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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,247,140**
(86) 1997/02/21
(87) 1997/09/04

(72) VOGDANIS, Lazaros, DE
(72) SCHMITZ, Arno, DE
(71) PPG INDUSTRIES, INC., US

(51) Int.Cl.^{6} C09D 163/00, C08J 3/09, C08L 63/00
(30) 1996/02/28 (196 07 435.5) DE

(54) **DISPERSION NON AQUEUSE STABILISEE STERIQUEMENT ET MATERIAU DE REVETEMENT A BASE DE CELLE-CI**

(54) **STERICALLY STABILIZED NON-AQUEOUS DISPERSION AND COATING MATERIAL MADE FROM IT**

(57) L'invention concerne un matériau de revêtement contenant a) une dispersion non aqueuse stabilisée stériquement produite par la réaction, dans un solvant organique en présence d'un stabilisant de dispersion, d'au moins une résine époxy (A) contenant une moyenne d'au moins deux groupes époxy par molécule avec au moins un diol (B) de la formule HOROH (I), dans laquelle R est un groupe de la formule -Ph-D-Ph- (II) où Ph- est un groupe phénylène et D un groupe méthylène ou propylène, et éventuellement avec un autre réactif (C) contenant des groupes réagissant avec des groupes époxy ou hydroxy, et b) au moins un agent de réticulation et, éventuellement, des solvants, des pigments, des charges et d'autres adjuvants et additifs, le diol (I) se présentant sous forme de dispersion non aqueuse stabilisée stériquement par un stabilisant renfermant de l'isoprène ou un composé dérivé de polyisoprène.

(57) The invention concerns a coating material containing: a) a sterically stabilized non-aqueous dispersion produced by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) containing an average of at least two epoxy groups per molecule with at least one diol (B) of the formula HOROH (I), in which R is a group of the formula -Ph-D-Ph- (II) in which Ph- is a phenylene group and D a methylene or propylene group, and optionally with a further reagent (C) containing groups which react with epoxy or hydroxy groups, and b) at least one cross-linking agent and, optionally, solvents, pigments, fillers and other auxiliaries and additives, the diol (I) being in the form of a non-aqueous dispersion which is sterically stabilized by a stabilizer containing isoprene or a compound derived from polyisoprene.

ABSTRACT

The invention concerns a coating material containing: a) a sterically stabilized non-aqueous dispersion produced by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) containing an average of at least two epoxy groups per molecule with at least one diol (B) of the formula HOROH (I), in which R is a group of the formula -Ph-D-Ph- (II) in which Ph- is a phenylene group and D a methylene or propylene group, and optionally with a further reagent (C) containing groups which react with epoxy or hydroxy groups, and b) at least one cross-linking agent and, optionally, solvents, pigments, fillers and other auxiliaries and additives, the diol (1) being in the form of a non-aqueous dispersion which is sterically stabilized by a stabilizer containing isoprene or a compound derived from polyisoprene.

Sterically stabilized nonaqueous dispersion, and coating composition based thereon

The present application relates to a sterically stabilized nonaqueous dispersion and to a coating composition based on this dispersion.

The present application also relates, in addition, to a process for preparing the said dispersion, for preparing the coating composition, and to its use for the coating of packaging containers.

In order to produce a can for use as packaging material, especially for the packaging of foodstuffs, sheet metal made from tinplate, chromated steel and aluminium in panel or strip form are coated. The coating acts as a protective layer in order, on the one hand, to protect the metal against attack by the contents, and resulting corrosion, and, on the other hand, to prevent the contents being influenced by corrosion products of the metal. Of course, the coating itself must not - for instance as a result of coating constituents that have leached out - impair or influence the contents in any way, neither in the course of the sterilization of the contents, which in the case of food packaging is carried out subsequent to filling, nor in the course of the subsequent storage of the packaged goods. In the case of technical packaging, the contents involved are often chemically reactive or aggressive, and the coats must likewise be resistant to such contents. Furthermore, the coatings must be of such a composition that they withstand the mechanical stresses which occur in the course of subsequent processing of the coated sheet metal to form the cans, for instance during forming, punching, flanging and crimping of the sheet metal.

Use is typically made of the so-called gold lacquers based on one or more epoxy resins and on one or more phenolic resins as interior protective coatings for sheet-metal packaging. A disadvantage with these customarily employed coating compositions, however, is the low solids content of in general from 30 to 40% by weight.

Furthermore, EP-A-321 088 discloses a process for preparing a sterically stabilized nonaqueous dispersion of a polyepoxide, in which polybutadiene is employed as dispersion stabilizer. A disadvantage of this process is the limited possibility of preparing dispersions having a defined composition. The possibility for incorporation of further resins requires improvement with this process. Moreover, various properties of the coatings produced using the dispersions are in need of improvement, for example flexibility, porosity and resistance to acidic test solutions such as, for example, 1% strength lactic acid or 3% strength acetic acid. Finally, the coat thicknesses of the applied coating compositions are too high. Adequate sterilization resistance and freedom from pores, especially in acidic media, can only be achieved with at least 7-8 g/m^2, whereas current requirements on can coating are below 5 g/m^2.

