, dimensional stability, and abrasion resistance to permit passage of traffic thereover to resume. The result of this in an application in the road traffic sector is that when the system of the invention is used it is no longer necessary that the traffiway section requiring marking is subjected to complicated and lengthy removal from use.

[0040] The expression capability to withstand wheeled traffic and the expression capability to permit resumption of passage of traffic, used synonymously, mean that the traffiway marking can be subjected to load, for example can support vehicular traffic. The period required to achieve capability to withstand wheeled traffic is the period from the application of the traffiway marking to the juncture at which it is no longer possible to discern any alterations in the form of abrasion, of adhesion loss in respect of the traffiway surface or in respect of the embedded glass beads, or of any deformation of the marking. Dimensional stability and stability of adhesion are measured in accordance with DIN EN 1542 99 in conjunction with DAfStb-RiLi 01.

The Impact Modifier

[0041] The person skilled in the art is aware of a large number of impact modifiers, e.g. elastomer particles. These are especially used in plastics which are intrinsically brittle, for example PVC or PMMA, in order to increase impact resistance. It is preferable that the impact modifiers involve core-shell particles.

The Core-Shell Particles

[0042] The core-shell particles, also termed impact modifiers, can be added in various embodiments, which lead to the same reactive resin of the invention.

[0043] In a first embodiment, the core-shell particles are added directly. This embodiment has the advantage that when the polymer that also has to be added is selected there is greater freedom in relation to the form in which it is added, example being the form of a fine-grain or suspension polymer.

[0044] The pure core-shell particles can be used directly in the form of coagulate, in the form of spray product, or in the form of freeze-dried product, or in the form of pelletized material obtained through extrusion of an emulsion polymer (extrusion with pressurized removal of material), as described in DE19927769 and in the publications cited therein.

[0045] The core of the core-shell particle mostly involves an engineering thermoplastic or elastomer that can be obtained through grafting or emulsion polymerization with use of a seed latex, or through sequential emulsion polymerization. Materials generally used as core material are amorphous copolymers with glass transition temperature below 0° C., for example acrylic rubbers, ASA rubbers, diene rubbers, organosiloxane rubbers, EPDM rubbers, SBS rubbers, SEBS
rubbers, ABS rubbers, and MBS rubbers, or else ethylene-based cores, examples being EnBA copolymers and EMA copolymers. The cores can optionally have been functionalized with reactive groups, e.g. epoxy groups or anhydride groups. These and other materials used for impact modification are described by way of example in DE 10 2005 034 999 and in the publications cited therein.

[0046] In other embodiments, the core-shell particles are added in the form of an impact-modified molding composition which comprises core-shell particles and at least a portion of the polymer. This embodiment has the advantage that dispersion of the core-shell particle in the reactive resin can be carried out more rapidly and more simply. Suspension polymers of this type comprising core-shell particles are marketed by way of example as ZK50 by Evonik Röhm GmbH. Other embodiments would be masterbatches comprising core-shell particles and comprising other polymers. This type of masterbatch can by way of example be obtained through extrusion.

[0047] Another possibility would be to use a specific reactive resin masterbatch.

[0048] Impact modifiers, e.g. for polymethacrylate plastics, are well known. Impact modifiers used in the invention are in particular polymer particles which can have a two- or three-layer core-shell structure, and which are obtained by emulsion polymerization. Impact modifiers of this type are described by way of example in EP-A-0 113 924, EP-A-0 522 351, EP-A-0 465 049, and EP-A-0 683 028. For the purposes of this invention, suitable particle sizes of said emulsion polymers are preferably in the range from 25 nm to 1000 nm, preferably from 50 nm to 700 nm, and particularly preferably from 80 nm to 500 nm.

[0049] The structure of the core-shell particles here can have two, three, or more shells. It is preferable that the core-shell particles comprise at least one hard phase and at least one tough phase. The hard phase here features a high glass transition temperature Tg of at least 70°C. At the same time, the glass transition temperature Tg of the tough phase is below -10°C. In the case of a two-shell core-shell particle, both the hard phase and the tough phase can form the core. The core is generally formed by the tough phase.

