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Kaksikomponenttinen aerosoliformulaatio

Tvåkomponentaerosolformulering

A two-component aerosol formulation

(57) Tiivistelmä - Sammandrag - Abstract

Esillä olevan keksinnön kohteena on kaksikomponenttinen aerosoliformulaatio käytettäväksi yksikammioisessa aerosolitölkissä, joka sisältää pinnoitteita muodostavia kemikaaleja käsittäen vähintään yhtä epoksihartsia, vähintään yhtä kovetusaineen esiaistetta pinnoitteita muodostavina kemikaaleina ja vähintään yhtä ponneainetta, jolloin ainakin osalla heikkoa hoppoa on dissosiaatiovakion pKa-arvo vaihteluväillä 1,2–5,2. Esillä olevan keksinnön kohteena on lisäksi kyseisen formulauksen valmistaminen ja formulauksen sisältävä aerosolitölki.

The present invention relates to a two-component aerosol formulation suitable for use in a single chamber aerosol can containing coating forming chemicals comprising at least one epoxy resin, at least one hardener precursor as coating forming chemicals, and at least one propellant, and least a portion of a weak acid having the dissociation constant pKa value in the range from 1.2 to 5.2. The present invention further relates to preparation of the formulation and to an aerosol can containing the formulation.

A two-component aerosol formulation

Field of the invention

The present invention relates to a stable two-component aerosol formulation
5 for aerosol cans.

Background art

A variety of aerosol formulations for aerosol paint and adhesive cans have
been known for years. One-component aerosol paint and adhesive formula-
10 tions have been the most important ones, but two-component systems have
been gaining more importance in the last few years.

The one-component aerosol formulations are suitable for use in conventional
aerosol cans, that is, in aerosol cans having one chamber. The two-component
aerosol formulations are suitable for aerosol cans having two chambers.

15 Two-component aerosol systems comprise a binder, a curing component such
as hardener or cross-linking component, a propellant and optionally a solvent
in an aerosol can. The binder and the hardener are typically packed in sepa-
rate chambers in the aerosol can. These types of aerosol cans are also re-
ferred to as "can in a can" cans or "2-chamber" cans. Just before using the can
20 one of the chambers is punctured so that the binder and the hardener are
brought into contact with each other inside the can. Reaction between the
binder and hardener starts immediately when they are contacted in the can
and the aerosol formulation is ready to be used for spraying.

25 Polyurethane system is one example of a two-component aerosol paint sys-
tem. The two-component polyurethane aerosol formulation comprises a binder
component, a hydroxyl group containing acrylate or polyester resin, and a
polyisocyanate as curing component in a separate chamber. Aerosol paint
cans of this type are employed to apply primers, undercoats, finishing coats,
etc., primarily for vehicles such as passenger cars, trucks, busses, railroads,
30 and containers.

EP 1125997 B1 discloses an aerosol formulation for two-component aerosol paint cans. The paint material, which consists of acrylic resins containing hydroxyl groups, and the hardener, which consists of aliphatic polyisocyanates are filled in two separate chambers within an aerosol can and united only immediately prior to their application. The components are jointly sprayed from the aerosol can via propellant gas consisting of a propane/butane mixture.

An epoxy system is another example of a two-component aerosol paint and adhesive system. The epoxy system comprises an epoxy parent compound as binder and usually an amine as hardener. The two-component epoxy systems are used, additionally to automotive purposes, for general industrial and household industrial purposes, for building sector, machinery construction industry etc. For example, EP 1427767 B1 discloses a two-component aerosol paint can with an epoxy paint system especially suited for repair purposes. The aerosol paint can contains an aerosol formulation based on two-component epoxy technology comprising (i) a parent epoxy resin, (ii) a solvent mixture, (iii) a propellant gas, and (iv) an epoxy curing agent in a separate chamber to be used as hardening constituent for the parent epoxy resin.

In the known two-component aerosol paint and adhesive systems the binder and the hardener are placed in separate chambers within an aerosol can so that reaction between the binder and hardener is not possible. As soon as the binder and hardener are brought into contact by puncturing one of the chambers, hardening reaction starts immediately. The aerosol paint or adhesive should be used entirely at once because the hardening reaction starts already inside the can. Shelf life of such two-component aerosol paint and adhesive systems is limited to maximum of 2-3 days. Additionally, the 2-chamber aerosol cans are complicated and expensive to manufacture.

Solutions utilizing one compartment i.e. single chamber cans are available, as well. In these systems the individual reactive components are in latent form before taking the can into use. For example, the abstract of JP2004035947 discloses a two component aerosol formulation for an aerosol can. The formulation comprises an epoxy resin such as bisphenol A type, an imine as hardener precursor and a propellant. The drawback and challenge in this type of solution is typically the presence of moisture in the aerosol formulation causing premature hardening already in the can. Therefore, zero ambient moisture for the precursors and the packaging ambient is a key requirement.

The abstract of WO2014057764 discloses an aerosol formulation for a one chamber aerosol can comprising a binder such as urethane resin and a latent hardener such as imine for the resin. The formulation hardens in contact with atmospheric moisture.

5 The abstract of JP2002249544 discloses a one-pack moisture-curable epoxy resin and an imine as hardener precursor for a formulation having excellent storage stability. The preparation of the formulation and precursor handling of the imine requires moisture free conditions obtained by use of nitrogen atmosphere and specifically predried precursors. Similarly, the formulation hardens
10 immediately when contacted with atmospheric moisture.

There is a need for a two-component aerosol paint, coating and adhesive system that has long shelf life, is simple to manufacture and use, and possibly re-use, and does not harder prematurely due to ambient moisture.

15 **Summary of the invention**

The object of the present invention is to provide a two-component aerosol formulation, such as paint and adhesive system, that has good stability and long shelf life.

20 A further object of the present invention is to provide a two-component aerosol formulation for use in a single chamber can which is simple to manufacture.

Yet, a further object of the present invention is to provide a two-component aerosol formulation for use in a can which is stable for a long time period enabling successful reuse after initial first usage anytime within at least a year.

25 The present invention provides a two-component aerosol formulation for use in an aerosol can as depicted by claim 1 and said can as depicted by claim 18.

The present invention further provides a method for preparing the stable two-component aerosol formulation as depicted by claim 14.

30 It has been found by the inventors that a stable two-component aerosol formulation i.e. epoxy paint or adhesive formulation, can be prepared and packed into a conventional aerosol can having one single chamber. All components of

the formulation can be placed within a common single chamber aerosol can without the components essentially reacting with each other.

