



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 163/00	A1	(11) International Publication Number: WO 98/40443 (43) International Publication Date: 17 September 1998 (17.09.98)
(21) International Application Number: PCT/EP98/01572 (22) International Filing Date: 11 March 1998 (11.03.98) (30) Priority Data: 97200740.5 12 March 1997 (12.03.97) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: CLAEYS-BOUUAERT, Pascale, Charlotte, Agnès, Marie, Gislaine; Avenue Jean Monnet 1, Lou- vain-La-Neuve, B-1348 Ottignies (BE). HENDERSON, Philippe, Gilbert, Jean-Marie, Ghislain; Avenue Jean Monnet 1, Louvain-La-Neuve, B-1348 Ottignies (BE).		(81) Designated States: AU, BR, CA, CN, HU, JP, KR, NZ, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: AQUEOUS EPOXY/PHENOLIC CODISPERSIONS USABLE FOR INTERIOR FOOD CAN COATING LACQUERS		
(57) Abstract <p>Stable aqueous coating dispersions, comprising a codispersion of at least a curable epoxy resin and a co-curable phenolic resin, and a combination of a non-ionic surfactant, comprising at least a reaction product of poly(ethylene oxide)polymer alcohols and a diglycidylether of a dihydric phenol having an epoxy group content in the range of from 1000 to 6000 mmol/kg, or a block copolymer of ethylene oxide and propylene oxide alcohol, and an anionic surfactant, comprising a random copolymer of at least one monovinyl arene, an alkyl acrylate, containing from 2 to 6 in the alkyl group, and acrylic acid, the copolymer having a weight average molecular weight in the range of from 3000 to 30.000, said composition partly neutralized by an amine to a neutralization degree of from 25 % to 95 %.</p>		

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AQUEOUS EPOXY/PHENOLIC CODISPERSIONS USABLE
FOR INTERIOR FOOD CAN COATING LACQUERS

The invention is relating to aqueous epoxy/phenolic codispersions, usable for interior food can coating lacquers.

5 More in particular the invention is relating to aqueous codispersions of an epoxy resin as curing resin and a phenolic resin as co-curing resin, both of which have dispersed during the same processing step, and showing a reduced Volatile Organic Compounds (VOC) content.

10 On the one hand, with increasing environmental concerns the coating industry puts more and more efforts in the reduction of the VOC emitted, and one of the possible alternatives is the replacement of the organic solvents, used in prior coating systems, by water.

15 On the other hand, further economical requirements compels the coating industry to put more efforts in the reduction of costs of manufacturing the lacquers and the final processing thereof.

20 Polymer coating compositions designed for use in the interior for food containers have to meet very stringent requirements.

High molecular weight epoxy resins are suitable for internal protective lacquers for tinsplate and aluminium packaging.

25 The cross-linking agents used are phenol formaldehyde, melamine formaldehyde and urea formaldehyde resins. Due to the prespecified application viscosity, can lacquers were based on organic solvents with a typical solvent content between 55 and 70 %wt.

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With reference to the hereinbeforementioned aims, the use of such organic solvents must be avoided as much as possible.

A currently desired volatile organic content (VOC)
5 level is lower than 200 g/kg solids.

Possible routes to reduce the use of solvents are, for example, those of powder coatings, high solids binders, or water based systems.

While chemical emissions are virtually absent in
10 powder coatings, said coating compositions do present some disadvantages with regard to can coating: the high layer thickness, requiring much more paint solids compared to liquid coatings, the high loss of material due to the insufficient transfer efficiency linked with
15 underdeveloped overspray recovery and recycling, danger of dust explosions and high initial investment.

There has been developed during the last decade a great variety of water based epoxy lacquer systems for internal can coating, which can be divided into three
20 main categories:

(a) products prepared by radically grafting an acrylic copolymer onto a backbone formed by an epoxy resin which is initially precondensed with a phenolic resin (e.g. as disclosed in GB-A-2152065); defunctionalized with a
25 polyester (e.g. as disclosed in US-A-5,114,993), or reacted with an anhydride which will be opened by the secondary OH of the epoxy resin (e.g. as disclosed in WO 93/19133);

(b) products prepared by defunctionalization of the epoxy
30 resin into a covalent ester bond with a preformed polycarboxylic polymer (e.g. as disclosed in US 4623680 and GB-A-2102807); and

(c) aqueous dispersions of blends made from a carboxyl-functional acrylic copolymer, phenolic resins and

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partially defunctionalized epoxy resin (e.g. as disclosed in US-A-5,296,525).