[0050] A three-layer or three-phase structure with a core and with two shells can take the following form. It is preferable that the core and the outermost shell are hard phases, while the middle shell is a tough phase. The outermost hard phase improves compatibility and provides good coupling to a matrix. The structure of this type of core-shell particle can by way of example take the following form:

[0051] The hard core can by way of example consist essentially of methyl methacrylate, of small proportions of comonomers, such as ethyl acrylate, and of a proportion of crosslinking agent, e.g. allyl methacrylate. The middle, soft shell (tough phase) can by way of example be composed of butyl acrylate and optionally styrene, while the outermost, hard shell in essence mostly corresponds to the matrix polymer. However, it is also possible to conceive of other embodiments, such as soft-hard-soft, soft-hard-hard, or hard-soft-soft. The composition of the outermost shell is preferably adapted to be appropriate to the ambient matrix, and at least one of the two inner shells should involve a tough phase, in order to improve impact resistance.

[0052] It is preferable that the core and/or at least one shell of the core-shell particle has/have been crosslinked. This crosslinking stabilizes the particle and improves impact-resistance properties to a marked extent.

[0053] The embodiment of a two-phase, impact-modified polymer can by way of example use a system known in principle from EP 0 528 196 A1:

[0054] a) from 10 to 95% by weight of a coherent hard phase composed of from 80 to 100% by weight of methyl methacrylate and from 0 to 20% by weight of one or more other ethylenically unsaturated monomers capable of free-radical polymerization, and

[0055] b) dispersed within the hard phase, from 5 to 90% by weight of a tough phase composed of from 50 to 90% by weight of a C6-C18 alkyl acrylate, of from 0.5 to 5% by weight of a crosslinking monomer having two or more ethylenically unsaturated moieties capable of free-radical polymerization, and optionally of other ethylenically unsaturated monomers capable of free-radical polymerization, where at least 15% by weight of the hard phase a) has covalent linkage to the tough phase b).

[0056] A two-phase impact modifier can be produced by a two-stage emulsion polymerization in water, as described by way of example in DE 38 42 796. The first stage by way of example produces the tough phase, which is composed of at least 50% by weight, preferably of more than 80% by weight, of lower alkyl acrylates, giving a glass transition temperature Tg below -10°C, for this phase. Crosslinking monomers used comprise (meth)acrylates of diols, for example ethylene glycol dimethacrylate or 1,4-butanediol dimethacrylate, aromatic compounds having two vinyl or allyl groups, for example divinylbenzene, or other crosslinking agents having two ethylenically unsaturated moieties capable of free-radical polymerization, e.g. allyl methacrylate, as graft-linking agent. Examples that may be mentioned of crosslinking agents having three or more unsaturated groups capable of free-radical polymerization, for example allyl groups or (meth)acrylic groups, are triallyl cyanurate, trimethylolpropane triacrylate, and trimethylolpropane trimethacrylate, and also pentaerythritol tetraacrylate, and pentaerythritol tetraethylacrylate. Other examples here are given in U.S. Pat. No. 4,513,118.

[0057] The ethylenically unsaturated monomers mentioned, capable of free-radical polymerization, can by way of example be acrylic or methacrylic acid, or else alkyl esters thereof having from 1 to 20 carbon atoms, where the alkyl moiety can be linear, branched, or cyclic. It is also possible to use other aliphatic comonomers capable of free-radical polymerization that are copolymerizable with the alkyl acrylates. However, significant proportions of aromatic comonomers, such as styrene, alpha-methylstyrene or vinyltoluene, should be avoided since they can lead to undesired properties of the final product—especially on exposure to weather.

[0058] The alternative addition form of an impact-modified molding composition, preferably of an impact-modified polyester molding composition or of an impact-modified PMMA molding composition, particularly preferably of a PMMA molding composition, is composed of from 1 to 80% by weight, preferably from 20 to 70% by weight, of a matrix polymer, preferably of a poly(meth)acrylate, and of from 99 to 20% by weight, preferably from 80 to 30% by weight, of core-shell particles, as described above.