The formulation may even be prepared under ambient conditions without any particular need for predrying the precursors or operating under inert gas, such 5 as nitrogen, atmosphere while preparing the formulation or filling the can. Even technical grade or industrial quality precursors may be used providing a portion of water into the formulation and inside the can.

By using at least one epoxy resin as binder and at least one hardener precursor and a small amount of a weak acid it is possible to make a stable mixture 10 of the components without a chemical reaction taking place between the components. The components may contain minor amounts of water originating from the transport, preparation or handling of the chemicals and containers.

The stable mixture of the epoxy resin and the hardener precursor and the weak acid, together with at least one propellant, is packed as an aerosol formulation into a conventional one-chamber aerosol can. As the two-component aerosol formulation is sprayed from the can, a cloud of fine particles suspended in gas or air is formed picking up water (moisture) from the air. The absorbance of water will have an effect on the hardener precursor, such as imine, 15 enamine, aldimine and/or Mannich base compound. When the water content is high enough it reacts with the hardener precursor forming an amine compound. The formed amine compound will act as a hardener and reacts in turn with the epoxy resin creating the final product, the two-component paint or adhesive layer or coating on a substrate.

As the reaction between the amine compound and the epoxy resin occurs outside 25 of the aerosol can, the formulation inside the can stays stable. No additional moisture from the air gets inside the can, because pressure inside the can is greater than the pressure outside of the can.

As the formulation stays stable inside the can, only a desired portion of the two-component aerosol formulation may be used at a time. That is, the whole 30 formulation does not have to be used at once, since the formulation remains stable inside the can. Shelf life of the can containing the formulation is at least a year, possibly up to 3 years or even more. Moreover, an aerosol can containing the formulation is easier and faster to use, because there is no need to first

separately mix the hardener and the binder as is the case with known solutions.

The preparation of the formulation and can containing the formulation is essentially simplified as no protection gas or predrying steps are necessary. The

5 manufacturing can take place in ambient conditions using regular mixing and can filling techniques.

Detailed description

In the present invention by hardener is meant a chemical capable of acting as

10 a hardener for an epoxy resin such as an amine that is formed when the hardener precursor such as imine, enamine, aldimine and/or Mannich base reacts with water. The hardener of the present invention is able to react with the epoxy resin used for providing the desired coating layers i.e. paint or adhesive.

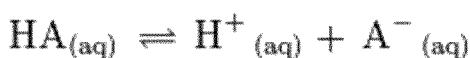
In the present invention by hardener precursor is meant a chemical capable of

15 forming a hardener i.e. containing the suitable amine produced by a chemical reaction.

By ambient is meant the typical environmental conditions, temperature, pressure and humidity, prevailing at the point of preparation of the formulation at regular industrial surroundings.

20 In the present invention by a weak acid is meant an acid that dissociates incompletely, releasing only some of its hydrogen atoms into the solution. Thus, it is less capable than a strong acid of donating protons. Weak acids ionize in water solution only to a moderate extent. If the weak acid is represented by the general formula HA, then in an aqueous solution a significant amount of undissociated HA still remains. Weak acids dissociate in water in the following way:

25



The strength of a weak acid may be represented by an equilibrium constant or percentage of dissociation. The equilibrium concentrations of reactants and products are related by the acid dissociation constant, K_a :

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The greater the value of K_a , the more the formation of H^+ is favored, and the lower the pH of the solution. The K_a of weak acids typically varies between 1.8×10^{-16} and 55.5. For many practical purposes it is more convenient to discuss using the logarithmic constant, pK_a

$$pK_a = -\log_{10} K_a$$

A weak acid typically has a pK_a value within the approximate range from -2 to 12 in water.

In one aspect, the present invention provides a two-component aerosol formulation suitable for use in an aerosol can, such as in a single chamber aerosol can. Naturally, also multiple chamber cans can be used, but eventually the components are brought into contact with each other once taking the can into use.

More particularly, the present invention provides a two-component aerosol formulation containing coating forming chemicals comprising at least one epoxy resin and at least one hardener precursor, and at least one propellant. The formulation further contains at least a portion of a weak acid having the dissociation constant pK_a value in the range from 1.2 to 5.2.

In one embodiment the weak acid is selected from those having the dissociation constant pK_a value within the range from 3 to 5, for efficiently maintaining the equilibrium of the formulation at the hardener precursor's side.

In another embodiment the weak acid is selected from those having the dissociation constant pK_a value within the range from 4.2 to 4.9 for optimized stability in storage and performance in use.

Naturally, the type of weak acid has a further influence on the formulation properties, as well as the amount of weak acid used.

In the formulation of the present invention, the epoxy resin does not substantially react with other components of the aerosol formulation when in a mixture inside the can i.e. with the hardener precursor and with the weak acid.

In one embodiment, the epoxy resin is selected from the group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, novolac epoxy resin, aliphatic epoxy resin, glycidylamine epoxy resin, and mixtures thereof.

In one embodiment, the epoxy resin is bisphenol A epoxy resin. The bisphenol 5 A epoxy resins are formed from reacting epichlorohydrin with bisphenol A. For example, the simplest bisphenol A epoxy resin is formed from reacting two moles of epichlorohydrin with one mole of bisphenol A to form bisphenol A di-glycidyl ether (DGEBA). Increasing the ratio of bisphenol A to epichlorohydrin during manufacture produces higher molecular weight polyethers with epoxide 10 groups (also referred to as glycidyl groups). This binder is particularly suitable for regular conditions. It has good water resistance and chemical resistance, and it provides flexible coatings.

In one embodiment, the epoxy resin is bisphenol F epoxy resin. The bisphenol F epoxy resins are formed from reacting epichlorohydrin with bisphenol F in 15 similar way to bisphenol A. This binder has better chemical resistance compared to bisphenol A epoxy resins, especially at low and high pH ranges.

In one embodiment, the epoxy resin is novolac epoxy resin. The novolac epoxy resins are formed from reacting phenols with formaldehyde and subsequent glycidylation with epichlorohydrin. Examples of particularly suitable novolac epoxy resins are epoxy phenol novolacs (EPN) and epoxy cresol novolacs (ECN). These provide high chemical resistance together with a high temperature resistance. The formed films are less flexible when the epoxy group content is increased.

In one embodiment, the epoxy resin is aliphatic epoxy resin. The aliphatic 25 epoxy resins comprise glycidyl epoxy resins and cycloaliphatic epoxides. These materials may act as dilutants, as well. They are preferably applied as auxiliary resins to the above discussed primary resins.