However, said conventional water based epoxy lacquers systems all have still relatively high VOC level of
5 400 g/kg solids and higher. Furthermore, the systems based on graft polymers are prepared by the use of a complicated lacquer preparation procedure in a complex equipment.

It will be appreciated that there is still a strong
10 need for further improvement of aqueous epoxy lacquer systems usable for internal can coating, characterized by avoiding the use of organic cosolvents, the use of complicated preparation routes and of complicated equipment, while maintaining or improving the final
15 lacquer properties after curing and the stability during storage.

Therefore an object of the present invention is to provide said stable aqueous epoxy resin lacquer systems, showing the required physical properties in the final can
20 coating layer and manufactured in cheap equipment and by using cheap, environmentally acceptable starting materials and auxiliaries.

Another object of the present invention is to provide an effective process for the manufacture of said stable
25 lacquer systems.

As a result of extensive research and experimentation such aqueous epoxy resin lacquers aimed at, have been surprisingly found.

Accordingly, the invention relates to stable aqueous
30 coating dispersions, comprising a codispersion of at least a curable epoxy resin and a co-curable phenolic resin, and a combination of a non-ionic surfactant, comprising at least a reaction product of poly(ethylene oxide)polymers and a diglycidylether of a dihydric phenol

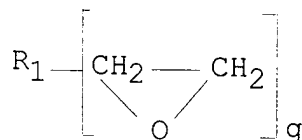
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having an epoxy group content in the range of from 1000 to 6000 mmol/kg, or a block copolymer of ethylene oxide and propylene oxide, and an anionic surfactant, comprising a random copolymer of at least one monovinyl arene, an alkyl acrylate, containing from 2 to 6 and preferably from 2 to 4 carbon atoms in the alkyl group, and acrylic acid, the copolymer having a weight average molecular weight in the range of from 3000 to 30.000, and preferably 4500 to 7000 and more preferably from 5500 to 6500, said composition partly neutralized by an amine, and preferably a tertiary amine, to a neutralization degree of from 25% to 95%, and preferably from 35 to 85%.

According to a preferred embodiment the non-ionic surfactant is a reaction product of poly(ethylene oxide) alcohol having an apparent molecular weight of from 5000 to 10.000 and more preferably from 6000 to 9000 and a diglycidyl ether of dihydric phenol.

The diglycidyl ether of dihydric phenol reactant more preferably has a viscosity of from 5 to 7 mPa.s at 25 °C in a MEK solution (40% by weight).

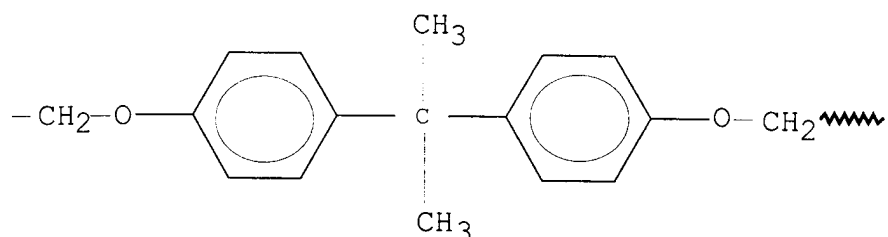
The epoxy resins to be dispersed in the practice of this invention comprise one or more polyglycidyl ethers of polyhydric phenols having two or more epoxide groups and one or more six carbon aromatic rings present in the molecule, as represented by the structural formula



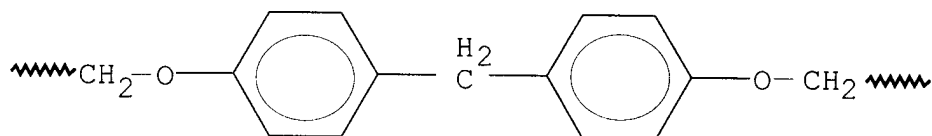
wherein R₁ represents a "g" valent C₆-C₅₀ organic radical comprising at least one six carbon aromatic ring and g is equal to or greater than 2, but less than or equal to 6.

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More in particular R_1 may represent a group



or a group



Suitable epoxy resins are commercially available from a variety of sources and include EPIKOTE or EPON epoxy resins (EPIKOTE and EPON are trade marks) from Shell Chemical Europe and Shell Chemicals Company and DER or DEN epoxy resins from Dow Chemical Company (DER and DEN are trade marks).