[0059] Said impact-modified molding compositions can be mixed in the melt in an extruder, as described in DE19927769, by adding the core-shell particles, used in coagulated or spray-dried form or in the form of dispersion in
water, and optionally the matrix polymer, to give impact-modified molding compositions. A possibility here is that during the coagulation of a dispersion that is used, water used is removed from the extruder and a dry melt is thus obtained. The material discharged is generally then chopped to give pellets. These can be subjected to further milling if necessary. The matrix polymer can by way of example be composed of from 60 to 100% by weight of methyl methacrylate units polymerized by a free-radical route and optionally from 0 to 40% by weight of other comonomers capable of free-radical polymerization, e.g. C₁₋₅-alkyl(meth)acylates, in particular methyl, ethyl, propyl, or butyl(meth)acrylate. It is preferable that the weight-average molar mass Mₚ of the matrix is in the range from 2000 g/mol to 200,000 g/mol, with preference from 25,000 g/mol to 150,000 g/mol, with particular preference from 50,000 g/mol to 150,000 g/mol (Mₚ being determined by means of gel permeation chromatography with reference to polymethyl methacrylate as standard).

Components of Cold Plastic or Reactive Resin

The sprayable or other cold plastic can also comprise other auxiliaries, such as wetting agents and/or dispersing agents, an (antisip) filler providing grip, and antisettling agents. It is also possible that the glass beads that are added in order to improve reflectance are already present in this component of the cold plastic.

Another possible alternative is that these are a constituent of the second component, and it is preferable, if the mechanism of application of the trafficway marking is appropriate, that the glass beads are applied in the form of third component. In this procedure, for example used with modern marking vehicles using a second nozzle, the beads are applied by spraying onto the first two components directly after these have been applied. An advantage of this procedure is that the portion of the glass beads wetted by the constituents of the other two components is only the portion embedded into the marking matrix, and ideal reflective properties are obtained. However, a very important consideration when this technology is used is particularly good embedment of the glass beads and correspondingly good adhesion of the marking matrix, or of the trafficway marking formulation, on the surface of the glass beads. Surprisingly, it has been found that the reactive resin of the invention, or the sprayable cold plastic of the invention, comprising said reactive resin, complies with these required properties at least at the level of the prior art. Detailed regulation of the properties required from a road-marking is provided by DIN EN 1436.

In order to achieve a further improvement in the required properties, the glass beads can be applied together with adhesion promoters or can be pretreated therewith. The retroreflective properties and the day- and night-visibility of the cold plastic of the invention are thus at least comparable with the prior art. The same applies to lifetime, in particular of the embedment of the glass beads.

The second component of the sprayable or other cold plastic comprises the initiator. Polymerization initiators used are in particular peroxides or azo compounds. It can sometimes be advantageous to use a mixture of various initiators. It is preferable to use halogen-free peroxides, such as dilauroyl peroxide, dibenzoyl peroxide, tert-butyl peroxycarbonate, di(tert-buty1) peroxide (DTBP), di(tert-amyl) peroxide (DTAP), tert-butyl 2-ethylhexyl peroxy-carbonate (TBPEHC), and other peroxides that decompose at high temperature, as free-radical initiator. For reactive resins for use by way of example for trafficway markings particular preference is given to dilauroyl peroxide or dibenzoyl peroxide. The general rule is that there is a diluent, for example a phthalate such as dibutyl phthalate, an oil, or another plasticizer admixed with the peroxide in the second component. The cold plastic of the invention, in the form of entirety of the first and of the second, and also optionally of the third, component comprises from 0.1% by weight to 7% by weight, preferably from 0.5% by weight to 6% by weight, and very particularly preferably from 1% by weight to 5% by weight, of the initiator of or the mixture of the initiator and of the diluent.

The preferred embodiment of a redox initiator system for reactive resins is peroxides combined with accelerators, in particular amines. Examples that may be mentioned of said amines are tertiary aromatically substituted amines, e.g. in particular N,N-dimethyl-p-toluidine, N,N-bis(2-hydroxyethyl)-p-toluidine and N,N-bis(2-hydroxypropyl)-p-toluidine. The reactive resin of the invention can comprise up to 5% by weight, and very particularly preferably up to 3% by weight, of an accelerator.

In an alternative embodiment of an alternative 2 C or 3 C system, the accelerator is present in the second component, for example in a diluent, and the initiator, for example the peroxide, is a constituent of the reactive resin of the invention. The optional third component in turn involves the glass beads and any adhesion promoters required.

