

Intumescent coating having improved low-temperature flexibility

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Field of the invention

10 The present invention relates to a novel reaction system for intumescent coating. Intumescent coatings are used in particular for fire protection of metallic building components, such as girders in building construction. In the event of a fire, such coatings undergo reactive foaming that results in the formation on the metal girder of a fireproof insulating layer having low thermal conductivity and that – through the insulation that this creates – retards any early, thermal-induced failure of said building component.

15 The present invention relates in particular to resin systems having improved low-temperature flexibility that ensure good metal adhesion and impact resistance even at low temperatures while avoiding the polymer components that are otherwise customary in resin systems.

20 Prior art

A first generation of intumescent coating systems was based on high-molecular-weight thermoplastic resins based on (meth)acrylates and/or vinyl monomers and needed a high content of solvent or water for application to metal surfaces. Because of the high solvent content, with aqueous systems also having been described, these systems require correspondingly long drying times.

It is customary for intumescent coatings to be applied on site during the construction phase. Off-site application prior to delivery to the construction site would however be preferable, since this can take place under controlled conditions. However, slow drying means an uneconomical, inefficient processing time. The long processing times are of particular importance here, since the resin must be applied from different sides one after the other and each side dried in order to obtain a complete coating.

35 Epoxy-based intumescent coatings are used mainly in the off-shore industry. They have the characteristic feature of good ageing resistance and relatively short drying times. Polyurethane systems have also been intensively investigated. They likewise have the characteristic feature of a relatively short drying time and good water resistance. However, the results of fire tests were unsatisfactory, since the coating has poor adhesion to steel. Details thereof can be found in Development of alternative technologies for off-site applied intumescent, Longdon, P.J., European Commission, [Report] EUR (2005), EUR 21216, 1-141.

A further generation of intumescent coatings is based on (meth)acrylate reactive resins. The application thereof has the great advantage that no solvent is required here; once applied, the resin does however cure relatively rapidly. This gives rise not only to more swift processing, but also to a lower content of residual volatile constituents in the applied coating. Such intumescent coating systems were disclosed for the first time in EP 1 636 318.

A further improvement in the (meth)acrylate-based systems was disclosed for example in EP 2 171 004. This has the characteristic feature of a particularly high content of acid groups to improve metal adhesion.

EP 2 171 005 discloses a further development of a system of this kind. This has the particular characteristic feature of copolymerization of diacids or copolymerizable acids having a spacer group. This can additionally improve metal adhesion.

All of these systems are however in need of further improvement. For example, there is very little freedom as regards formulation options. Also, only relatively thick layers can be applied. The combined effect of these disadvantages means also, for example, that the foam height in the event of need or fire can be preset only to a minimal extent.

In addition, disadvantages can also arise from the relatively complex production process of the resins. What all otherwise very advantageous (meth)acrylate systems described in the prior art have in common is that the solid thermoplastic polymer present in the resin is here produced only separately, then dissolved in the monomer components and preformulated with additives before finally undergoing final formulation shortly before application as a 2C system. This process chain is relatively complicated and there is great interest in making it simpler.

The European patent application having filing reference number 20162308.9 discloses resin systems produced by means of a novel process. In this process, a monomer mixture is polymerized to a maximum degree of polymerization of 70%. The glass transition temperature of the methacrylate-based polymeric component formed thereby is -20°C to 23°C and is thus significantly lower than that described in the abovementioned prior art. Despite this, the low-temperature flexibility of these systems remains limited, especially when using exclusively (meth)acrylate polymer components.

Object

The object of the present invention was, with regard to the prior art, to provide a reactive resin system that is particularly flexible at low temperatures for the production of (meth)acrylate-based intumescent coatings that have improved impact resistance and can be applied off-site.

There was a need here for a simplified production process for a reactive resin system for intumescent coatings in which, by comparison with the prior art, the introduction of a solid (meth)acrylate polymer component, which is energetically costly, can be dispensed with.