Examples of suitable epoxy resins are:

- I) Polyglycidyl and poly(beta-methylglycidyl) esters obtainable by reacting a compound having at least two carboxy groups in the molecule with epichlorohydrin or beta-methyl-epichlorohydrin respectively. The reaction is advantageously carried out in the presence of bases. Examples of aromatic polycarboxylic acids which may be used include, for example, phthalic acid, isophthalic acid or terephthalic acid.
- II) Polyglycidyl or poly(beta-methylglycidyl) ethers obtainable by reacting a compound having at least two free phenolic hydroxy groups with epichlorohydrin or beta-methyl-epichlorohydrin, respectively, under alkaline conditions, or in the presence of an acid catalyst and with subsequent alkali treatment.

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The epoxy compounds of this type may be derived from mononuclear phenols, such as for example, resorcinol or hydroquinone; or they are based on polynuclear phenols, such as, for example, bis(4-hydroxyphenyl)methane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, and from novolacs obtainable by condensation of aldehydes, such as formaldehyde, acetaldehyde, chloral or furfuraldehyde, with phenols, such as phenol, or with phenols that are substituted in the nucleus by halide atoms or C₁-C₁₈ (preferably C₁-C₉) alkyl groups, such as, for example, 4-chlorophenol, 2-methylphenol or 4-tert-butylphenol, or by condensation with bisphenols, in the manner described above.

There are preferably used epoxy resins that have an epoxy content of from 2 to 10 equivalents/mole and that are glycidyl ethers or glycidyl esters of aromatic or alkyaromatic compounds. Especially preferred epoxy resins are polyglycidyl ethers of bisphenols, such as, for example, of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) or bis(4-hydroxyphenyl)methane (bisphenol F), or novolacs formed by reacting formaldehyde with a phenol.

Illustrative examples of suitable epoxy resins are described in for instance The Handbook of Epoxy Resins by H. Lee and K. Neville, McGraw-Hill, New York (1967), Epoxy Resins, Chemistry and Technology, edited by C.A. May, Marcel Dekker (1988) and Chemistry and Technology of Epoxy Resins, edited by B. Ellis, Blackie Academic & Professional (1993).

For reasons of cost and availability, the most preferred epoxy resins are polyglycidyl ethers based on bisphenol A.

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Preferably epoxy resins are used, having an epoxide equivalent weight of at least 700 and more preferably at least 1500.

Suitable examples thereof are aromatic polyglycidylethers, which are commercially available under the trade names EPIKOTE 1001, EPIKOTE 1004, EPIKOTE 1007, EPIKOTE 1008, EPIKOTE 1055 and EPIKOTE 1009.

As co-curable phenolic resins can be used those which were disclosed in e.g. U.S. patent No. 5,491,031, Japanese patent applications J 08081532 A, J 08041170 A and J 08067743 A, Rumanian patent No. 2041904 C, and Journal of Coatings Technology, K. Bourlier, vol. 68, No. 853, February 1996.

Generally, the phenolic resin utilized in the present composition is a condensation product, resulting from a reaction between a phenol and formaldehyde, and has a low molecular weight of 1,000 to 8,000 and preferably 3,000 to 5,000. Phenol or essentially any other compound including a hydroxyphenyl moiety, like cresols acid, can be used as the phenol component of the phenolic resin. Non-limiting examples of suitable phenol compounds include phenol, o-cresol, p-cresol, m-cresol and bisphenol A. Bisphenol A is the preferred phenol component of the phenolic resin.

To achieve the full advantage of the present invention, bisphenol A and formaldehyde are used as the components of the phenolic resin. The combination of bisphenol A and formaldehyde provides a phenolic resin that, when incorporated into a coating composition of the present invention, imparts excellent adhesion of the coating composition both to the primer coating and to a variety of plastisol gaskets that can be applied over the cured composition coating. Cresol (cresylic acid) can be

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included in the phenolic resin to further enhance the corrosion-inhibiting properties of the coating composition.

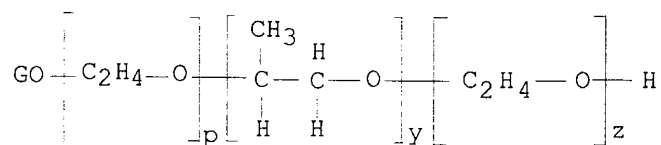
An exemplary phenolic resin utilized in the present coating composition includes about 24% by weight bisphenol A, and about 7% by weight formaldehyde. This phenolic resin is incorporated into a present coating composition as a solution containing about 50% by weight of the phenolic resin.

Suitable examples of phenolic resins are those, which are commercially available under the trade names EPIKURE DX-200-MN-70 or DX-200-N-60, or PHENODUR 217.