In one embodiment, the epoxy resin is glycidyl epoxy resin. The glycidyl epoxy resins are formed by reaction of epichlorohydrin with aliphatic alcohols or polyols to give glycidyl ethers or aliphatic carboxylic acids to give glycidyl esters. Examples of preferred glycidyl epoxy resins are dodecanol glycidyl ether, di-glycidyl ester of hexahydrophthalic acid, and trimethylolpropane triglycidyl 30 ether. The purpose of these chemicals is to provide a reactive dilutant for its low viscosity. Preferably, they are used in combination with the primary resins

as auxiliary binders to balance the reaction taking place. Typically, their reaction rate is clearly lower to the primary resins.

In one embodiment, the epoxy resin is cycloaliphatic epoxide. The cycloaliphatic epoxides contain at least one cycloaliphatic ring in the molecule to which an oxirane ring is fused. The cycloaliphatic epoxides are formed by reaction of cyclo-olefins with a peracid, such as peracetic acid. An example of preferred cycloaliphatic epoxide is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate. The purpose of these chemicals is to provide a reactive dilutant for its low viscosity. The reaction rate is lower to the primary resins.

10 In one embodiment, the epoxy resin is glycidylamine epoxy resin. The glycidylamine epoxy resins are formed when aromatic amines are reacted with epichlorohydrin. Examples of preferred glycidylamine epoxy resins are triglycidyl-p-aminophenol and N,N,N,N-tetraglycidyl-4,4-methylenebis benzylamine. These provide a very high temperature resistant coating and very high reactivity, as there are as many epoxy groups in the chain.

In one embodiment a combination of selected different types of primary and auxiliary resins, and optional solvents, is used to ensure linear and steady evaporation of the solvents, and to enhance the forming of the coating and exhibiting desired properties.

20 A wide range of different epoxy resins, such as the ones mentioned above, are produced industrially and are commercially available.

The epoxide content is a characteristic feature of the epoxy resins. The epoxide content is commonly expressed as epoxide number, which is the number of epoxide equivalents in 1 kg of resin (Eq./kg), or as the equivalent weight, 25 which is the weight in grams of resin containing 1 mole equivalent of epoxide (g/mol). One measure may be converted to another with formula:

$$\text{Equivalent Weight (g/mol)} = 1000 / \text{epoxide number (Eq./kg)}$$

30 Preferably, the epoxy resin of the present invention is selected from a group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, epoxy phenol novolacs (EPN), epoxy cresol novolacs (ECN), dodecanol glycidyl ether, di-glycidyl ester of hexahydrophthalic acid, trimethylolpropane triglycidyl ether, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, triglycidyl-p-

aminophenol, N,N,N,N-tetraglycidyl-4,4-methylenebis benzylamine, or mixtures thereof. More preferably, the epoxy resin of the present invention is selected from bisphenol A epoxy resin or bisphenol F epoxy resin. The characteristics of these two types of binders are the most suitable for the aimed products. They 5 further enable the use of reactive dilutants of high temperature resistant type.

In one embodiment, the epoxy resin has an Equivalent Weight from 100 to 1500 g/eq, preferably from 120 to 700 g/eq, and more preferably from 450 to 500 g/eq.

10 In another embodiment the epoxy resin is an epoxy with an epoxy group content of 2000- 2220 mmol/kg and an epoxy molar mass of 450-500 g/Eq.

In one embodiment the amount of epoxy by weight of the formulation is from 18 to 30 %. Preferably, the amount of epoxy by weight of the formulation is from 15 % to 30 %. Most preferably, the amount of epoxy by weight of the formulation is from 15 to 23 %

15 The aerosol formulation of the present invention comprises at least one hardener precursor which is preferably selected from the group consisting of an imine, an enamine, a Mannich base, aldimine and mixtures thereof.

The imine which is also referred to as Schiff base, enamine, aldimine and Mannich base do not substantially react with the epoxy resin as such, when no 20 water is present, for example inside a dry aerosol can atmosphere. As soon as the imine, enamine, aldimine and/or Mannich base are in contact with water, the water reacts with the hardener precursor, and as a result of this reaction an amine reactant is formed. Subsequently, the formed amine compound functions as hardener and reacts with the epoxy resin providing the coating.

25 When the two-component aerosol formulation of the present invention is sprayed from an aerosol can, a cloud of particles suspended in gas or air is formed effectively picking up moisture from the air due to large surface area. The moisture or water will react with the hardener precursor of the formulation forming the amine compound. The formed amine compound reacts further with 30 the epoxy resin. This reaction is also referred to as curing reaction. And, finally a coating or adhesive layer is formed on a substrate on which the formulation is sprayed.

Figure 1 presents, as an example, the reversible reaction of an imine with water resulting in an amine and a ketone:

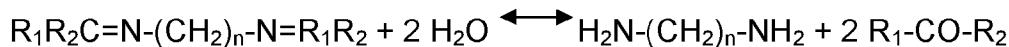


Figure 1.

5 Figure 2 presents, as an example, the reversible reaction of an enamine with water resulting in an amine and a ketone:

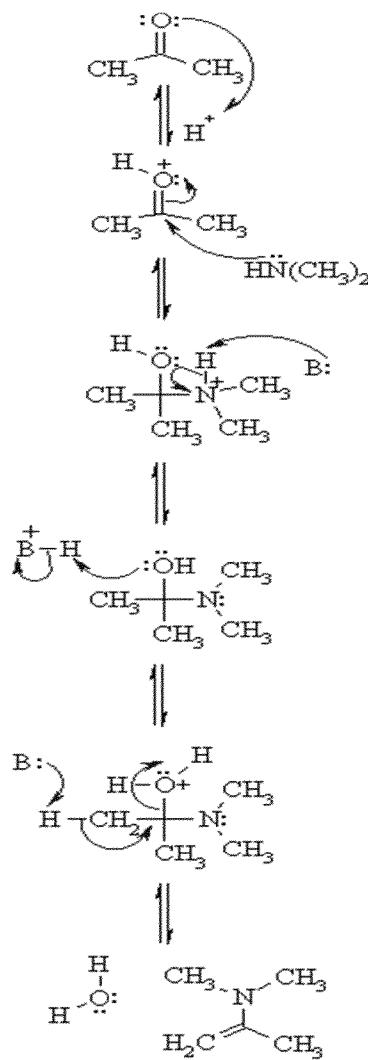


Figure 2.