In addition, German Patent Application P 44 23 309.4 discloses a process for preparing a sterically stabilized nonaqueous dispersion of a polyepoxy resin and its use in coating compositions for the interior coating of packaging containers. The addition of phenolic resins to the coating compositions, however, is not described in that application.

Finally, German Patent Application P 44 41 684 discloses a coating composition based on a sterically stabilized nonaqueous dispersion and phenolic resins. Polybutadiene serves here as dispersion stabilizer. The same disadvantages as with the product according to EP-A-321 088 occur here.

The object of the present invention, accordingly, is to provide a coating composition comprising a) a sterically stabilized nonaqueous dispersion which can be prepared by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) having on average at least 2 epoxide groups per molecule with at least one diol (B) of the formula HOROH (I) in which R is a group of the formula -Ph-D-Ph- (II), in which -Ph- is a phenylene group and D is a methylene or a propylene group, and, if desired, with a further component (C) which has groups which are reactive towards epoxide groups or hydroxyl groups, and b) the coating composition comprises at least one crosslinking agent. The coating composition should have as high as possible a solids content and should meet the requirements which are commonly placed on coating compositions employed for the interior coating of cans. These coating compositions should therefore possess, for example, good application properties and ensure good adhesion, good flexibility and good sterilization resistance and also freedom from pores in the resulting coatings. Moreover, the coating composition should be easy and very inexpensive to prepare.

This object is surprisingly achieved by a coating composition which is characterized in that the compound (I) is present in the form of a nonaqueous dispersion which is sterically stabilized by a stabilizer which comprises isoprene or a component derived from polyisoprene.

The present application additionally provides a process for preparing the coating compositions based on a sterically stabilized nonaqueous dispersion which can be prepared by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) having on average at least 2 epoxide groups per molecule with at least one diol (B) of the formula HOROH (I) in which R is a group of the formula -Ph-D-Ph- (II) in which -Ph- is a phenylene group and D is a methylene or a propylene group, and, if desired, with a further component (C) which has groups which are reactive towards epoxide groups or hydroxyl groups, and the coating composition comprises at least one crosslinking agent.

This process is characterized in that the reaction of the diol (B) and, if used, of the component (C) with the epoxy resin component (A) takes place in the presence of a steric dispersion stabilizer which comprises isoprene or a component derived from polyisoprene.

The invention additionally relates to a sterically stabilized nonaqueous dispersion which can be prepared by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) having an average of at least 2 epoxide groups per molecule with at least one diol (B) of formula HOROH (I) in which R is a group of the formula -Ph-D-Ph- (II) in which -Ph- is a phenylene group and D is a methylene group or a propylene group, and, if desired, with a further component (C) which has groups which are reactive towards epoxide groups or hydroxyl groups, characterized in that the compound (I) is present in the form of a nonaqueous dispersion which is sterically stabilized by a stabilizer which comprises isoprene or a component derived from polyisoprene.

Accordingly, a further subject of the invention is a process for preparing a sterically stabilized nonaqueous dispersion which can be prepared by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) having on average at least 2 epoxide groups per molecule with at least one diol (B) of the formula HOROH (I) in which R is a group of the formula -Ph-D-Ph- (II) in which -Ph- is a phenylene group and D is a methylene or a propylene group, and, if desired, with a further component (C) which has groups which are reactive towards epoxide groups or hydroxyl groups, characterized in that the reaction of the diol (B) and, if used, of the component (C) with the epoxy resin component (A) takes place in the presence of a steric dispersion stabilizer which comprises isoprene or a component derived from polyisoprene.

The preparation of the sterically stabilized nonaqueous dispersion preferably takes place in a one-stage process. Alternatively, the dispersion can also be prepared in a two-stage process.

In the first stage of the process the epoxy resin component (A) is reacted with at least one diol (B) and, if desired, with the component (C) to form a reaction product which contains phenolic hydroxyl groups as end groups and has a phenoxy equivalent weight of at least 246, preferably of at least 642, particularly preferably of from 642 to 26,500. The amounts of epoxy resin component (A) and diol (B) in this reaction are preferably chosen such that 1 equivalent of epoxy resin component (A) is reacted with from 3 to 1.001 equivalents, preferably from 1.5 to 1.01 equivalents, of at least one diol (B), where up to 100% by weight of component (B) can be replaced by the component (C). Preferably, a proportion of from 0 to 20% by weight of component (C) is present in the component (B).

The reaction of the epoxy resin component (A) with the diol or diols (B) and, if used, (C) in the first stage of the process is preferably carried out by combining the epoxy resin or resins, the diol or diols and, if used, (C), the dispersion stabilizer and the solvent, and slowly heating them with stirring. Heating is preferably carried out at temperatures of between 80 and 140°C. Dispersion is preferably carried out first of all for some time at this slightly elevated temperature. Then, the catalyst - if used - is added and the mixture is heated to the desired reaction temperature. The reaction of the epoxy resin with the diol and, if used

(C) takes place usually at a temperature of between 120 and 250°C, preferably at a temperature of between 160 and 180°C.