The weight ratio between the epoxy resin and the cocurable phenolic resins to be dispersed may be in the range of from 90/10 to 20/80 and preferably from 85/15 to 65/35.

The non-ionic surfactant may be derived from poly(ethoxy)polymers of the formula

$GO[C_2H_4-O]_xH$, wherein G represents the residue of a dihydric alcohol and more preferably polyalkylene glycol, has and wherein X has a value from 100 to 250 and preferably from 150 to 200, which is prereacted with diglycidylether, and is a more preferred surfactant, or



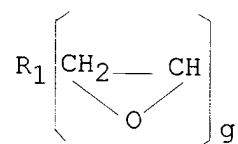
wherein $x = 100$ to 250 , preferably 150 to 200 , $p = 50$ to 200 , preferably 75 to 125 , $y = 10$ to 100 , preferably from 25 to 50 and $z = 0$ to 200 , to be used as such.

Examples of the dihydric alcohols which can be used for the preparation of the non-ionic surfactant component

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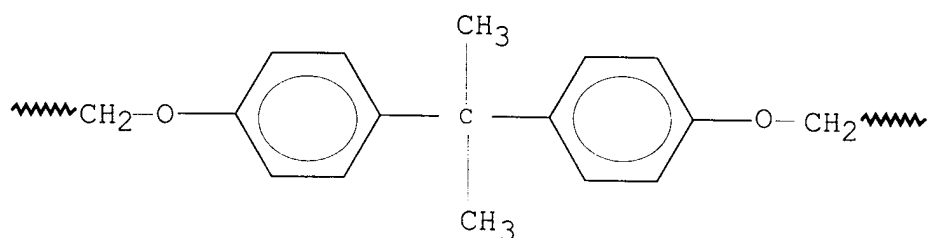
derived from ethylene oxide and propyleneoxide are polyethylene glycol, polypropylene glycols, or a mixture thereof. The use of polyethylene glycol is most preferred.

5 The epoxy resin reactant is preferably selected from diglycidyl ethers derived from dihydric phenols, having one or more six carbon aromatic rings present in the molecule, represented by the structural formula

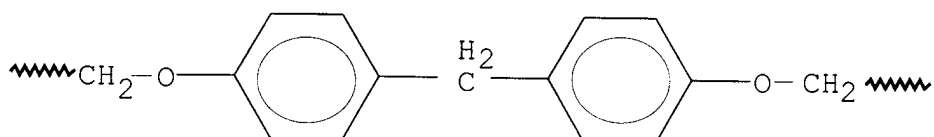


wherein R_1 and g are as defined hereinbefore.

10 Preferably R_1 represents a group



or a group



15 More preferably epoxy resins are used for the preparation of the non-ionic surfactants, having an epoxide equivalent weight of at least 700 and most preferably of at least 1500.

Suitable examples of such epoxy resins are aromatic polyglycidyl ethers, which are commercially available under the trade name EPIKOTE 1001, EPIKOTE 1004, EPIKOTE 1007, EPIKOTE 1008, EPIKOTE 1009, EPIKOTE 1055, 20 of which EPIKOTE 1001 is the most preferred.

The non-ionic surfactant is generally included in amounts in the range of from 1 to 15 wt% and preferably

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from 4 to 10 wt% relative to the total weight of solids. More preferably the amounts are in the range of from 6 to 8 wt%.

5 The anionic co-surfactant is preferably a terpolymer of styrene, ethyl acrylate and acrylic acid in a weight ratio of from 40 to 50 wt% styrene, from 15 to 25 wt% ethylacetate, and from 30 to 35 wt% acrylic acid, the sum of the percentages of the three comonomer components being 100%.

10 More preferably co-surfactant terpolymers are used, derived from 44 to 46 wt% styrene, from 20 to 22 wt% ethyl acetate and from 33 to 34 wt% acrylic acid, the sum of the percentages of the three comonomer components being 100%.

15 Said terpolymers and their preparation are known from US patent No. 4,623,680 and more in particular from column 5, example 1.

20 The anionic terpolymer surfactant is generally included in amounts of from 2 to 15 wt%, relative to the total weight of the solids, and preferably from 5 to 10 wt% and more preferably from 6 to 8 wt%.

As neutralizing amines are preferably used dimethyl-ethanol amine (DMEA) and/or N-ethyl-morpholine (NEM).

25 The codispersions are physically stable, if as far as the neutralization degree is in the range of from 25 to 95.

Preferably this neutralization degree will be in the range from 30 to 60% for optimum results.

30 Another aspect of the present invention is formed by a process for the manufacture of the hereinbefore specified aqueous lacquers.