10 Mannich reaction is an organic reaction which consists of an amino alkylation of an acidic proton placed next to a carbonyl functional group by formaldehyde and a primary or secondary amine or ammonia. The final product is a β -amino-carbonyl compound also known as a Mannich base. Reactions between al-

dimines and α -methylene carbonyls are also considered Mannich reactions because these imines form between amines and aldehydes.

The Mannich reaction is an example of nucleophilic addition of an amine to a carbonyl group followed by dehydration to the Schiff base.

5 Figure 3 presents, as an example, a reversible reaction of a Mannich base with water resulting in an amine and a ketone:

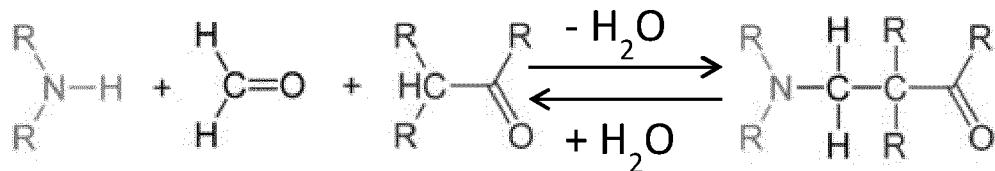


Figure 3.

10 In the present invention, the imine, enamine, aldimine and Mannich base are selected in a way that they react with water by forming an amine. Additionally, the imine, enamine, aldimine and Mannich base are selected in a way that they do not substantially react with the epoxy resin or other components inside an aerosol can.

In one embodiment, the formed amine is primary, secondary or tertiary amine.

15 In one embodiment, the formed amine is mono-, di- or polyfunctional amine.

In one embodiment, the formed amine is aliphatic, cycloaliphatic or aromatic amine.

20 Preferred amines are di- and polyfunctional primary amines. The di- and polyfunctional primary amines undergo a reaction with an epoxide group of the epoxy resin to form a hydroxyl group and a secondary amine. The secondary amine can further react with an epoxide group to form a tertiary amine and an additional hydroxyl group.

In one embodiment the imines are reaction products of ethylenediamine and methyl isobutyl ketone; diethyl ketone-based di-imine, preferably *N,N*-di(1-

25 ethylpropylidene)-*m*-xylylenediamine, or mixtures thereof. Ethylenediamine

and m-xylylenediamine are very good hardeners for epoxy coatings without side effects like Bernard cells and blushing. The solvent formed after hydrolysing the imine is compatible with the reaction product. The amine hydrogen equivalent weight (AHEW) values are in the dosage range of about 1:10 of binder.

In another embodiment enamine is a reaction product of 3,3,5-trimethylcyclohexanone with secondary diamines; a reaction product of isopheronediamine and methyl isobutyl ketone; N,N, bis(1,3-dimethylbutylidene)ethylenediamine. The diamines give a higher reactivity than monoamines and provide therefore a faster hardening that can lead to a harder film but less flexible film formation.

In one embodiment aldimine is any Schiff base of the general formula RCH—NH or RCH—NR' formed by condensation of an aldehyde with ammonia or a primary amine. Preferred aldimines are N-butyl-2-(1-ethylpentyl)-1,3-oxazolidine or 3-Oxazolidineethanol,2-(1-methylethyl)-,3,3-carbonate.

A wide range of imines and Mannich bases are commercially available. Also enamines and aldimines are commercially available. Suitable imines, enamines, aldimines and Mannich bases can also be synthesized with known procedures.

In one embodiment Mannich base is the reaction product between an aldehyde, such as formaldehyde, and a secondary amine, such as diethanol amine, in a weak acid environment dissolved in organic solvent, such as methyl ethyl ketone, as depicted by figure 4:

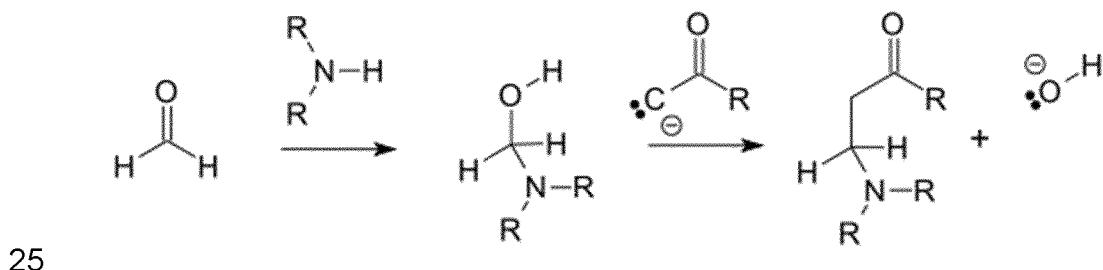


Figure 4.

In yet another embodiment the Mannich base is Ancamine 1110 (Airproducts) i.e. dimethylaminomethylphenol as active ingredient, as depicted by figure 5:

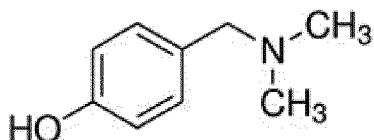


Figure 5.

5 In yet another embodiment the Mannich base is selected from D.E.H™ 613, D.E.H™ 614, D.E.H™ 615, D.E.H™ 618, D.E.H™ 619 and D.E.H™ 620, or mixtures thereof, available commercially from company DOW.

The weight ratio between the epoxy resin binder to the hardener precursor is based on the epoxy molar mass of the binder and the equivalent weight of the 10 hardener precursor, the amine content of the hardener precursor. The amount of hardener may vary +/- 10%.

In one embodiment weight ratio of the epoxy resin to hardener precursor is from 8:1 to 15:1, preferably from 9:1 to 12:1, more preferably from 10:1 to 11:1 when using the preferred resins and hardener precursors.

15 In one embodiment the epoxy resin is an epoxy binder with an epoxy molar mass of 450-500, and the hardener precursor is a reaction product of ethylenediamine and methyl isobutyl ketone.

The two-component aerosol formulation of the present invention may further comprise at least one solvent, sometimes also referred to as diluent. Function 20 of the solvent is to lower the viscosity of the epoxy resin and the hardener precursor. The solvent type and the amount of the solvent are selected in a way that the viscosity of the epoxy resin and the hardener precursor mixture is such that the mixture is viscous enough to be suitably sprayed with aid of the propellant from a regular aerosol can.

25 The solvent is preferably selected from a group consisting of ketones, acetates, glycol ethers, aromatic solvents, aliphatic solvents, or mixtures thereof. More preferably, the solvent is dimethyl ketone, methyl iso-butylketone, methyl ethyl ketone, xylene, 1-methoxy-2-propanol, di-propylene glycol methyl ether cyclohexanone, or mixtures thereof.