In addition to this, however, it is also possible in the first stage of the process first of all to introduce, as initial charge, the epoxy resin component (A) with the solvent and the dispersion stabilizer, and to disperse the epoxy resin component by stirring and, if desired, with gentle heating, preferably at temperatures of between 80 and 140°C. Then, subsequently, the dispersion can be heated to the desired reaction temperature and the diol (B) and, if used (C) added.

Then, in a second stage, from 50 to 100%, preferably from 80 to 100% of the phenolic hydroxyl groups present in the reaction product obtained in stage (1) are reacted with further epoxy resin component (A) and/or with component (C). Preferably, in the second stage from 50 to 100%, preferably from 80 to 100%, of the phenolic hydroxyl groups present in the reaction product obtained in stage (1) are reacted with further epoxy resin component (A).

The reaction with the epoxy resin component and/or, if desired, further modifying components (C) is preferably carried out by slowly adding the epoxy resin and, if used, the further modifying components dropwise at an elevated temperature, preferably at a temperature of from 60 to 120°C. It is also possible to add the epoxy resin component in one portion in stage (2) of the process. Preferably, after the end of the addition of epoxy resin and/or addition of the modifying components, further catalyst is added and the temperature is raised, preferably to levels of between 160 and 180°C.

The reaction is then continued until the desired degree of conversion is reached.

In addition, however, it is also possible to add the epoxy resin component and/or the further modifying components (C) at room temperature to the phenoxy-terminated product obtained in stage (1) of the process and then to heat the mixture at a temperature of from 120 to 180°C, to carry out dispersion and to continue the reaction until the desired degree of conversion is reached.

Finally, the invention is directed to the use for the coating of packaging containers.

It is surprising and was not foreseeable that the coating compositions prepared using the novel dispersion stabilizer, despite a very high solids content, have good application properties and at the same time also meet the other requirements which are customarily placed on coating compositions for the interior coating of packaging containers. For instance, the coatings produced from the novel coating compositions exhibit good adhesion and good flexibility, good sterilization resistance and also freedom from pores. In particular, sterilization-resistant and pore-free films can be produced with these coating compositions with lower coat thicknesses than those produced using dispersion stabilizers comprising polybutadiene in accordance with EP-A-321 088. This can readily be achieved with coat thicknesses of $\leq 5\ g/m^2$. A further advantage is that the coating compositions are easy and inexpensive to prepare. Finally, it is advantageous that the coatings exhibit a high degree of freedom from pores.

In the text below, the components employed to prepare the novel coating compositions will first of all be elucidated in more detail:

Epoxy resins (A) suitable for preparing the nonaqueous polyepoxide dispersion employed in accordance with the invention are epoxides having on average at least 2 epoxide groups per molecule. Preference is given as component (A) to the use of epoxy resins which are liquid at room temperature. Particular preference is given to the use of epoxy resins having an epoxide equivalent weight of from 150 to 450, preferably from 170 to 192.

Epoxy resins particularly suitable for use are aromatic epoxy resins (A), but also aliphatic and araliphatic epoxy resins (A) as well. Examples which may be mentioned are diglycidyl ethers of polyphenols, diglycidyl ethers of dialcohols and diglycidyl esters of dicarboxylic acids. Preference is given to diglycidyl ethers of polyphenols, especially diglycidyl ethers of bisphenol A, and to epoxidized novolak resins, particularly preferably to the use of epoxy resins based on bisphenol A. It is of course also possible to employ mixtures of different epoxy resins. Furthermore, it is also possible - where operating by the two-stage procedure - to employ different epoxy resins (A) in stage (1) and stage (2). In particular, it is also possible in stage (2) to employ epoxy resins (A) having a functionality < 2, i.e. for example including monoepoxides.

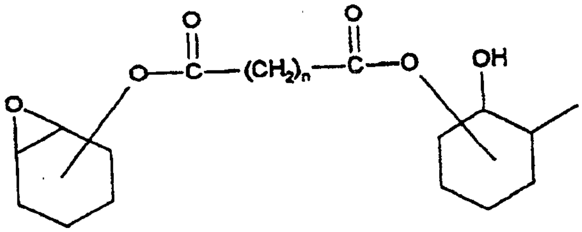
Examples of suitable epoxy resins (A) are the products obtainable commercially under the following names based on bisphenol A:
Epikote[R] 828 from Shell-Chemie;
DER[R] 330 and 333 from Dow Chemicals;
GY[R] 250 from Ciba-Geigy.

Other suitable examples are the products obtainable commercially under the following names, based on epoxidized novolak resins:
XPY 307 and EPN 1139 from Ciba-Geigy and DEN[R] 438 from Dow Chemicals.