Accordingly the invention relates to a process for the manufacture of stable aqueous coating dispersions comprising heating of the hereinbefore specified starting

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materials to be dispersed and surfactants and stirring until a homogeneous liquid mixture at a stirring speed in the range of from 50 to 150 RPM, adjusting the temperature to the desired Phase Inversion Temperature (PIT) and adding water dropwise and an aqueous solution of the neutralizing amine just before inversion occurs, continuation of adding water dropwise to avoid back inversion and stirring the obtained aqueous dispersion at a few degrees below the PIT for an extra one to four hours and preferably from two to three hours, optionally further dilution of the obtained aqueous dispersion and cooling.

A typical temperature/time profile has been depicted in the attached Fig. 1.

In general, during the process of the present invention due care will have to be taken that shock cooling or heating should always be avoided and that the water addition rate is such that the formation of a water layer is not observed.

It has been found that, when preparing a (co)-dispersion by inversion, the final particle size can be strongly influenced by the Phase Inversion Temperature (PIT).

Smaller particles are usually produced at a lower inversion temperature. However, if the temperature is too low, the viscosity increases and either inversion cannot be completed or the particles have a bad shape.

If the temperature is too high, inversion cannot be achieved either, due to a loss of solubility in water of the non-ionic hydrophilic chains of the polymeric surfactant at high temperature.

Depending on the final chemical composition and PIT, inversion occurs between 68% and 77% weight of

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non-volatile compounds. The maximum PIT is between 60 and 83 °C.

Above the maximum PIT, water simply cannot be incorporated and two separated phases are produced.

5 It has been found that the tertiary amines catalyze reactions with epoxy groups and a hard network is formed during the melting of the resins if the tertiary amine such as DMEA is introduced from the beginning. On the other hand, if the amine/terpolymer blend is introduced
10 after inversion, the terpolymer does not provide its electrostatic stabilization during inversion and a bad quality dispersion is formed. Bad quality dispersions are produced as well if the anionic surfactant is used in the absence of non-ionic surfactant.

15 The aqueous coating dispersions according to the present invention are stable over a long storage period and have average particle sizes $DW < 2 \mu m$ and $D_n < 1 \mu m$ of at least 90% of the particles.

20 More in particular, homogeneous codispersions, having small particles and a sharp particle size distribution e.g. $D_n = 0.66 \mu m$ and $DW = 0.84 \mu m$ can be obtained which are physically stable for months at ambient temperature. There is no or very little settling after six months.

25 The codispersions according to the present invention show VOC values significantly lower than the usual 400 g/kg solids of the prior art aqueous dispersions and in particular VOC values lower than 200 g/kg solids in combination with high performance.

30 It is true that from US patent No. 3,249,412 there was known a process of sizing glass fibres with an epoxy resin emulsion, which contained from 5 to 15 wt% of the epoxy resin of a cationic emulsifying agent selected from imidazolines or amides of a specific structure and from 5 to 15 percent by weight of the epoxy resin of a non-ionic

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emulsifying agent consisting of a poly(oxyalkylene) polymer chain, bearing one or two hydroxyl groups and having a molecular weight from 3000 to 20,000.

However, it will be appreciated that the use of the said epoxy resin emulsion is completely different from that of the aqueous lacquer compositions of the present invention, while the surfactant components are of a completely different type as well.

The invention will be further illustrated by means of the following examples, however, without restricting its scope to these embodiments.

EXAMPLE 1

A codispersion made of a EPIKOTE 1001 (EGC = 2220 mmol/kg)/EPIKURE DX 200 blend (ratio 70/30 based on weight solids) has been prepared according to the temperature/time profile described in Fig. 2 in the presence of 6% on solids of a non-ionic surfactant Q comprising of a 32% by weight of the reaction product of an 1/2 molar ratio mixture of EPIKOTE 1001 and of a poly(ethylene oxide)alcohol, containing 181 ethylene oxide units (i.e. 2 moles of PEO per mole E1001) and of 8% on solids of anionic surfactant A which has been specified in subsequent Table 1.