Viscosity of liquid phase of the formulation is preferably from 50 to 300 cSt, more preferably from 50 to 150 cSt, measured at 20°C and at atmospheric conditions. By the liquid phase is meant mixture of the epoxy resin and the hardener precursor, and optionally the solvent.

5 The propellant may be any suitable propellant known in the art. Preferably, the propellant is selected from a group consisting of dimethyl ether, propane, butane, isobutene, nitrogen, dinitrogen oxide, 1,1,1,2-tetrafluoroethane, or mixtures thereof. Most preferably, the propellant is dimethyl ether.

10 The two-component aerosol formulation may further comprise any additional suitable additives, such as colorants, color pigments and curing accelerators. Preferred colorants and color pigments are iron(II)oxide, iron(III)oxide, phthalo green, titanium(II)oxide and carbon black.

15 The epoxy resin, the imine, the enamine, the aldimine and the Mannich base, the solvent, the propellant and any additional additives typically need to be totally water free. In the present invention, due to the addition of a weak acid into the formulation, this requirement is not that strict. The precursors may suitably be water free but the formulation of the present invention tolerates a moderate amount of water present.

20 In one embodiment, the formulation further contains water. The amount of water is preferably less than 2500 ppm, more preferably less than 2000 ppm. In moist ambient the water content included into a formulation from surrounding atmosphere may be up to 250 ppm depending on the temperature and relative humidity. Whereas, the varying grade of precursors used may carry considerably more water into the formulation without using any pre-treatment, such as up to 2000 ppm.

25 It was found by the inventors that the reversible Mannich base hardener precursor reaction with water discussed above resulting in an amine and a ketone may be modified using an addition of a weak acid into the reaction mixture. When a weak acid, such as carboxylic acid or carbonyl acid is present, the reaction equilibrium is shifted towards the hardener precursor side as shown in figure 6:

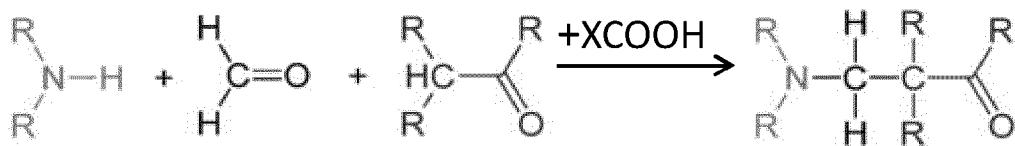


Figure 6.

Now the reaction balance favours the presence of the hardener precursor instead of the amine formation. By adjusting the amount, and type, of the weak acid to be added, the equilibrium of the amine formation reaction may be adjusted to favour the presence of the hardener precursor. The amount of weak acid depends on the pKa value of the acid.

5

When the amount of water increases considerably i.e. the ejected droplets of the formulation aerosol spray having a very small particle size, 75 -100 micrometer, are exposed to environmental conditions and subjected into contact with ambient humidity the equilibrium will eventually shift to favour the formation of the amine. Moreover, the evaporation of the weak acid will further favor the reaction towards the forming of the amine which will enhance the reaction with the epoxy groups of the binder.

10

15 Preferably, the weak acid is selected from the group consisting of carboxylic acids and carbonic acids.

In one embodiment the weak acid to be applied comprises formic acid (methanoic acid) HCOOH (pKa=3.8), acetic acid (ethanoic acid) CH₃COOH (pKa=4.7), propionic acid (propanoic acid) CH₃CH₂COOH (pKa=4.9), butyric acid (butanoic acid) CH₃CH₂CH₂COOH (pKa=4.8), valeric acid (pentanoic acid) CH₃CH₂CH₂CH₂COOH (pKa=4.8), caproic acid (hexanoic acid) CH₃CH₂CH₂CH₂CH₂COOH (pKa=4.9), oxalic acid (ethanedioic acid) (COOH)(COOH) (pKa=1.2), lactic acid (2-hydroxypropanoic acid) CH₃CHOHCOOH (pKa=3.9), malic acid (2-hydroxybutanedioic acid) (COOH)CH₂CHOH(COOH) (pKa=3.4), citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) CH₂(COOH)COH(COOH)CH₂(COOH) (pKa=3.1), benzoic acid (benzenecarboxylic acid or phenylmethanoic acid) C₆H₅COOH (pKa=4.2) or carbonic acid (hydroxymethanoic acid) OHCOOH or H₂CO₃ (pKa=3.6).

20

25

Preferably, the weak acid is acetic acid, benzoic acid, propionic acid or mixtures thereof, as these are the most efficient weak acids for the preferred hardener precursors of the present invention.

In one embodiment the weak acid is propionic acid, having a high pKa value.

5 In another embodiment the weak acid is acetic acid. Acetic acid has the advantage that it is a volatile liquid which readily evaporates when sprayed.

In yet another embodiment the weak acid is benzoic acid. This acid is a solid which facilitates the handling in preparation.

10 The amount of acid is dependent on the pKa value of the acid, the higher the pKa, the less acid is required.

15 Preferably, the amount of the weak acid to be added into the formulation of the present invention is from 0.1 to 10 % by weight (w/w) of the two-component aerosol formulation, preferably from 0.2 to 5.0 %, more preferably from 0.5 to 2.0 %. The amount of weak acid used depends on the type of acid, the pKa value, and the selected hardener precursor.

20 In one embodiment the formulation according to the present invention contains 8 - 45 %, preferably about 20 % by weight epoxy binder with an equivalent weight of 120-800, preferably 475, which is preferably a bisphenol epoxy binder; and 1.5 – 35 % by weight, preferably about 3.2 % by weight of the hardener, which is preferably the reaction product of isophoronediamine and methyl isobutyl ketone; and 10-30 % by weight, preferably about 18,3 % by weight solvent, which is preferably 1-methoxy-2-propanol; and 10-30 % by weight, preferably about 16.8 % by weight of additional solvent, which is preferably butanon-2; and 0.5-3 % by weight, preferably about 1.7% of the weak acid, which is preferably acetic acid; and 25-45 % by weight, preferably about 40 % by weight propellant, which is preferably dimethyl-ether. This composition is especially well suited as fuel, water and chemical resistant clear coat.

25 In a further aspect, the present invention provides a method for producing a two-component aerosol formulation as depicted above wherein the formulation is prepared under ambient conditions. The method further provides for increasing the storage stability and shelf life of a two-component aerosol formulation when stored in a single chamber aerosol can.