A further object was to provide a novel formulation for a 2C intumescent coating that, in addition to very good metal adhesion and easy processibility, additionally permits freedom as regards additivation and the adjustment of subsequent foaming control, particularly as regards the presetting of subsequent foam heights and foam quality, for example a particularly high fraction of closed-pore foam.

Further objects that are not mentioned explicitly may become apparent hereinbelow from the description or the examples, or from the overall context of the invention.

Achievement of objects

These objects are achieved by a novel intumescent formulation and a reactive resin system for such intumescent formulations and by the coatings produced therewith. In particular, the invention relates to liquid, foamable intumescent formulation that comprise a resin system, said resin system being characterized in that it comprises at least one first polymer having an average molecular weight M_n of between 1500 and 35 000 g/mol and a glass transition temperature of less than 15°C, at least one vinylic monomer, and at least one component that acts as a blowing agent at a temperature of above 200°C. A coating produced from said intumescent formulations is curable by polymerization. In addition, the intumescent formulations of the invention is characterized in that, prior to initiation of said polymerization, this comprises no component having an acid function and at the same time a molecular weight of greater than 1500 g/mol.

This first polymer preferably has a functionality that is copolymerizable with vinylic monomers. By means of this functionality, the polymer chain is, during curing of the reactive resin, incorporated into the vinylic polymer chain formed during the polymerization. The first polymer may here also contain more than one of said copolymerizable vinylic functionalities per chain. The chains here preferably contain more than 2, particularly preferably more than 2.1, and especially preferably more than 2.3, of said functionalities per chain. The greater the proportion of said functionalities per chain, the higher the degree of crosslinking in the cured intumescent coating, which, if a high

degree of crosslinking is present, increases the hardness in particular. The brittleness of the coating can also increase as the degree of crosslinking rises, but this can be countered by a suitable choice of polymers and of monomers in particular.

- 5 The first polymer is particularly preferably a liquid urethane (meth)acrylate, a liquid epoxy (meth)acrylate, a liquid polyether (meth)acrylate, a liquid polyester (meth)acrylate or mixtures thereof. It is particularly preferably a liquid urethane (meth)acrylate. A commercially available example of a urethane acrylate produced from polyols, isocyanates, and hydroxy-functional acrylates is EBECRYL 230 from Allnex.

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It is possible to use commercial liquid polymers and mixtures thereof with (meth)acrylate-based reactive diluents, for example methyl methacrylate.

- Alternatively, the liquid polymers can be prepared for example by reacting isocyanates with hydroxyalkyl (meth)acrylates and macromolecular polyols in a first step, for example in a stirred-tank reactor, before further components of the reactive resin are in a second step mixed in. This approach can be described as an in-situ process.

- The term "liquid polymer" is in accordance with the invention understood as meaning a polymer having an average molecular weight M_n of between 1000 and 35 000 g/mol, preferably between 1500 and 20 000 g/mol, more preferably between 1500 and 10 000 g/mol. In addition, this liquid polymer has a glass transition temperature of less than 15°C, preferably less than 10°C, more preferably less than 0°C.

- Liquid polymer does not in this context necessarily mean thin or even free-flowing. Rather, it is preferable that this first polymer present in the reactive resin of the intumescent formulation has a dynamic viscosity at room temperature of 23°C, determined in accordance with DIN EN ISO 2555 using a rotational viscometer (Brookfield DV2T), of less than 250 000 mPa·s, preferably less than 100 000 mPa·s.

- In accordance with the invention, when selecting the liquid polymers care must be taken to ensure they impart sufficient low-temperature flexibility to the reactive resin system. Particular preference is therefore given to using urethane (meth)acrylates. The liquid polymers should therefore have a glass transition temperature (T_g) of from -80°C to 15°C, preferably from -70°C to 0°C, and more preferably from -60°C to -20°C. It is preferable that the liquid polymer has an average of two or more (meth)acrylate groups in one molecule. If the number of groups is less than 2, the coating would have poor physical mechanical properties, but also solvent resistance and scratch resistance.