The crosslinking agents are a constituent of decisive importance in the reactive resin of the invention. In particular polyeutathane methacrylates, such as allyl(meth)acrylate. Particular preference is given to di- or tri(meth)acrylates, for example 1,4-butane diol di(meth)acrylate, poly(urethane) (meth)acrylates, tetrathylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, or trimethylolpropane tri(meth)acrylate. The proportion of crosslinking agent is markedly higher than in the prior art, and is from 13% by weight to 35% by weight, preferably from at least 20% by weight to at most 30% by weight. Surprisingly, it has been found that this relatively high proportion of crosslinking agent provides not only a high degree of initial curing but also, in combination with the other components, provides rapid capability of the trafficway marking, comprising the resin of the invention, to withstand wheeled traffic.

For the purposes of this invention, the urethane (meth)acrylates optionally present are compounds which have (meth)acrylate functionalities linked to one another by way of urethane groups. They are obtainable through the reaction of hydroxyalkyl(meth)acrylates with polyisocyanates and polyoxyalkylenes which have at least two hydroxy functionalities. Instead of hydroxyalkyl(meth)acrylates it is also possible to use esters of (meth)acrylic acid with oxiranes, such as ethylene oxide or propylene oxide, or with corresponding oligo- or polyoxiranes. An overview by way of example of urethane(meth)acrylates having a functionality greater than two is found in DE 199 02 685. A commercially available example produced from polyols, isocyanates, and hydroxy-functional (meth)acrylates is EBECRYL 210-5129 from UCB Chemicals. Urethane(meth)acrylates increase flexibility, ultimate tensile strength, and tensile strain at break in a reactive resin without any major temperature dependency. This has surprisingly been found to have two types of effect on the trafficway marking: The resistance of the marking to temperature changes increases and, particularly surprisingly, it is possible to achieve compensation for the dis-
advantages of a relatively high degree of crosslinking resulting from the relatively high content of crosslinking agent in relation to embrittlement and adhesion to the trafficway surface, or even to make improvements in comparison with cold plastics of the prior art. For this, the concentration of the urethane(meth)acrylates in the reactive resin has to be relatively high for trafficway markings. The reactive resin of the invention comprises from 5% by weight to 30% by weight, preferably from 10% by weight to 20% by weight, of the urethane(meth)acrylates described.

[0069] The monomers present in the reactive resin involve compounds selected from the group of the (meth)acrylates, such as alkyl(meth)acrylates of straight-chain, branched, or cycloaliphatic alcohols having from 1 to 40 carbon atoms, for example methyl(meth)acrylate, ethyl(meth)acrylate, n-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, stearyl(meth)acrylate, lauryl(meth)acrylate; ary(meth)acrylates, for example benzyl(meth)acrylate; mono(meth)acrylates of ethers, of polyethylene glycols, or of propylene glycols, or mixtures thereof of having from 5 to 80 carbon atoms, examples being tetrahydro-furfuryl(meth)acrylate, methoxy(meth)acrylate, benzyl(meth)acrylate, 1-ethoxybutyl(meth)acrylate, 1-ethoxyethyl(meth)acrylate, ethoxyethyl(meth)acrylate, poly(ethylene glycol) methyl ether(meth)acrylate, and poly(propylene glycol) methyl ether(meth)acrylate.

[0070] Other suitable constituents of monomer mixtures are additional monomers having a further functional group, for example, &beta;-unsaturated mono- or dicarboxylic acids, e.g. acrylic acid, methacrylic acid, or itaconic acid; esters of acrylic acid or methacrylic acid with dihydric alcohols, for example hydroxyethyl(meth)acrylate or hydroxypropyl(meth)acrylate; acrylamide and methacrylamide; or dimethylaminomethyl(meth)acrylates. Other suitable constituents of monomer mixtures are by way of example glycidyl(meth)acrylate and silyl-functional (meth)acrylates.

[0071] The monomer mixtures can also comprise, alongside the (meth)acrylates described above, other unsaturated monomers which are copolymerizable with the above-mentioned (meth)acrylates and by means of free-radical polymerization. Among these are inter alia 1-alkenes or styrenes.

[0072] The detailed selection of the proportion and composition of the poly(meth)acrylate will advantageously depend on the desired technical function.

[0073] The monomer content of the reactive resin here is from 20% by weight to 85% by weight, preferably from 30% by weight to 40% by weight.