By ambient conditions is meant regular environmental conditions typically comprising water vapour the amount dependent on the temperature and humidity, and water originating from precursor chemicals.

Typically, the stability without the acid and when prepared at water-free conditions using water-free precursors is about a few weeks or months. And especially, if traces of water remain in the can the stability of the formulation decreases rapidly. The formulation of the present invention is stable at least over a year, with preferred choice of precursors at least up to 3 years. The can may be reused several times without any decrease in the storage stability.

10 Moreover, in the method of the present invention the preparation of the formulation may be performed under ambient conditions simplifying the manufacturing considerably as no protection gasses or drying agents need to be applied. No nitrogen atmosphere is necessary to avoid excess water contamination. In the preparation method according to the present invention merely a weakly acidic formulation is created by adding a suitable small amount of a weak acid thus preventing immediate reactions of the hardener precursors with moisture.

15 In one embodiment the formulation of the present invention is prepared by first mixing the coating forming chemicals comprising the epoxy resin and the hardener precursor, and the weak acid having the dissociation constant pK_a value in the range from 1.2 to 5.2. The obtained mixture is directed into a single chamber can. Subsequently, the propellant is introduced into the can, and the can is sealed, and ready for use.

20 In one embodiment, when the coating forming chemicals comprise an auxiliary resin or solvent, the weak acid is first dissolved into the solvent, auxiliary resin or mixture thereof, after which at least one resin builder i.e. primary resin is introduced into this mixture. Subsequently, at least one hardener precursor is introduced thereto.

25 In one embodiment, the solvents, if more than one, are first mixed together. Subsequently, the acid is introduced and mixed with the solvents. The primary, and optionally, the auxiliary resin builder(s) are introduced into the mixture, whereafter the hardener precursor(s) is introduced.

30 Preferably, after introducing all the compounds of the coating forming chemicals into the formulation, it is mixed for a short period, such as 15 min per 1000

I of formulation, prior to directing the mixture into cans and sealing the cans. Excess exposure to ambient should be avoided, if possible.

In a yet further aspect, the present invention provides an aerosol can containing the two-component aerosol formulation discussed above.

5 The mechanical vessel, the aerosol can, also referred to as a spray can or an aerosol spray can, may be any conventional aerosol can known in the art. Preferably, the aerosol can is a conventional aerosol can having one single chamber.

10 The aerosol can may be a 2-chamber aerosol can, commonly used for two-component aerosol formulations. In the 2-chamber aerosol can the hardener precursors are in one chamber and the epoxy resin in a separate chamber.

In the aerosol can having a single chamber all components of the formulation are in the same chamber. Examples of single chamber aerosol cans are straight-walled and necked-in cans.

15 Material of the aerosol can is metal based, for example, aerosol can is made of aluminium or tinplate.

Aerosol cans are commercially available in a diversity of diameters, heights, fill volumes, brim volumes and pressures. As for the shape, there is a wide range of variations available.

20 Special provisions apply for, especially metal, aerosol cans. These provisions are well known for a skilled person in the art. The special provisions define, for example, total capacities of aerosol cans, pressures of the aerosol cans, volume of liquid phase etc.

25 An example of such provision is, in Europe, "The Pressure Equipment Directive" (97/23/EC) together with: the directives related to simple pressure vessels (2009/105/EC), transportable pressure equipment (99/36/EC), and Aerosol Dispensers (75/324/EEC); for an adequate legislative framework on European level for equipment subject to a pressure hazard.

30 Aerosol cans are commercially available, for example from company G. Staehle GmbH u. Co. KG, Germany.

In one embodiment, the aerosol may additionally contain silica gel and/or molecular sieve filters to absorb excess water. The amount of the silica gel and/or molecular sieve filters is selected so that the silica gel and/or molecular sieve filters absorbs the excess water present in the formulation and in the can, and

5 thus prevents the water from reacting with the hardener precursor inside the can.

In one embodiment the aerosol may additionally contains one or several mixing balls, preferably two mixing balls, which enhance mixing of the two-component aerosol formulation when the can is shaken before spraying. The

10 mixing balls, also referred to as shaking balls or peas, are well known and commonly used in the art.

The two-component aerosol formulation of the present invention can be packed into an aerosol can with known procedures.

In one embodiment, first an epoxy resin, weak acid and solvent are mixed together. Optionally, color paste or other additives are added to the mixture and the mixing is continued. The hardener precursor is added to the mixture and mixing is continued. The obtained mixture is filled in a 1-chamber aerosol can with a liquid filling machine. Shaking balls may be added, a valve is put on the can and clinched on the can. The can is finally filled with a suitable amount of

15 liquefied propellant through the valve. An actuator is put on the valve, and the can is ready to be used. All these procedures may be performed under ambient conditions.

20

The valve may be any common aerosol can valve used in the art. Suitable aerosol can valves are commercially available, for example from company

25 Aptar GmbH, Germany.

The actuator may be any common actuator used in the art. Suitable actuators are commercially available. Example of such actuator is Aptar W2AX from company Aptar GmbH, Germany.

In addition to the weak acid application, the time between mixing and filling the

30 formulation into an aerosol should be kept as short as possible in order to avoid unnecessary water contamination.

In one embodiment the precursor chemicals are treated for removal of excess water prior to application into the formulation.

When the two-component aerosol formulation is sprayed from an aerosol can there should be a sufficient amount of water, such as humidity, present in the

5 surrounding environment for the hardener precursor to react efficiently with the water to form the amine.

Preferably, the temperature of the environment during the spraying should be such that the two-component aerosol formulation is viscous enough to be sprayed. More preferably, the temperature is from 10 to 50 °C, most preferably

10 from 15 to 35 °C, and even such as from 17 to 27°C.

In one embodiment the two-component aerosol formulation is used in under-water applications. The pressure inside the can is adjusted to overcome the ambient pressure. Preferably, water displacement additives are used to ensure sufficient contact of the paint spray to the surface to be coated.

15 The epoxy resin and/or formed amine combinations cure at ambient temperature. In one embodiment the curing is expedited by heating, with temperatures up to 75 °C.

Spray pattern, when the aerosol formulation is sprayed from an aerosol can, is a fine mist of aerosol droplets forming a film on sprayed surface. The spray pattern can be flat, such as fan spray, or round depending on the actuator.

20

In one embodiment, the spray will give a dry film of approx. 15-20 µm after 1 cross layer, with a hardness of persoz hardness at least 180 sec. The coating layer is dust dry after 15 min, touch dry after 30 min, and sufficient hardened after 24 h.