Also suitable are the polyepoxides of the formula (4)

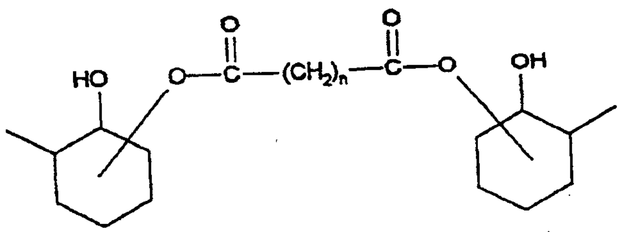
$$A^1OBO(A^2OBO)_aA^1 \qquad (4)$$

in which a is a number such that the epoxide equivalent weight is in the range from 350 to infinity, B is a group of the formula (2) and A^1 is hydrogen or a group of the formula (6)



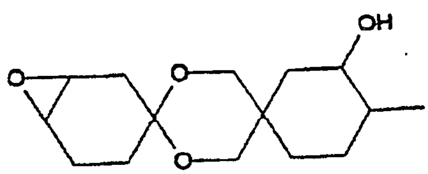
(6)

in which n is from 1 to 4, and A^2 is a group of formula (7)



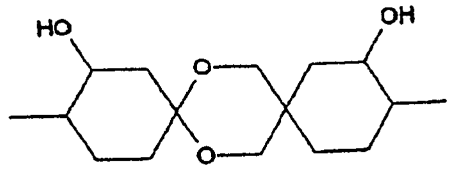
(7)

in which n has the same meaning as in formula (6), or A^1 is hydrogen or a group of formula (9)



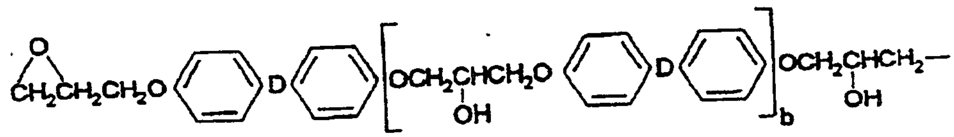
(9)

and A^2 is a group of the formula (10)



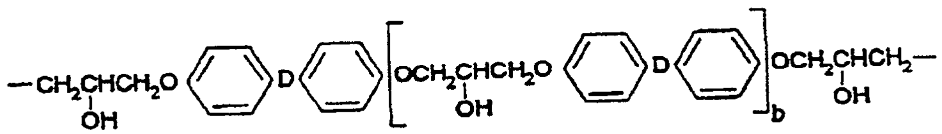
(10)

or A^1 is hydrogen or a group of formula (12)



(12)

in which D is a methylene group or a propane-2,2-diyl group and b is from 0 to 2, and A^2 is a group of the formula (13)



(13)

in which D and b have the same meaning as in formula (12).

In further embodiments, A^1 is hydrogen or a group of formula (12), A^2 is a group of formula (13) and D is a group of propane-2,2-diyl and b is from 0.1 to 1. Furthermore, A^1 can be hydrogen or a group of formula (6), A^2 a group of the formula (7), and n 4. Preferably, the compound having at least two epoxide groups is an epoxide-novolak compounds [sic].

The epoxide equivalent weight is in the range from 350 to 500,000, preferably in the range from 350 to 250,000 and, with very particular preference, in the range from 350 to 25,000.

Further suitable compounds are the epoxides described in Karsten, Lackrohstofftabellen, 9th edition, chapter 31, section 31.2 and 31.2.

To prepare the nonaqueous dispersions of the polyepoxide, diols (B) of the formula HOROH (I) are employed in which R is a group of the formula -Ph-D-Ph- (II) in which Ph is a phenylene group and D is a methylene or a propylene group.

Bisphenol A is preferably employed as diol (B).

If desired, small amounts, preferably less than 20% by weight, particularly preferably from 1 to 15% by weight, of the diol (B) and/or of the epoxy resin component (A) can be replaced by other components (C) which are reacted with the epoxy resin component (A) or - where operating the two-stage process - with the reaction product obtained in stage (1). In particular, difunctional compounds are employed as component (C). Through the use of these additional compounds (C) it is possible to bring about specific improvements in the physical properties of the resulting polyepoxy resins.

For example it is thus possible, as component (C) for the reaction with the epoxy resin, to incorporate adipic acid, sebacin [sic] or dimeric fatty acid or other flexibilizing components. Polyesters, polyacrylates, diamines and fatty acid amides can additionally be employed for this purpose. Where the two-stage process is employed, component (C) is preferably reacted in stage (1).

The reaction of the diol (B) and, if used, of component (C) with the epoxy resin component (A) takes place in the presence of a steric dispersion stabilizer.

A steric dispersion stabilizer is a compound having one part which associates with the epoxy resin which is to be stabilized (commonly referred to as the anchor component) and one part which associates with the solvent (commonly referred to as solvated component).

Suitable dispersion stabilizers are (co)polymers of isoprene or components derived therefrom. Accordingly, it is also possible to use copolymers of isoprene and butadiene. The stabilizer is preferably in the form of a solvated component.

The proportions of isoprene are from 1 to 99% by weight, preferably from 10 to 70% by weight, and those of the polybutadiene from 1 to 99% by weight, preferably from 30 to 90% by weight.

The dispersion stabilizers can be employed such that the anchor component is based on an acrylate polymer. Suitable acrylate polymers are homo- and copolymers of (meth)acrylic alkyl esters (e.g. polymethyl methacrylate, polyethyl methacrylate, polymethyl acrylate, polyethyl acrylate, polymethyl acrylate/polyethyl methacrylate, etc.) and also copolymers of (meth)acrylic alkyl esters and methacrylic and/or acrylic acid, the proportion of copolymerized (meth)acrylic acid usually being below 10% by weight. It is also possible for small proportions of other ethylenically unsaturated monomers to be copolymerized into the copolymers, for example small amounts of crotonic acid, isocrotonic acid, maleic acid and/or alkyl esters of these acids.