[0074] Systems known as MO-PO systems comprise not only the monomers listed but also polymers, preferably polyesters or poly(meth)acrylates, and for the purposes of this patent the term prepolymer is used for these in order that they are more clearly distinguishable. These polymers are used to improve polymerization properties, mechanical properties, adhesion to the substrate, and also the optical requirements placed upon the resins. The prepolymer content of the reactive resin here is from 10% by weight to 30% by weight, preferably from 15% by weight to 25% by weight. The polyesters, and also the poly(meth)acrylates, can have additional functional groups to promote adhesion or for copolymerization in the crosslinking reaction, for example taking the form of double bonds. However, it is preferable with a view to better colorfastness of the trafficway marking that the prepolymer have no double bonds.

[0075] Said poly(meth)acrylates are generally composed of the monomers already listed in relation to the monomers in the resin system. They can be obtained by solution polymerization, emulsion polymerization, suspension polymerization, bulk polymerization, or precipitation polymerization, and are added in the form of pure substance to the system.

[0076] Said polyesters are obtained in bulk via polycondensation or ring-opening polymerization, and are composed of the units known for these applications.

[0077] Chain-transfer agents, plasticizers, paraffins, stabilizers, inhibitors, waxes, and/or oils can also be used as auxiliaries and additives.

[0078] The paraffins are added in order to prevent inhibition of the polymerization by the oxygen in air. To this end, it is possible to use a plurality of paraffins with different melting points, in different concentrations.

[0079] Chain-transfer agents that can be used are any of the compounds known from free-radical polymerization. It is preferable to use mercaptans, such as N-dodecyl mercaptan.

[0080] Plasticizers used are preferably esters, polyols, oils, or low-molecular-weight polyethers, or phthalates.

[0081] Dyes, glass beads, fine and coarse fillers, wetting agents, dispersing agents, and flow control agents, UV stabilizers, anti-foams, and rheology additives can also be added to the formulations for trafficway markings. Preferred auxiliaries and additives added for the field of application of the formulations as trafficway marking or surface marking are dyes. Particular preference is given to white, red, blue, green and yellow inorganic pigments, and white pigments such as titanium dioxide are particularly preferred.

[0082] Glass beads are preferably used as reflectors in formulations for trafficway markings and surface markings. The commercially available glass beads used have diameters of from 10 μm to 2000 μm, preferably from 50 μm to 800 μm. The glass beads can be provided with a coupling agent in order to facilitate operations and improve adhesion. The glass beads can preferably be silanized.

[0083] One or more mineral fillers having fine particles and fillers having coarse particles can moreover be added to the formulation. These materials also serve to reduce slip, and are therefore in particular used to improve grip, and for additional coloring of the trafficway marking. Fillers used having fine particles are selected from the group of the calcium carbonates, barium sulfates, powdered and other quartzes, precipitated and fumed silicas, pigments, and cristobalites, and also corundum. Fillers used having coarse particles are quartzes, cristobalites, corundums, and aluminum silicates.

[0084] It is also possible to use conventional UV stabilizers. It is preferable that the UV stabilizers are selected from the group of the benzophenone derivatives, benozatriazole derivatives, thioxanthone derivatives, piperidinocarboxylic ester derivatives, or cinnamic ester derivatives.

[0085] From the group of the stabilizers and inhibitors, it is preferable to use substituted phenols, hydroquinone derivatives, phosphines, and phosphites.

[0086] The following components can optionally also be present in formulations for trafficway marking:

[0087] wetting agents, dispersing agents, and flow-control agents are preferably selected from the group of the alcohols, hydrocarbons, glycol derivatives, polyethers, polysiloxanes, polycarboxylic acids, saturated and unsaturated polycarboxylic aminoamides, and derivatives of glycolic esters, of acetic esters, and of polysiloxanes.
Preferred rheology additives used are polyhydroxy-carboxamides, urea derivatives, salts of unsaturated carboxylic esters, alklylammonium salts of acidic phosphoric acid derivatives, ketoximes, amine salts of p-toluenesulfonic acid, amine salts of sulfonic acid derivatives, and also aqueous or organic solutions or mixtures of the compounds. Rheology additives based on fumed or precipitated, optionally also silanized, silicas with BET surface area of from 10 to 700 m²/g have been found to be particularly suitable.

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.

These elements of freedom of formulation show that the reactive resin of the invention and the sprayable or other cold plastic of the invention, comprising the reactive resin, is precisely equivalent to any established sprayable or other cold plastic of the prior art in its capability for formulation and for use of additives. Abrasion resistance, lifetime, whiteness, pigmentation, and grip capability are thus at least as good as in systems of the prior art. Surprisingly, however, it has been found that lifetime and adhesion, based on the particular mechanical properties explained, and on the additional adhesion-promoting properties of the urethane(meth)acrylates, are actually better than described in the prior art.