25 More particularly, there is provided use of the aerosol can as defined above for applying coatings and adhesives.

In one embodiment, the two-component aerosol formulation of the present invention and the method for preparation thereof is used for providing a clear coat.

30 In one embodiment the aerosol can is used for spraying primers, undercoats, finishing coats, varnishes, lacquers and adhesives, or any other coatings.

The aerosol can may be used to spray adhesives, primers, undercoats, finishing coats, varnishes, lacquers, or other coatings in any suitable applications, such as industrial, automotive, marine, construction industry and/or flooring applications.

5 The following non-limiting examples will further illustrate the present invention.

Examples

Example 1

A two-component aerosol formulation is prepared for production of approx. 625 aerosol cans with filling of 400 ml.

10 Formulation

Component 1: Epikote 1001-x-75 (epoxy resin in xylene); 113.7 kg; from company Momentive Specialty Chemicals, Netherlands.

15 Component 2: Epicure 3502 (hardener precursor: reaction product of ethylenediamine and methyl isobutyl ketone); 9.3 kg; from company Momentive Specialty Chemicals, Netherlands.

Component 3: Methyl ethyl ketone; 7.8 kg; from company Brenntag Nordic Oy, Finland.

Component 4: Xylene; 23.6 kg; from company Brenntag Nordic Oy, Finland.

20 Component 5: Dimethyl ether; added per can 96.6 g; from company Dupont de Nemours, Netherlands.

Component 6: acetic acid, 6.86 g; about 2% by weight; from Taminco

Mixing and filling

25 To a 200 l barrel were added components 1, 6, 3 and 4, in this order, under ambient conditions. The mixture was mixed with a normal mixer (not high shear) for less than 15 minutes. Component 2 was added to the mixture and it was mixed for further 15 minutes until the mixture was homogeneous and did not separate.

A three piece tinplate aerosol can (a 1-chamber aerosol can) without inner coating was used. Dimensions of the can were: diameter 65 mm; height 157

mm; 400 ml filling (520 ml brimful volume). Supplier for the can was G. Staehle GmbH u. Co. KG, Germany.

Two mixing balls were added to the can and the can was filled with 247.1 g of the prepared mixture containing components 1, 6, 3, 4 and 2 with a liquid filling machine.

An aerosol valve (commercially available from Aptar GmbH, Germany) was put on the can. Specifications of the valve were: Aptar: cup tinplate, stem 0.50 mm, housing 2.4 mm, VPH 0.45 mm, inner gasket: chlorbutyl, outer: gasket n-buna sh 85.

10 The valve was clinched on the can and the clinch was checked with clinch measurement equipment from company Kroepelin, Weith 27.2 mm, Depth 5.10 mm.

15 The closed can was filled with liquefied propellant dimethyl ether (component 5) 96.6 g. An actuator (Aptar W2AX from company Aptar) was put on the valve, after which the can filled with the formulation was ready for use.

Visual testing

One cross layer of the formulation was sprayed on a white metal paint card having a black stripe.

Observations:

20 The layer was dust dry in 18 minutes.

The layer was touch dry in 35 minutes.

Transparencies of clearcoat, Garder ASTM 1544 < 1.

No dripping after spraying one cross layer wet in wet.

Dry film thickness

25 Film thickness of one cross layer was measured after 1 h drying time. The film thickness was measured with BYKO-Test MPOR from company BYK. Thickness of the film was 45 - 50 micrometers.

Hardness

Hardness was measured after 10 h, 36 h, 61 h and 120 h. The hardness was measured with pendel hardness meter from company BYK. Units of hardness are König and Persoz.

5 Hardness was measured from dry film of 75 micrometers on a glass plate. In Table 1 is presented the results of the hardness measurements.

Table 1. Hardness measurements.

Measured after	Hardness	Unit
10H	49	König
10H	110	Persoz
36H	60	König
36H	160	Persoz
61H	85	König
61H	217	Persoz
120H	135	König
120H	325	Persoz

Adhesion test

10 Adhesion was measured after 36 h and 72 h. The adhesion was measured with PosiTTest AT-A (from company BYK) with 20 mm Doly size. The adhesion was measured from dry film of 75 microns.

Measured adhesion was > 450 psi.

Gloss

15 A conventional gloss meter applicable for paint that measures under an angle of 60° was used in gloss measurements. Used equipment was Erichsen Pico-gloss meter 560 MC.

Measured gloss was 96.

Reuse

After 2 years the can was reused. The formulation was fully operational and the spray result was the same as of the freshly produced can. Also the characteristics of the drying and the dry film were according the values of the tests 5 performed with the freshly produced can.

Reference Example

A formulation clear coat without the weak acid was produced in % w/w:

Density content: 0.861 g/ml 400 ml = 344.4 g

		%w/w	H ₂ O cont	H ₂ O /400 ml can
		H ₂ O%	in g	ppm
10	Binder epoxy	20	-	-
	Blocked hardener (ketamine)	2	-	-
	MethylEthylKeton	20	0.5%	0.3444
	Propylene glycol methyl ether	10	0.1%	0.0344
15	Aceton	13	0.5%	0.2239
	Dimethylether	35	0.05%	0.0603
		total 100	0.663 g	1925 ppm

20 The formed product had a shelf life of less than two weeks.

Example 2

A formulation clear coat with the weak acid was produced in % w/w, similarly to the reference example:

Density content: 0.861 g/ml 400 ml = 344.4 g

		%w/w		H ₂ O cont in gr	H ₂ O /400 ml can ppm
			H ₂ O%		
	Binder epoxy	20	-	-	
5	Blocked hardener (ketamine)	2	-	-	
	MethylEthylKeton	20	0.5%	0.3444	1000
	Propylene glycol methyl ether	10	0.1%	0.0344	100
	Acetic acid	1.7	-	-	-
	Aceton	13	0.5%	0.2239	650
10	Dimethylether	33.3	0.05%	0.0573	350
		total	100	0.6148 g	1916 ppm

15 The addition of 1.7 %w/w acetic acid did not influence the manufacturing and testing of the formulation. The can was aged 3 months in an oven at 45 °C. From previous experience it is well known that aging simulation can be used to accelerate the stability loss. Three months at 45 °C corresponds to a shelf life of 3 years or more at 25 °C.

Examples 3-8

20 The further formulations were made similarly to example 1 with the exceptions of the used component materials. Table 2 lists the tested chemicals and chemical compositions.

The manufacturing of the liquid phase and the filling of the aerosol can were made similarly to the description in Example 1.