The dispersion stabilizers can be prepared by the normally employed methods, for example by reacting the polymer desired as anchor component with the polymer desired as solvated component (for example derived from the polyisoprene).

For preparing the nonaqueous dispersion use is made in particular of solvents which do not dissolve the resulting polyepoxide, examples being apolar organic solvents. As solvents it is preferred to employ aliphatic hydrocarbons which may, if desired, also contain up to 20% by weight of other solvents, for example aromatic hydrocarbons, such as, for example, xylene and Solvesso^R 150.

Preferred solvents employed are high-boiling aliphatic hydrocarbons, especially those having a boiling point of between 120 and 280°C. Examples of suitable solvents are Hydrosol^R P 230 EA from Deutsche Hydrocarbures GmbH, Exxold^R 240 to 270, Norpar^R 12 and Isopar^R M from Deutsche Exxon Chemical GmbH.

When using the two-stage process, the amount of solvent is preferably chosen such that the reaction of the diol (B) with the epoxy resin component (A) (stage (1)) is carried out with a dispersion solids content of from 20 to 80% by weight, preferably from 50 to 70% by weight, and the reaction of the reaction product from stage (1) with the diol (B) (stage (2)) is carried out at a dispersion solids content of from 25 to 85 % by weight, preferably from 55 to 75% by weight.

The reaction of the diol (B) of the epoxy resin component (A) takes place preferably in the presence of a catalyst. Examples of suitable catalysts are alkali metal carbonates, such as potassium and sodium carbonate, alkali metal hydroxides, such as sodium and potassium hydroxide, quaternary ammonium salts, amines, such as dibenzylamine, and also trialkylphosphonium salts, for example triphenylethylphosphonium iodide and triphenylethylphosphonium acetate. A preferred catalyst employed is triphenylethylphosphonium iodide.

The nonaqueous dispersions obtained in the manner described above are, in order to prepare the novel coating compositions, combined with a phenolic resin or with a mixture of phenolic resins as crosslinking agent.

Phenolic resins preferably employed are reaction products of phenol, substituted phenols and bisphenol A with formaldehyde, which have preferably been prepared under alkaline conditions. Under such conditions, the methylol group is linked either in ortho or para position with the aromatic ring.

As etherifying alcohol for the methylolic hydroxyl groups, use is made of lower alcohols such as, for example, ethanol, propanol, butanol and isobutanol, n-butanol preferably being employed as etherifying alcohol.

The coating compositions are with particular preference prepared using low-viscosity phenolic resins. Phenolic resins employed in particular are those whose from 50 to 70% strength solutions have a viscosity at 20°C of less than 1000 mPas, preferably from 300 to 900 mPas.

Examples of phenolic resins which are suitable as cross-linking agent are the products obtainable commercially under the following tradenames:

Phenodur[R] resins, for example Phenodur[R] PR 285, from Hoechst AG
Epikure[R] resins, for example Epikure[R] DX 200 N 60, from Shell Chemicals
Bakelike[R] resins, for example Bakelite[R] 7576 LB, from Rütgerswerke AG
Uravar[R] resins, for example Uravar[R] FB 209, from DSM
Varcum[R] resins, for example Varcum[R] 2890, from Reichold Chemie GmbH.

With very particular preference, the novel coating compositions are prepared using the products obtainable commercially under the following names:

SFC 123 from Schenectady Europe S.A.

SFC 112 from Schenectady Europe S.A.

The novel coating compositions may additionally comprise further binders such as, for example, epoxy resins, polyester resins, polyacrylate resins or polyurethane resins.

The novel coating compositions may, in addition to the solvent employed for preparing the nonaqueous dispersion, optionally contain further solvents as well. Examples of suitable further solvents that may be mentioned are aromatic, aliphatic and cycloaliphatic hydrocarbons, for example Solventnaphta[R], various Solvesso[R] and Shellsol[R] grades, Deasol and various white spirits. These additional solvents are employed in amounts such that the overall solvent content of the coating compositions (i.e. including the solvent content of the nonaqueous dispersion and, if appropriate, of the phenolic resin) is from 30 to 50% by weight.

The additional solvent can be employed in order to establish a viscosity which is favourable for the application of the coating compositions and/or in order to form a paste of the phenolic resins and/or pigments and/or fillers.

Also suitable for use in the novel coating compositions are organic and inorganic pigments, for example titanium dioxide, iron oxides and diarylides. Preferably, however, the coating compositions are employed in unpigmented form.

Also suitable for use in novel coating compositions are customarily employed fillers, for example talc, mica, kaolin, chalk, quartz flour, slate flour, barium sulphate, various silicic acids, silicates and the like. Preference is given, however, to coating compositions which contain no fillers or only transparent fillers.