The shelf life of the reactive resin is also at least comparable with the prior art.

The system can also be optimized in relation to the substrate to be coated, by means of selection of suitable monomers, prepolymer, and/or adhesion promoters. The systems of the invention can accordingly be variably optimized for the marking of asphalt surfaces, concrete surfaces, or natural stone surfaces.

Use of the Reactive Resins or Sprayable or Other Cold Plastics

The systems of the invention are also versatile in relation to application technology. The reactive resins or cold plastics of the invention can by way of example be applied either by spraying, by pouring, or else by extrusion, or manually by means of a trowel, a roller, or a doctor system.

The individual components of the cold plastic, for example the reactive resin of the invention, can be mixed before, after, or during further operations, e.g. application on a trafficway surface. An established method is incorporation by mixing before further operations, but a factor requiring attention here is that only a limited amount of open time, e.g. 2 or 40 min, remains for the application process once mixing to incorporate the hardener component has been carried out.

Mixing during operations can be carried out by way of example in modern marking machines which have a mixing chamber preceding the application nozzle.

Mixing to incorporate the hardener after the application process can be achieved by way of example through a subsequent application, using two or more nozzles, or through application of glass beads coated with hardener. As an alternative, a primer comprising the hardener component can be sprayed in advance before the sprayable or other cold plastic is applied.

It is preferable that the reactive resins of the invention and the cold plastics produced therefrom are used for the production of trafficway markings with long lifetime.

In particular, the reactive resins and cold plastics are used in a process in which glass beads are added before, during, or directly after the application of the cold plastic on a trafficway surface.

As an alternative, the reactive resins and/or cold plastics of the invention can also be used in other technical fields. Examples of these are floorcoverings, preferably for industrial applications, production of cast parts, sealing of bridges or joints thereof, in particular in the form of vapor-barrier membrane, bridge coating generally, vapor-barrier membrane on roofs, production of sheets, e.g. for subsequent use as worktop, drainage-system resin, crack-filling, for example in buildings, and use in the orthopedic sector.

The examples given below are provided for further illustration of the present invention, but do not restrict the invention to the features disclosed therein.

EXAMPLES

The production of the test specimens and the measurement of tensile strength, of modulus of elasticity, of tensile strain at yield, of yield stress, and of tensile strain at break were carried out as in ISO 527.

The core-shell-shell particles used are composed of 23% by weight of core, 47% by weight of shell 1, and 30% by weight of shell 2.

The core here has the following constitution:

95.5% by weight of methyl methacrylate, 4% by weight of ethyl acrylate, 0.5% by weight of allyl methacrylate.

Shell 1 has the following constitution:

81% by weight of n-butyl acrylate, 17.5% by weight of styrene, 1.5% by weight of allyl methacrylate.

Shell 2 has the following constitution:

96.5% by weight of methyl methacrylate, 4% by weight of ethyl acrylate, 0.5% by weight of n-dodecyl mercaptan.

Example 1

0.05 part of topanol-O, 15 parts of Degacryl M339 (Evonik Röhm GmbH), 10 parts of core-shell-shell particles, and 0.5 part of paraffin were intimately mixed with 63 parts of methyl methacrylate and 5 parts of triethylene glycol dimethacrylate and heated, with vigorous stirring, to 63°C until all of the polymer constituents had been dissolved or dispersed. For curing, 1 part of benzoyl peroxide (50% by weight formulation in dioctyl phthalate) and 1.9 parts of N,N-diisopropylamine were added and incorporated by stirring for 1 minute at room temperature (21°C). For hardening, the composition was poured onto a metal sheet, and test specimens were produced in accordance with DIN 50125.

Pot life: 11 min; curing time: 22 min; flow time (8 mm): 74 sec.

Example 2

0.05 part of topanol-O, 13 parts of Degacryl M339, 9 parts of core-shell-shell particles, and 0.5 part of paraffin were intimately mixed with 63 parts of methyl methacrylate and 5 parts of butyl diglycol dimethacrylate and heated, with vigorous stirring, to 63°C until all of the polymer constituents had been dissolved or dispersed. For curing, 1 part of benzoyl peroxide (50% by weight formulation in dioctyl...
Phthalate) and 2 parts of N,N-diisopropoxytoluidine were added and incorporated by stirring for 1 minute at room temperature (21°C).