70 Gr of EPIKOTE 1001, 42.9 gr of EPIKURE DX 200-NM-70, 18.8 gr of a non-ionic surfactant Q and 14.2 gr of anionic surfactant A (56.2% solids, VOC:727 gr/kg solids) were introduced in a classical round bottom reactor of 500 ml with anchor stirrer and reflux condenser and stirred at 100 RPM during the whole process. After heating at 65-70 °C until a homogeneous liquid was obtained (during + 90 min; see Fig. 2), the heating was stopped but the mantle not removed. When the temperature of the mixture was at 45 °C (about 30 min. later), a mixture of 1.73 gr of dimethylethanolamine (60%

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neutralization of the acid groups of anionic surfactant A) in 4.8 gr of deionized water was added dropwise and followed by the addition of 14 gr of deionised water, still dropwise. This took about 15 min. during which the temperature decreased to 39 °C. The inversion took place at this point (68.5% non-volatile content [NVC]). Deionised water (11 gr) was again added dropwise. The mixture was stirred for 1 extra hour and then cooled to R.T. After one hour, 25 gr of deionized water were added dropwise and the mixture was stirred for another hour. Finally, 82.6 gr of deionized water were added dropwise over one hour under stirring before dumping.

Ex. 1: 40% Solids; VOC: 179.0 gr/kg solids; Brookfield viscosity (spindle 2, 60 RPM, 76% torque):~382cP (day 0).

The quality of the codispersion is very good: homogeneous, small particles and sharp particle size distribution (see Fig. 3). As previously explained, the distribution increases during storage and reaches and equilibrium (Fig. 3). The resulting codispersion is physically stable for months at room temperature (R.T.); there is no or very little settling after 6 months.

Table 1

Preparation of acrylic copolymer anionic surfactants A and B as disclosed in US patent 4,623,680.

About 1 kg of acrylic co-polymer is prepared in a 2 l glass reactor, equipped with an anchor stirrer, refridgerator, nitrogen inlet and thermocouple.

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Preparation	Anionic surfactant A	Anionic surfactant B
water	36.90 g	36.90 g
n-butanol	236.47 g	236.47 g
butylOXITOL	144.02 g	144.02 g

- Heated at 99 °C, stirring at 100 rpm

Styrene	234.00 g	234.00 g
ethylacrylate	109.89 g	109.89 g
acrylic acid	176.03 g	176.03 g

dibenzoyl peroxide

(75% in water)	36.90 g	49.20 g
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- The monomers and initiator are pre-blended at room temperature and added over 150 min. with an addition funnel to the reactor.

ButylOXITOL	11.40 g	11.40 g
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- used to rinse the funnel and added to the reactor
- The mixture is cooled to 93 °C in 10 min.
The system is maintained at 93 °C for 1 h.

dibenzoyl peroxide	5.18 g	6.91 g
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(75% in water)

- Maintain 1 h at
93 °C

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Table 1 (Cont'd)

butyLOXITOL	9.21 g	9.21 g
<ul style="list-style-type: none"> Cool 54 °C in 1 h 		
Preparation	Anionic surfactant A	Anionic surfactant B
PROPERTIES		
viscosity, Brookfield	7.6 Pa.s	4.8 Pa.s
solids content	55.2 %	55.4 %
acid value	241 mgKOH/- gsolid	242 mgKOH/- gsolid
VOC	727 gsolvent/- kgsolid	714 gsolvent/- kgsolid
GPC results Mn	2900 g/mol	2500 g/mol
Mw	5930 g/mol	5140 g/mol

EXAMPLE 2

Co-inversion of EPIKOTE 1055/EPIKURE DX 200-NM-70

A similar process to the one described for Example 1 (Fig. 2) can be applied in this case for EPIKOTE 1055 (Fig. 5). The main difference is the viscosity before inversion which is higher in this case. The inversion temperature has to be somewhat higher for this reason and EPIKURE DX 200-70-MN.

Codispersions made of a E 1055/DX 200 blend (ratio 70/30 based on weight solids) have been prepared (code: Ex. 2) in the presence of 7% on solids of non-ionic surfactant Q and of 6% on solids of anionic surfactant A.

70 Gr of E 1055, 42.9 gr of DX 200-NM-70, 21.9 gr of and 10.7 gr of anionic surfactant A (56.2% solids,

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VOC:727 gr/kg solids) were introduced in a classical round bottom reactor of 500 ml with anchor stirrer and reflux condenser and stirred at 100 RPM during the whole process. After heating at 85-90 °C until a homogeneous liquid was obtained (during + 80 min.), the power of the heating mantle was reduced. When the temperature of the mixture was around 55 °C (about 60 min. later), a mixture of 1.3 gr of dimethylethanolamine (60% neutralization of the acid groups of anionic surfactant A) in 4.2 gr of deionized water was added dropwise and followed by the addition of 13 gr of deionized water, still dropwise. This took about 20 min. during which the temperature decreased to ~50 °C. The inversion took place at this point (69% NVC). Deionized water (15 gr) was again added dropwise. The mixture was stirred for two extra hours and then diluted dropwise with deionized water (103.6 gr for Ex. 2A and 72.2 gr for Ex. 2B over one hour under stirring before dumping.