In addition, the novel coating compositions may also comprise customary auxiliaries and additives, such as levelling agents, wetting agents, antifoams, PVC-free plasticizers (for example adipic esters), wax (e.g. polyolefin waxes, carnauba waxes, beeswax, lanolin wax) and crosslinking catalysts (for example acid catalysts, such as phosphoric acid solutions and p-toluenesulphonic acid solutions).

The novel coating compositions preferably comprise

- from 30 to 60% by weight, preferably from 35 to 50% by weight, of one or more novel nonaqueous dispersions and

- from 5 to 30% by weight, preferably from 15 to 20% by weight, of one or more phenolic resins,

the percentages by weight being based in each case on the overall weight of the coating composition and on the solids content of the nonaqueous dispersion and of the phenolic resin.

The coating compositions may additionally contain further solvents and, if desired, further binders, optionally pigments and/or fillers and also, if desired, customary auxiliaries and additives in customary amounts. With particular preference the novel coating compositions comprise, in addition to the sterically stabilized nonaqueous dispersion and the phenolic resin, also from 0 to 40% by weight of further binders, from 30 to 50% by weight of solvents (including the solvent portion of the nonaqueous dispersion), from 0 to 50% by weight of pigments and/or fillers, and from 1 to 10% by weight of customary auxiliaries and additives.

The preparation of the coating compositions is normally carried out by first of all preparing the nonaqueous dispersion of a polyepoxy resin and then adding the phenolic resin and, if used, the solvent, pigments, fillers and customary auxiliaries and additives, and, if desired, in processing these components, if desired by dispersion, to form the coating composition.

The coating compositions are preferably employed for the coating of packaging containers, especially for the coating of food packaging. In this context, the packaging containers may consist of a very wide variety of materials and may have a very wide variety of geometries. Particularly suitable materials are black plate, tin- plate and various ferrous alloys, which may have been given a passivating coat based on compounds of nickel, of chromium and of zinc. The packaging containers can be coated in the form, for example, of can halves, i.e. bodies and lids, as 3-part cans and as 2-part cans, as deep-drawn wall-ironed cans or otherwise deep-drawn cans, for example beverage and preserve cans.

The novel coating compositions cure fully within the substrate temperature range from 150 to 400°C over a period of from 2 s to 15 minutes. They can be applied by rolling, knife coating, brushing, spraying, flow coating or dipping using customary equipment, the film subsequently being fully cured to form a firmly adhering coating. The coating compositions are preferably applied by means of roller application.

The invention will now be illustrated in more detail with reference to working examples. In these examples, all parts and percentages are by weight unless expressly stated otherwise.

Preparation of a dispersion stabilizer

In feed 1,

8.961 parts of methyl methacrylate and
0.572 part of methacrylic acid

are weighed out and mixed.

In feed 2,

0.191 part of tert-butyl per-2-ethylhexanoate

is weighed out and mixed.

Then,

14.185 parts of xylene
9.445 parts parts [sic] of a commercial mixture of paraffinic and naphthenic hydrocarbons in the range C15-C17, with a boiling range between 230 and 265°C (commercial product Hydrosol[R] P 230 EA from Deutsche Hydrocarbures GmbH)
9.529 parts of a commercial, solvent-free polymer based on polyisoprene, having a weight-average molecular weight of about 40,000 (commercial product Isolene 40 S from Hermann ter Hell & Co. GmbH, Hamburg)

are mixed and heated with stirring to 125°C. Then feed stream 1 and feed stream 2 are metered in simultaneously but separately. Feed stream 1 is metered in over the course of 90 minutes and feed stream 2 over the course of 100 minutes. The temperature therein is held at 125°C for 1 h. Then 4.720 parts of xylene are distilled off under a slight vacuum. Subsequently,

52.383 parts of a commercial mixture of paraffinic and naphthenic hydrocarbons in the range C15-C17, with a boiling range of between 230 and 265°C (commercial product Hydrosol[R] P230 EA from Deutsche Hydrocarbures GmbH)

are added dropwise with stirring over the course of 30 minutes at a temperature of 125°C. The batch is then cooled.

The resulting dispersion has a solids content (90 minutes, 180°C) of 18.4% and an acid number of 22.2 mg of KOH/g and a viscosity (ICI plate/cone viscometer, 23°C) of 0.4 dPas.

Preparation of a nonaqueous dispersion

35.554	parts of a commercial liquid epoxy resin based on bisphenol A, having an epoxide equivalent of 186 and a molecular weight of 350-380 (commercial product Epicote[R] 880 from Shell Chemie)
19.321	parts of bisphenol A
29.333	parts of the above-described dispersion stabilizer and
15.682	parts of a commercial mixture of paraffinic and naphthenic hydrocarbons in the range C15-C17, having a boiling range between 230 and 265°C (commercial product Hydrosol[R] P230EA from Deutsche Hydrocarbures GmbH)

are weighed into a 4 l steel reactor and heated to 120°C with slow stirring (about 80 revolutions per minute). The stirring speed is then raised to 300 revolutions per minute and dispersion is carried out for 1 h. Then,

0.110 part of ethyltriphenylphosphonium iodide as catalyst

is added and the temperature is raised to 170°C. The batch is held at this temperature until the epoxy equivalent weight is 3700. The batch is then cooled and the product is filtered through a nylon mesh (mesh size 30 μm).