**Example 3**

0.05 part of topanol-O, 25 parts of Degalan LP 66/02, and 0.5 part of paraffin were intimately mixed with 63 parts of methyl methacrylate and 5 parts of triethylene glycol dimethacrylate and heated, with vigorous stirring, to 63°C. until all of the polymer constituents had been dissolved or dispersed. For curing, 1 part of benzoyl peroxide (50% by weight formulation in dioctyl phthalate) and 2.5 parts of N,N-diisopropoxytoluidine were added and incorporated by stirring for 1 minute at room temperature (21°C). For hardening, the composition was poured onto a metal sheet, and test specimens were produced in accordance with DIN 50125.

**Example 4**

0.05 part of topanol-O, 22 parts of Degalan LP 64/12 and 0.5 part of paraffin were intimately mixed with 63 parts of methyl methacrylate and 5 parts of butyl diglycol dimethacrylate and heated, with vigorous stirring, to 63°C. until all of the polymer constituents had been dissolved or dispersed. For curing, 1 part of benzoyl peroxide (50% by weight formulation in dioctyl phthalate) and 2 parts of N,N-diisopropoxytoluidine were added and incorporated by stirring for 1 minute at room temperature (21°C). For hardening, the composition was poured onto a metal sheet, and test specimens were produced in accordance with DIN 50125.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>43.7 MPa</td>
<td>50.6 MPa</td>
<td>41.8 MPa</td>
<td>52.7 MPa</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>2181 MPa</td>
<td>2488 MPa</td>
<td>2731 MPa</td>
<td>2630 MPa</td>
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<tr>
<td>Tensile strain at yield</td>
<td>3.9%</td>
<td>3.9%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Yield strength</td>
<td>43.8 MPa</td>
<td>50.8 MPa</td>
<td>0 MPa</td>
<td>0 MPa</td>
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<tr>
<td>Tensile strain at break</td>
<td>5.1%</td>
<td>6.7%</td>
<td>1.8%</td>
<td>3.1%</td>
</tr>
</tbody>
</table>

**Example 5**

0.05 part of topanol-O, 15 parts of ZK 50, and 0.5 part of paraffin were intimately mixed with 75 parts of methyl methacrylate and 5 parts of butyl diglycol dimethacrylate and heated, with vigorous stirring, to 63°C. until all of the polymer constituents had been dissolved or dispersed. For curing, 1 part of benzoyl peroxide (50% by weight formulation in dioctyl phthalate) and 2 parts of N,N-diisopropoxytoluidine were added and incorporated by stirring for 1 minute at room temperature (21°C). For hardening, the composition was poured onto a metal sheet, and test specimens were produced in accordance with DIN 50125.

**Example 6**

0.1 part of topanol-O, 8 parts of Degacryl M339, 8 parts of core-shell-shell particles, and 1.5 parts of paraffin were intimately mixed with 162 parts of methyl methacrylate and 7 parts of butyl diglycol dimethacrylate and heated, with vigorous stirring, to 63°C. until all of the polymer constituents had been dissolved or dispersed. For curing, 1.5 parts of benzoyl peroxide (50% by weight formulation in dioctyl phthalate) and 2.5 parts of N,N-diisopropoxytoluidine were added and incorporated by stirring for 1 minute at room temperature (21°C). For hardening, the composition was poured onto a metal sheet, and test specimens were produced in accordance with DIN 50125.

**Example 7**

0.1 part of topanol-O, 26 parts of Degalan LP 66/02, and 1.5 parts of paraffin were intimately mixed with 162 parts of methyl methacrylate and 7 parts of butyl diglycol dimethacrylate and heated, with vigorous stirring, to 63°C. until all of the polymer constituents had been dissolved or dispersed. For curing, 1.5 parts of benzoyl peroxide (50% by weight formulation in dioctyl phthalate) and 2.5 parts of N,N-diisopropoxytoluidine were added and incorporated by stirring for 1 minute at room temperature (21°C). For hardening, the composition was poured onto a metal sheet, and test specimens were produced in accordance with DIN 50125.