- The vinylic monomers in the resin system are in turn preferably a (meth)acrylate and/or a mixture of different (meth)acrylates and/or monomers copolymerizable with (meth)acrylates. Examples of such copolymerizable monomers are styrene, itaconic acid or maleic acid.

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The vinylic monomers are particularly preferably (methyl) methacrylate, (ethyl) methacrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, styrene or a combination of one or more of said monomers.

- 5 The (meth)acrylate monomers may for example be, in particular, alkyl (meth)acrylates of straight-chain, branched or cycloaliphatic alcohols having 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; aryl (meth)acrylates, for example benzyl (meth)acrylate; mono(meth)acrylates of ethers, polyethylene glycols, polypropylene glycols or mixtures thereof
- 10 having 5 to 80 carbon atoms, such as tetrahydrofurfuryl (meth)acrylate, methoxy(m)ethoxyethyl (meth)acrylate, benzyloxymethyl (meth)acrylate, 1-ethoxybutyl (meth)acrylate, 1-ethoxyethyl (meth)acrylate, ethoxymethyl (meth)acrylate, poly(ethylene glycol) methyl ether (meth)acrylate, and poly(propylene glycol) methyl ether (meth)acrylate. Suitable as constituents of monomer mixtures are also additional monomers having a further functional group, such as esters of acrylic acid or
- 15 methacrylic acid with dihydric alcohols, for example hydroxyethyl (meth)acrylate or hydroxypropyl (meth)acrylate; acrylamide or methacrylamide; or dimethylaminoethyl (meth)acrylate. Examples of further suitable constituents of monomer mixtures are glycidyl (meth)acrylate or silyl-functional (meth)acrylates.
- 20 Adhesion promoters that are very preferably present in the intumescent composition are silane-functional (meth)acrylates such as 3-methacryloxypropyltrimethoxysilane, silane-functional vinyl compounds such as vinyltrimethoxysilane, or preferably acid-functional monomers such as acrylic acid, methacrylic acid, 2-methacryloyloxyethyl phosphate, bis(2-methacryloyloxyethyl) phosphate, 2-acryloyloxyethyl phosphate, bis(2-acryloyloxyethyl) phosphate, 2-methacryloyloxethyl maleate,
- 25 acryloyloxethyl maleate, itaconic acid and/or 2-carboxyethyl acrylate, particularly preferably 2-carboxyethyl acrylate. Other examples, depending on the composition, include maleic acid, for which the presence of styrene in the monomer mixture is absolutely essential for the copolymerization. Preference is given to using from 0.2% by weight to 10% by weight, more preferably from 0.4% by weight to 4% by weight, of adhesion promoter in the resin composition.
- 30 In addition, combinations of two or more of these adhesion promoters are also possible.

Methyl methacrylate is, on account of its ability to produce low-viscosity solutions, the particularly preferred methacrylic acid ester. However, its high volatility and characteristic odor can mean that

35 alternative (meth)acrylic acid esters may be preferable for certain uses.

The intumescent formulation preferably contains between 20% and 60% by weight of the resin system. Likewise preferably, said resin system in the intumescent formulation contains between 5% and 65% by weight, preferably between 20% and 55% by weight, of the first liquid polymer

and/or between 30% and 90% by weight, preferably between 40% and 75% by weight, of vinylic monomers.

Irrespective of the composition of the reactive resin, the intumescent formulation preferably
5 contains between 35% and 60% by weight, more preferably between 40% and 50% by weight, of blowing agent.

For the blowing agents, there are various alternatives. In a particularly preferred alternative, polyphosphates may be used, which at 190 to 300°C are converted into phosphoric acid. The formulation additionally includes pentaerythritol, which above 300°C in the presence of the
10 phosphoric acid then forms a carbon foam with the elimination of water and carbon dioxide. In this process, water and carbon dioxide act as blowing agents. An additional advantage of this alternative is that both the polyphosphates and the phosphoric acid act as additional flame retardants.