Ex. 2A: 45% Solids; VOC: 163 gr/kg solids; Brookfield viscosity (spindle 2, 60 RPM, 92% torque): ~460 cP (day 0).

The quality of the codispersion is very good: homogeneous, small particles and sharp particle size distribution ($D_n=0.66 \mu\text{m}$, $D_w=0.84 \mu\text{m}$). The resulting codispersion is physically stable for months at R.T.; there is no or very little settling after six months. No indication about chemical stability.

Here again, the viscosity of the codispersion becomes stabilized after two to three days. After this short period, the viscosity hardly varies (Fig. 4).

EXAMPLE 3

The replacement of DX 200-MN-70 in Example 2 PHENODUR 217 does not negatively affect the quality of the codispersion (PCB 98: VOC = 191 gr/kg solids; $D_n=0.5\mu\text{m}$;

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$D_w=0.8\mu\text{m}$; no settling over storage). At a solids content of 45%, the viscosity stabilizes after few days of storage at R.T. at about 300 cP which is similar to what was observed with Ex. 2B (Fig. 4).

5 EPIKOTE/resole codispersions containing binary blends of phenolic resins (DX 200 + another resol) have also been prepared.

From these experiments it may be concluded that DX 200-MN-70, which is definitely a good phenolic resin
10 for water-borne dispersions, is not the only one which can be co-inverted with EPIKOTE resins.

EXAMPLES 5 AND 6 AND COMPARATIVE EXAMPLE A

Codispersions have been prepared via the process described in Example 2 with various amounts of non-ionic
15 surfactants Q with the aim of optimising the level to the minimum required (Table 2).

Table 2

Compositions of co-dispersions with various amounts of non-ionic surfactants Q

Code	Comp. Ex. A	Ex. 5	Ex. 6	Ex. 2
E 1055/DX 200*	70/30	70/30	70/30	70/30
NIS-Q/AIS-A**	0/8.2	4/7	5.5/7	7/6
% neutralization***	60%	70%	70%	60%
Inversion point	47 °C, 62% NVC	44 °C, 73% NVC	43 °C, 71%	53 °C, 69% NVC
% solids	54%	50%	50%	45%
viscosity ****	100 cP	260 cP	980 cP	230 cP
VOC (gr/Kg solids)	190	178	176	164

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- * Ratio on solids
- ** Ratio on solids for 100 parts of solid resins
- *** % Neutralization of the acid groups of AIS-A by DMEA
- **** Brookfield, spindle 2, measured after 10 days of storage at R.T.

5

As shown in Table 2, the anionic-surfactant A (AIS-A) level was slightly increased when the amount of non-ionic surfactant Q (NIS-Q) was lowered. The neutralization degree was raised as well in Ex. 5 and Ex. 6 in order to increase the chance of success. From Table 2, it is clear that the more non-ionic surfactant Q (NIS-Q) which is present, the higher the viscosity is. The final solids content was subsequently lowered to keep a suitable viscosity. One can also say that the inversion point is similar for Ex. 5 and Ex. 6; the difference is not significant. At higher temperature, the NVC could be expected to be lower which is in agreement with what was observed when preparing Ex. 2 (Fig. 6). On the other hand, it is clear that the inversion point of Comp. Ex. A is far away from the expected area. Inversion could only occur at a much lower NVC, i.e. with more water, showing therefore that this blend is more difficult to invert.

10

15

20

The quality/stability of those four codispersion does increase with increasing amount of NIS-Q (Table 3). On the basis of these experiments, it seems difficult to get stable codispersions with less than 7 parts (solids) of NIS-Q per 100 parts of solid resins.

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- 20 -

Table 3

Influence of level of non-ionic
surfactant Q on co-dispersion quality

Code	Comp. Ex. A	Ex. 5	Ex. 6	Ex. 2
Visual quality	inhomo- geneous	homo- geneous	homogeneous	homo- geous
Particle size	bimodal $D_n=0.8 \mu\text{m}$; $D_w=3.5 \mu\text{m}$	monomodal $D_n=0.7 \mu\text{m}$; $D_w=1.1 \mu\text{m}$	monomodal $D_n=0.6 \mu\text{m}$; $D_w=0.9 \mu\text{m}$	monomodal $D_n=0.6 \mu\text{m}$; $D_w=0.8 \mu\text{m}$
Coale- scence*	complete phase separa- tion	yellowing 5% of large particles	slight yellowing slight broadening of particle size distributions	no
Settling	a lot	no	no	no

* After 6 weeks of storage at R.T.