25 The test results give the same results as discussed in example 1 within a margin of approximately 5 %. This represents an extraordinary high quality, prepared with an aerosol can that can be reused at any desired moment and has the shelf life of approximately 3 years.

Table 2.

	example 2	example 3	example 4	example 5	example 6	example 7	example 8
component 1:	bisphenol A epoxy resin	bisphenol A epoxy resin	novolac epoxy resin	bisphenol F epoxy resin	bisphenol A epoxy resin	bisphenol A epoxy resin	bisphenol F epoxy resin
component 2:	ethylenediamine and methyl isobutyl ketone	3,3,5-trimethylcyclohexanone with secondary diamine	N,N' Bis(dimethylbutylidene)ethylenediamine (curamine 33-672)	Isophoronediamine,MIBK reaction product (curamine 33-891)	N,N' Bis(dimethylbutylidene)ethylenediamine (curamine 33-672)	Isophoronediamine,MIBK reaction product curamine 33-891	3,3,5-trimethylcyclohexanone with secondary diamine
component 3:	Methylethyl ketone	Methylethyl ketone	Methylethyl ketone	Methylethyl ketone	Methylethyl ketone	Methylethyl ketone	Methylethyl ketone
component 4:	xylene	xylene	methyl isobutylketone	methyl isobutylketone	1-methoxy-2-propanol	1-methoxy-2-propanol	methyl isobutylketone
component 5:	Dimethyl ether	Dimethyl ether	Dimethyl ether	Dimethyl ether	Dimethyl ether	Dimethyl ether	Dimethyl ether
component 6:	acetic acid	propionic acid	Benzoic acid	acetic acid	Benzoic acid	Acetic acid	Benzoic acid

Claims

1. A two-component aerosol formulation suitable for use in a single chamber aerosol can containing coating forming chemicals comprising at least one epoxy resin, at least one hardener precursor as coating forming chemicals, and at least one propellant, **characterized** in that the formulation further contains at least a portion of a weak acid having the dissociation constant pKa value in the range from 1.2 to 5.2.
5
2. The formulation of claim 1, **characterized** in that the weak acid is selected from carboxylic acids and/or carbonic acids.
10
3. The formulation of claim 1 or 2, **characterized** in that the weak acid comprises formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, oxalic acid, lactic acid, malic acid, citric acid, benzoic acid, carbonic acid, or mixtures thereof.
15
4. The formulation of any one of claims 1-3, **characterized** in that the weak acid is comprises propionic acid, acetic acid, benzoic acid or mixtures thereof.
20
5. The formulation of any one of claims 1-4, **characterized** in that the amount of the weak acid is from 0.1 to 10 % by weight (w/w) of the two-component aerosol formulation, preferably from 0.2 to 5 %, more preferably from 0.5 to 2 %.
25
6. The formulation of any one of claims 1-5, **characterized** in that the hardener precursor is selected from the group consisting of an imine, an enamine, a Mannich base, aldimine and mixtures thereof.
7. The formulation of claim 6, **characterized** in that the imine is a reaction product of ethylenediamine and methyl isobutyl ketone; diethyl ketone-based di-imine, preferably *N,N'*-di(1-ethylpropylidene)-*m*-xylylenediamine; or mixtures thereof.
30

8. The formulation of claim 6, **characterized** in that the enamine is a reaction product of 3,3,5-trimethylcyclohexanone with secondary diamines; a reaction product of isophoronediamine and methyl isobutyl ketone; N,N, bis(1,3-dimethylbutylidene)ethylenediamine

5

9. The formulation of claim 6, **characterized** in that the Mannich base is dimethylaminomethylphenol.

10. The formulation of claim 6, **characterized** in that the aldimine is 3-oxazolidineethanol,2-(1-methylethyl)-,3,3-carbonate or N-butyl-2-(1-ethylpentyl)-1,3-oxazolidine.

15

11. The formulation of any one of claims 1-10, **characterized** in that the formulation further comprises at least one solvent.

20

12. The formulation of any one of claims 1-11, **characterized** in that the epoxy resin is selected from a group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, novolac epoxy resin, aliphatic epoxy resin, glycidylamine epoxy resin, or mixtures thereof.

25

13. The two-component aerosol formulation according to claims 1-12, **characterized** in that the formulation further contains water, preferably less than 2500 ppm, more preferably less than 2000 ppm.

30

14. A method for producing a two-component aerosol formulation according to any one of claim 1-14, **characterized** in that the formulation is prepared under ambient conditions.

15. The method of claim 14, **characterized** in that the formulation is prepared by mixing the coating forming chemicals comprising the epoxy resin and the hardener precursor, and the weak acid having the dissociation constant pKa value in the range from 1.2 to 5.2; and directing the obtained mixture into a single chamber can; and providing the propellant into the can; and sealing the can.

35

16. The method of claim 14, **characterized** in that the epoxy resin is mixed with the weak acid and optionally with a solvent, subsequently introducing the hardener precursor into the mixture.
- 5 17. The method of claim 15 or 16, **characterized** in that mixing time for the coating forming chemicals after the addition of the hardener precursor is less than 15 minutes per 1000 litres of the mixture.
- 10 18. An aerosol can containing the two-component aerosol formulation of any one of claims 1-13.

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SEARCH REPORT

PATENT APPLICATION No.		CLASSIFICATION	
20155933		IPC C09D 163/00 (2006.01) C09K 3/30 (2006.01) C08G 59/40 (2006.01)	CPC C09D 163/00 C09K 3/30 C08G 59/4014
PATENT CLASSES SEARCHED (classification systems and classes)			
IPC: C08G, C08L, C09D, C09J, C09K			
DATABASES CONSULTED DURING THE SEARCH			
EPO-Internal, WPI			

DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Bibliographic data on the document and relevant passages	Relevant to claims
D, Y	JP 2004035947 A (SHIKOKU RESEARCH INST INC) 05 February 2004 (05.02.2004) & abstract [online] EPOQUENET WPI & machine translation into English by EPO [online] EPOQUENET TXPJPEA, paragraph [0026]	1-18
Y	JP 2000038542 A (SHINTO PAINT CO LTD) 08 February 2000 (08.02.2000) & abstract [online] EPOQUENET WPI & machine translation into English by ThomsonReuters [online] EPOQUENET TXPJPOEA, paragraph [0016]	1-18
A	US 2004019161 A1 (ENDO TAKESHI [JP] et al.) 29 January 2004 (29.01.2004) paragraphs [0001], [0011]-[0012] and [0024]-[0027]	

Continued on the next sheet

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