**Measurement**

<table>
<thead>
<tr>
<th></th>
<th>Example 6</th>
<th>Example 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>39.8 MPa</td>
<td>58.5 MPa</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>2265 MPa</td>
<td>2471 MPa</td>
</tr>
<tr>
<td>Tensile strain at break</td>
<td>3.2%</td>
<td>5.5%</td>
</tr>
</tbody>
</table>

1. A (meth)acrylate-based reactive resin, comprising: a crosslinking agent; a monomer; a polymer; and an impact modifier.

2. The (meth)acrylate-based reactive resin of claim 1, comprising: a core-shell particle as the impact modifier.

3. The (meth)acrylate-based reactive resin of claim 2, comprising:

   from 0.5% to 30% by weight of the crosslinking agent, from 20% to 85% by weight of the monomer, from 0% to 20% by weight of a urethane(meth)acrylate, from 3% to 40% by weight of a prepolymer, from 0% to 5% by weight of an accelerator, from 1% to 25% by weight of the core-shell particle, and optionally an auxiliary.
4. The (meth)acrylate-based reactive resin of claim 3, comprising:
from 20% to 30% by weight of a dimethacrylate,
from 50% to 40% by weight of a (meth)acrylate, a component copolymerizable with a (meth)acrylate or a combination thereof,
from 0% to 20% by weight of the urethane(meth)acrylate,
from 15% to 25% by weight of a poly(meth)acrylate,
from 0% to 5% by weight of an amine,
from 1% to 15% by weight of a core-shell particle comprising a polymethacrylate, and
optionally an auxiliary,
wherein the (meth)acrylate-based reactive resin is halogen-free.
5. The (meth)acrylate-based reactive resin of claim 1,
wherein the core-shell particle comprises a particle comprising poly(meth)acrylate, with a core and at least one shell,
the core, the at least one shell, or a combination thereof has a glass transition temperature above 70°C, and
the core, the at least one shell, or a combination thereof which does not have a glass transition temperature above 70°C has a glass transition temperature below −10°C.
6. The (meth)acrylate-based reactive resin of claim 5,
wherein the core, the at least one shell, or a combination thereof has been crosslinked.
7. The reactive (meth)acrylate-based resin of claim 5,
wherein a diameter of the core-shell particle is from 25 nm to 1000 nm.
8. The (meth)acrylate-based reactive resin of claim 1,
wherein a core-shell particle is added together with a prepolymer in a form of a molding composition to the (meth)acrylate-based reactive resin, and the molding composition comprises from 20 to 80% by weight of the prepolymer and from 20 to 80% by weight of the core-shell particle.
9. The (meth)acrylate-based reactive resin of claim 8,
wherein the molding composition comprises from 1 to 80% by weight of the prepolymer and from 20 to 99% by weight of the core-shell particle.
10. A cold plastic, comprising:
from 1% to 5% by weight of a mixture comprising an initiator,
from 7% to 15% by weight of an inorganic pigment, and
from 50% to 60% by weight of a metal filler.
11. The cold plastic of claim 17,
wherein the peroxide comprises dilauroyl peroxide, dibenzoyl peroxide or a combination thereof, and
an amine comprises a tertiary, aromatically substituted amine.
12. The cold plastic according to claim 17,
wherein the peroxide is a constituent of the (meth)acrylate-based reactive resin, and
an accelerator is not a constituent of the (meth)acrylate-based reactive resin, but instead is a separate component of the cold plastic.
13. A method for producing a long-life trafficway marking, comprising:
producing the long-life trafficway marking with the (meth)acrylate-based reactive resin of claim 1.
14. A method for producing a cast part, for sealing or coating a bridge or a roof, for producing a sheet, in a drainage-system resin, for crack-filling, or for utilize in an orthopedic sector, the method comprising:
producing the cast part, sealing or coating the bridge or the roof, producing the sheet, in the drainage-system resin, crack-filling, or utilizing in the orthopedic sector with the (meth)acrylate-based reactive resin.
15. A method for producing a long-life trafficway marking, comprising:
producing the long-life trafficway marking with the cold plastic of claim 10.
16. The method of claim 15,
wherein a glass bead is added to a surface of the trafficway marking before, during, or directly after application of the cold plastic.
17. The cold plastic of claim 10, wherein the mixture is peroxide.
18. The cold plastic of claim 11, the inorganic pigment is titanium dioxide.