The resulting dispersion has a solids content (90 minutes, 180°C) of 60.0% and a viscosity (ICI plate/cone viscometer) 23°C) of 1.6 dPas. The dispersion thus obtained has a storage stability at 23°C of more than 30 days.

Examples 1 to 4

The components indicated in Table 1 are processed by stirring to form homogeneous coating compositions.

The properties of the resulting coating compositions 1 to 4 are set out in Table 2.

These coating compositions 1 to 4 are then applied as one coat to tinplate E 2.8/2.8 and stoved for 12 minutes at an ambient air temperature of 200°C. The properties of the resulting coating are set out in Table 3.

Table 1

	1	2	3
NAD[1)]	73.5	66.5	69
SFC123[2)]	26.5	-	-
SFC112 (65% in butanol)[2]	-	26.2	-
Epicure DX200[3)]	-	-	26.5
Hydrosol EA230[4)]	-	7	4.5
Butyl titanate (10% in Solvesso 150)	-	0.3	-
Solids content (15 min, 200°C)	58%	56%	59%
Viscosity (DIN-4 mm/20°C)	40 s	50 s	60 s
Wedge bend test	28 mm	43 mm	60 mm
Colour	light gold	gold	light gold
Coating add-on	5 g/m^2	5 g/m^2	5 g/m^2

Key to Table 1:

1) Above-described nonaqueous dispersion of a polyepoxy resin
2) Product from Schenectady Europe S.A., phenolic resin based on butylphenol and formaldehyde.
3) Epikure[R] DX-200-N-60 from Shell Chemicals, a commercial resol-phenol-formaldehyde resin, 60%

strength in n-butanol, with a viscosity (Brookfield) at 25°C of 450-800 mPas

4) Hydrosol

Table 2: Sterilization properties of the coated specimens in accordance with Examples 1 to 4 (assessment: water uptake/porosity)

	1	2	3	4
Water	0/0	0/0	0/0	0/0
3% NaCl	0/0-1	0/1-2	0/0-1	0/0-1
3% acetic acid	0/1	0/3	0/2	0/2
2% NaCl, 3% acetic acid	0/0-1	0/1-2	0/0-1	0/0-1
2% lactic acid	0/1	0/2	0/1-2	1/1-2
0.5 g/l cysteine	0/0	0/2	0/0	0/0-1
marbling	2	0-1	0-1	0-1

Notes regarding Table 2:

The sterilization resistance was determined by sterilizing the coated metal panels (o 99 mm) in an autoclave at 129°C for a period of 60 minutes and subjecting them to the action of water or 3% strength sodium chloride solution (3% NaCl) or 3% strength acetic acid (3% HAc) or 2% strength acetic acid and 3% strength sodium chloride solution, or 1% strength lactic acid (lact.) or cystein solution (0.5 g cystein/l water). Following sterilization, the test panels were subjected to the action of copper sulphate solution (10% copper sulphate, 10% concentrated hydrochloric acid) for a period of 3 minutes at room temperature. The adhesion was assessed in accordance with DIN 53 151, and a visual assessment was carried out of water uptake (number before the oblique) and of the porosity (number after the oblique) in accordance with the following evaluation scale:

0 = very good

5 = very poor.

The assessment of sulphur resistance (marbling) was carried out in accordance with the specification in Verpackungs-Rundschau <u>28</u> (1977), 7, technical supplement, page 58.

Examples of the novel mixtures using component (C)

Example 5

35.764 parts of a commercial epoxy resin based on bisphenol A, having an epoxide equivalent of 186 and a molecular weight of 350-380 (commercial product Epikote[R] 880 from Shell Chemie)

12.971 parts of bisphenol A

29.606 parts of the above-described dispersion stabilizer and

5.751 parts of sebacic acid

15.794 parts of a commercial mixture of paraffinic and naphthenic hydrocarbons in the range C15-C17, having a boiling range between 230 and 265°C (commercial product Hydrosol[R] P230EA from Deutsche Hydrocarbures GmbH)

0.111 part of ethyltriphenylphosphonium iodide as catalyst

are weighed into a 4 l steel reactor and are heated to 120°C with slow stirring (80 revolutions/minute). The stirrer speed is then raised to 300 revolutions/minute and dispersion is carried out for 1 h. Raise the temperature further to 170°C. Maintain at this temperature until an EEW of 3700 g/mol is reached. The batch is then cooled and the product is filtered through a nylon mesh (mesh size 30 m [sic]).

The resulting dispersion has a solids content (90 minutes, 180°C) of 60% and a viscosity (ICI plate/cone viscometer 23°C) of 2.1 dPas.