A second alternative uses melamine, which above 350°C decomposes to ammonia, nitrogen and
15 carbon dioxide, with all three of these acting as blowing agents. A combination of these two alternatives makes it possible to additionally achieve further benefits besides a flame retardant action. In this way, it is possible to fine-tune the degree of foaming. Moreover, foaming takes place gradually, which is in turn advantageous in respect of foam stability.

The reactive resin is produced in a simple manner by mixing the abovementioned liquid
20 components, typically in stirred-tank reactors in a batch mixing process.

Exemplary formulations of the invention can be summarized as follows:

Such a formulation for 2C intumescent coating may, at a point in time after mixing the 2C system, contain 30% to 50% by weight of the reactive resin produced by the process of the invention, 35%
25 to 60% by weight of a blowing agent, 0.1% to 2.5% by weight of a peroxide and/or azo initiator, preferably only peroxides such as for example benzoyl peroxide, optionally up to 2% by weight of an accelerator, optionally 4.9% to 15% by weight of additives and 5% to 30% by weight of fillers. Optionally, the formulation can include additional pigments.

30 The initiator system generally consists of one or more peroxides and/or azo initiators, preferably a peroxide, and of an accelerator, generally one or more tertiary amines, especially an aromatic tertiary amine. A particularly suitable example of such an initiator is dibenzoyl peroxide, which can be used for example also in the form of a safe, preformulated paste in which the auxiliaries contained in said paste, for example paraffins, do not in the employed concentrations interfere with
35 the formulation. Examples of accelerators include in particular N,N-dialkyl para-toluidines, for example N,N-bis(2-hydroxypropyl)-para-toluidine or N,N-dimethyl-para-toluidine or N,N-dimethylaniline.

Besides the constituents mentioned, the intumescent compositions or the reactive resin contained
40 therein may include further optional constituents.

An optional constituent of the reactive resin is monomeric crosslinkers. In particular, polyfunctional (meth)acrylates such as allyl (meth)acrylate. Particular preference is given to di- or tri(meth)acrylates such as butane-1,4-diol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate or trimethylolpropane tri(meth)acrylate. These monomeric crosslinkers may be present alongside crosslinking liquid polymers as described above.

Additives that may be optionally present in the intumescent composition or already present in the reactive resin include in particular wetting agents, film formers, deaeration reagents and/or dispersing agents. Optional fillers may for example be silica, titanium dioxide, quartz or other, in particular thermally stable, inorganic compounds. Inorganic fillers such as carbonates that can undergo thermal decomposition may be used only to a more minor extent, in order to avoid uncontrolled additional foaming of the coating in the event of fire. A particularly preferred filler is titanium dioxide.

The accelerators optionally used for faster curing as cold plastic are usually tertiary aromatic amines.

Besides the novel intumescent formulation, a process for curing this liquid foaming intumescent formulation also forms part of the present invention.

In this process of the invention, an initiator or a component of an initiator system is added to the intumescent formulation and the formulation is applied to a substrate within 20 min and cured within a further 120 min after application.

In an alternative process of the invention, the curing coating composition is a 2C system. Here, the two part-compositions of the 2C system are mixed together, then applied to a substrate within 20 min and cured within a further 120 min after application.

The formulation of the actual coating composition in this second alternative can take place as follows: the reactive resin is formulated with the blowing agents, additives, optional fillers and further optional fillers. Such intermediate formulations are then split into two fractions that are for example equal in size. One of these fractions is then additionally mixed with the accelerator. These two fractions are subsequently storage-stable even for long periods.

Before the actual application, the accelerator-free fraction is then mixed with the initiator or initiator mixture. After a long period of storage or transport, it may first be necessary to stir both fractions again, since fillers, for example, may have settled. After stirring in or otherwise mixing in the initiator, the two fractions of the 2C system are then mixed together. This starts the polymerization

of the monomeric constituents of the reactive resin, this being the start of the so-called pot life within which the application to the substrate, for example to a steel girder, must take place. With modern application devices, the mixing of the two fractions of the 2C system can also take place in a mixing chamber of an application nozzle immediately before pressure-indicated spraying. The pot life derives from a combination of nature and concentration of the initiator and accelerator, the monomer composition and external influencing factors, for example the ambient temperature. These factors can be easily estimated and adjusted by those skilled in the art. Working with pot lives of several minutes to several hours is generally customary; these can also exceed the 20-hour mark. Preference is however given to significantly shorter pot lives that match the preferred process times given above. Such a pot life would be, for example, between 3 and 30 min, with pot lives of less than 10 minutes possible with fully automated application using spray machines.

In one of the two alternatives of the process, it is preferable that the initiator, a component of the initiator system or a constituent in a component of a 2C system is an organic peroxide. This organic peroxide is particularly preferably a diacyl peroxide, a ketone peroxide, a peroxyester, a dialkyl peroxide, a hydroperoxide such as cumene hydroperoxide, a peroxyketal or a combination thereof.

In addition, as already stated, the present invention provides a process for the intumescent coating of a metal surface. In this process, the above-described formulation for the 2C intumescent coating is prepared, applied to the metal surface within 1 to 20 minutes and cured thereon at a temperature of between 0 and 30°C, preferably between 17 and 23°C, within a period of 120 min, preferably within 60 min. The preferred layer thickness of the unfoamed coating is 1 to 20 mm, preferably 2.5 to 7.5 mm. This would be formulated such that, in the event of a fire, the coating would preferably result in the foam having a layer thickness of 20 to 100 mm, preferably 30 to 50 mm.

The total loss of weight by evaporation in the intumescent formulation during mixing, application to the substrate, and curing is particularly preferably less than 5% by weight. This can be ensured by a correspondingly suitable formulation, especially with regard to the selection of the monomers in the reactive resin.

Examples

Example 1: Production according to the invention of a reactive resin

DEGADUR MDP Membran SG is a methacrylate-based, accelerator-free reactive resin commercially available from Röhm GmbH that comprises urethane methacrylates for flexibility.

DEGADUR MDP Membran SG does not contain any solid polymeric components.

To 970.0 g of DEGADUR MDP Membran SG was added 20.0 g of 2-carboxyethyl acrylate and 10.0 g of N,N-bis(2-hydroxypropyl)-para-toluidine and the mixture was stirred at 50°C until completely dissolved. The reactive resin was then cooled to room temperature.

5 Example 2: Inventive formulation 1 of an intumescent coating

Composition of formulation 1 from example 2

Reactive resin from example 1	40.0% by weight
Titanium dioxide	10.0% by weight
Ammonium polyphosphate	30.0% by weight
Pentaerythritol	8.5% by weight
Melamine	11.0% by weight
Byk D410	0.5% by weight

10 It is understood that the embodiment described above is exemplary only. Many modifications or variations are possible.

Comparative example 1: Noninventive formulation 2 of an intumescent coating

DEGALAN 1710 is a commercially available meth(acrylate)-based reactive resin produced by R hm GmbH having a solid (glass transition temperature > 50 C) thermoplastic polymer component.

Composition of formulation 2 from example 3

DEGALAN 1710	40.0% by weight
Titanium dioxide	10.0% by weight
Ammonium polyphosphate	30.0% by weight
Pentaerythritol	8.5% by weight
Melamine	11.0% by weight
Byk D410	0.5% by weight

Properties of the intumescent coatings

Determination of pot life and curing time:

Immediately before application, 1 part by weight of Perkadox GB50-X (50% dibenzoyl peroxide powder, Nouryon) was mixed into 99 parts by weight of each of the above example formulations.

The formulations were then each applied in a layer thickness of 3000  m to steel plates. The pot life and the maximum temperature during curing were additionally measured on a smaller portion of the sample. The pot life corresponds to the length of time after addition of the initiator during which the viscosity is still low enough for application of the coating to be possible.