Example 6

29.134 parts of a commercial epoxy resin based on bisphenol A, having an epoxide equivalent of 186 and a molecular weight of 350-380

(commercial product Epikote 880 from Shell Chemie)

8.045 parts of Pripol 1013

are weighed into a 4 l steel reactor and heated with stirring. Then

0.008 part of ethyltriphenylphosphonium iodide as catalyst

is added and the temperature is raised to 165°C. Maintain this temperature until an EEW of 290 g/mol is reached. Then cool to 60°C and add

12.642 parts of bisphenol A
27.057 parts of the above-described dispersion stabilizer
23.032 parts of a commercial mixture of paraffinic and naphthenic hydrocarbons in the range C15-C17, having a boiling range of between 230 and 265°C (commercial product Hydrosol P230EA from Deutsche Hydrocarbures GmbH) and
0.082 part of ethyltriphenylphosphonium iodide as catalyst

and raise the temperature to 120°C with slow stirring (80 revolutions/minute). The stirrer speed is then raised to 300 revolutions/minute and dispersion is carried out for 1 h. Raise the temperature further to 170°C. Maintain at this temperature until an EEW of 3700 g/mol is reached. The batch is then cooled and the product is filtered through a nylon mesh (mesh size 30 m [sic]).

The resulting dispersion has a solids content (90 minutes, 180°C) of 55% and a viscosity (ICI plate/cone viscometer, 23°C) of 1.5 dPas.

Example 7

In this example, the proportion of component C is 100%:

38.384 parts of a commercial epoxy resin based on bisphenol A, having an epoxide equivalent of 186 and a molecular weight of 350-380 (commercial product Epikote[R] 880 from Shell Chemie)

29.076 parts of the above-described dispersion stabilizer and

13.373 parts of adipic acid

19.048 parts of a commercial mixture of paraffinic and naphthenic hydrocarbons in the range C15-C17, having a boiling range between 230 and 265°C (commercial product Hydrosol[R] P230EA from Deutsche Hydrocarbures GmbH)

0.119 part of ethyltriphenylphosphonium iodide as catalyst

are weighed into a 4 l steel reactor and are heated to 120°C with slow stirring (80 revolutions/minute). The stirrer speed is then raised to 300 revolutions/minute and dispersion is carried out for 1 h. Raise the temperature further to 170°C. Maintain at this temperature until an EEW of 3700g/mol is reached. The batch is then cooled and the product is filtered through a nylon mesh (mesh size 30 m [sic]).

The resulting dispersion has a solids content (90 minutes, 180°C) of 57%.

PCT Application No. PCT/EP97/00833
Applicant: PPG Industries, Inc. et al.

Patent Claims:

1. Process for preparing a sterically stabilized nonaqueous dispersion by reacting, in an organic solvent in the presence of a dispersion stabilizer, at least one epoxy resin (A) having on average at least 2 epoxide groups per molecule with at least one diol (B) of the formula HOROH (I) in which R is a group of the formula -Ph-D-Ph- (II), in which Ph- is a phenylene group and D is a methylene or a propylene group, and, if desired, with a further component (C) which has groups which are reactive towards epoxide groups or hydroxyl groups, characterized in that the reaction of the diol (B) and, if desired, of component (C) with the epoxy component (A) takes place in the presence of a steric dispersion stabilizer which comprises isoprene or a component derived from polyisoprene, with the exception of degraded natural rubber.

2. Process according to Claim 1, characterized in that the nonaqueous dispersion has been prepared by
1) reacting the epoxy resin component (A) in a first stage (stage (1)) with at least one diol (B) and/or with the component (C) to form a reaction product containing phenolic hydroxyl groups as end groups and having a phenoxy equivalent weight of at least 246, and
2) then, in stage (2), reacting from 50 to 100% of the phenolic hydroxyl groups present in the reaction product obtained in stage (1) with further epoxy resin component (A) and/or with the component (C).

3. Process according to one of the preceding claims, characterized in that the stabilizer is a copolymer of butadiene and isoprene.

4. Process according to Claim 3, characterized in that the proportion of isoprene is from 1 to 99% by weight, preferably from 10 to 70% by weight and the proportion of the polybutadiene is from 1 to 99% by weight, preferably from 30 to 90% by weight.

5. Sterically stabilized nonaqueous dispersion preparable by a process according to one of Claims 1 to 4.

6. Coating composition comprising

a) a sterically stabilized nonaqueous dispersion according to Claim 5
and

b) at least one crosslinking agent and also, if desired, solvents, pigments, fillers and customary auxiliaries and additives.

7. Coating composition according to Claim 6, characterized in that the crosslinking agent comprises a phenolic resin or a plurality of phenolic resins.

8. Coating composition according to one of Claims 6 and 7, characterized in that the coating composition comprises
from 30 to 60% by weight, preferably from 35 to 50% by weight, of one or more nonaqueous dispersions according to Claim 5 and
from 5 to 30% by weight, preferably from 15 to 20% by weight, of one or more phenolic resins,

the percentages by weight being based in each case on the overall weight of the coating composition and on the solids content of the nonaqueous dispersion and of the phenolic resin.

9. Process for preparing a coating composition based on a sterically stabilized nonaqueous dispersion by adding at least one crosslinking agent and also, if desired, solvents, pigments, fillers and customary auxiliaries and additives to a sterically stabilized nonaqueous dispersion according to Claims 5.

10. Use of the coating compositions according to one of Claims 6 to 8 for coating packaging containers, especially for the coating of food packaging containers.