	Inventive example formulation 1	Noninventive formulation 2
Pot life	10 min	16 min
Time until maximum temperature	14 min	34 min
Maximum temperature	84�C	70�C
Time until tack-free curing	19 min	43 min

Determination of low-temperature flexibility

Immediately before application, 1 part by weight of Perkadox GB50-X (50% dibenzoyl peroxide powder, Nouryon) was mixed into 99 parts by weight of each of the above example formulations. The formulations were then each applied in a layer thickness of 1000  m to sheet steel with a thickness of 1 mm.

Once curing was complete, the plates were cooled to -20 C and the coated steel sheets were at this temperature bent through 90  over a right-angled edge. The coating at the bending point was then examined for cracks and flaking.

	Inventive example formulation 1	Noninventive formulation 2
Low-temperature flexibility of the coating at -20°C	No flaking or cracks visible.	The coating shows clear cracks and flaking.

In the bending test at -20°C, example formulation 1 of the invention shows significantly improved low-temperature flexibility compared to noninventive formulation 2 of the prior art.

Claims

1. A liquid, foamable intumescent formulation comprising a resin system, characterized in that
5 the resin system comprises at least one first polymer having an average molecular weight M_n of between 1000 and 35 000 g/mol and a glass transition temperature of less than 15°C, at least one vinylic monomer, and at least one component that acts as a blowing agent at a temperature of above 200°C, wherein a coating produced from the intumescent formulation is curable by polymerization and, prior to initiation of said polymerization,
10 comprises no component having an acid function and at the same time a molecular weight of greater than 1500 g/mol.
2. The intumescent formulation as claimed in claim 1, characterized in that the first polymer
15 has a dynamic viscosity of less than 250 000 mPa·s and a functionality that is copolymerizable with vinylic monomers.
3. The intumescent formulation as claimed in claim 2, characterized in that the first polymer is
20 a liquid urethane (meth)acrylate, a liquid epoxy (meth)acrylate, a liquid polyether (meth)acrylate, a liquid polyester (meth)acrylate or mixtures thereof, preferably a liquid urethane (meth)acrylate.
4. The intumescent formulation as claimed in at least one of claims 1 to 3, characterized in
25 that the vinylic monomers in the resin system are a (meth)acrylate and/or a mixture of different (meth)acrylates and/or monomers copolymerizable with (meth)acrylates.
5. The intumescent formulation as claimed in claim 4, characterized in that the vinylic
30 monomers are selected from (methyl) methacrylate, (ethyl) methacrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, styrene, and combinations of said monomers.
6. The intumescent formulation as claimed in at least one of claims 1 to 5, characterized in
that the intumescent formulation contains between 20% by weight and 60% by weight of resin system.
7. The intumescent formulation as claimed in at least one of claims 1 to 6, characterized in
35 that the resin system contains between 5% and 65% by weight of the first liquid polymer.
8. The intumescent formulation as claimed in at least one of claims 1 to 7, characterized in
40 that the resin system contains between 30% and 90% by weight of vinylic monomers.

9. The intumescent formulation as claimed in at least one of claims 1 to 8, characterized in that the intumescent formulation contains between 35% by weight and 60% by weight of blowing agent.
- 5 10. A process for curing a liquid foaming intumescent formulation as claimed in any of claims 1 to 9, characterized in that an initiator or a component of an initiator system is added to the intumescent formulation or that the curing coating composition is a 2C system and the two part-compositions of the 2C system are mixed together, then applied to a substrate within 20 min and cured within a further 120 min.
- 10 11. The process as claimed in claim 10, characterized in that the initiator, a component of the initiator system or a constituent in a component of a 2C system is an organic peroxide.
- 15 12. The process as claimed in claim 11, characterized in that the organic peroxide is a diacyl peroxide, a ketone peroxide, a peroxyester, a dialkyl peroxide, a hydroperoxide such as cumene hydroperoxide, a peroxyketal or a combination thereof.
- 20 13. The process as claimed in at least one of claims 10 to 12, characterized in that the intumescent formulation is cured in less than 60 minutes at a temperature of between 17°C and 23°C.
14. The process as claimed in claim 13, characterized in that the total loss of weight by evaporation in the intumescent formulation during mixing, application to the substrate, and curing is less than 5% by weight.