5 EXAMPLES 7, 8 and 9

Amount and type of neutralizing amine.

It is known in the literature that various amines and
neutralization degrees can provide the aimed
stabilization effect in the so-called Glidden technology,
as known from US patent 4623,680, col 1, ex 1; Belgian
10 patent BE 854.476; S Kojima "Development of high
performance, waterborne coatings and the analysis of
their levelling flow" Doct Diss. Nagoya Inst. of
Technol.(1995) 46.

15 Beside the dispersion stabilization, it has also been
shown that it can influence the coating properties. It

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has been found that the use of ammonia or morpholine derivatives allow the wet adhesion to be improved.

In all the experiments carried out, the acrylic copolymer was neutralized by another frequently used amine species, DMEA, at a neutralization level of 60%.
Therefore, the DMEA was replaced by N-ethyl-morpholine (NEM), which has also been used for Glidden type products.

The replacement of DMEA in Ex. 2 by NEM at constant neutralization degree (60%) yields the codispersion. It is worthwhile to mention that, for Ex. 7, the particle size reduction by stirring after inversion was kept to its minimum: 50 RPM during one hour in place of 100 RPM for two hours. Despite this difference, a good quality codispersion similar to Ex. 2 was obtained (very little settling after three months of storage at R.T.; $D_n=0.2 \mu\text{m}$; $D_w=1.0 \mu\text{m}$).

The stabilized viscosity in both cases but the viscosity decrease after production takes more time with NEM (Fig. 7). The same applies to Ex. 2 when Ex. 7 is diluted to a solids of 40%.

Still following the procedure described in paragraph 2.2.2, the neutralization degree was either lowered to 35% (Ex. 8) or increased to 85% (Ex. 9). Good quality codispersions were obtained as well. However, it is clear that the weight average particle size is decreasing as the neutralization degree is raised. The particle size distribution becomes very sharp at 85% neutralization, as shown by the polydispersity (Table 3). The high polydispersity of Ex. 7 is presumably due to the poor particle size reduction applied after inversion in this particular case (50 RPM during 1 hour in place of 100 RPM for two hours).

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Code	Ex. 8	Ex.7	Ex. 9
Neutr. degree	35%	60%	85%
VOC (gr/kg solids)	161 gr/kg solids	167 gr/kg solids	173 gr/kg solids
D _n	0.33 µm	0.16 µm	0.60 µm
D _w	1.16 µm	1.00 µm	0.74 µm
D _w /D _n (poly-idispersity)	3.52	6.25	1.23

The viscosity behaviour is the same whatever the neutralization degree but the viscosity is higher for high neutralization degrees.

EXAMPLE 10

5 The same procedure as described in Example 2 is followed but with the following compounds:

EPIKOTE 1055 : 70 parts solids

EPIKURE DX 200-MN-70 : 25 parts solids

Bakelite 100 : 5 parts solids

10 This blend of unroles is used instead of DX 200 alone.

Nonionic surfactant Q : 7 parts solids

Anionic surfactant B : 6 parts solids

ButyLOXITOL : 10 parts (= additional
solvent added to
the other
chemicals).

N-Ethyl-Morpholine

(instead of dimethyl- : 1.8 parts
ethanolamine)

20 Inversion temperature was 61 °C (instead of 50 °C in example 2).

Properties: . D_n = 1.10 nm

. D_w = 1.56 nm

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. VOC = 250 gr/Kg solids

. Stable

List of materials used:

Epoxy resin EPIKOTE 1055 ex SHELL Nederland Chemie

5 Pernis (EGC = 1120)

Cocuring resin Phenol-formaldehyde resins (resole type)
EPIKURE DX 200 ex Shell (70% in butanol/
butyl OXITOL 2:1)10 PHENODUR PR 217 ex Hoechst (65% in
butanol)

Bakelite 100 ex Bakelite AG (solid)

Varcum 29101 via BASF (solid) equivalent
to Varcum 2890 from Reichhold

Surfactant PHB3 anionic surfactant B

15 propionic surfactant Q

Amine N-Ethyl Morpholine

Solvent butyLOXITOL

EXAMPLE 1120 Exactly the same procedure as described Example 10
was followed, excepted that Bakelite 100 is replaced by
VARCUM 29101.

Properties . stable

. VOC = 250 gr/kg solids

. D_n = 0.75 nm25 . D_w = 1.05 nmEXAMPLE 12Exactly the same procedure as described in Example 10
followed, excepted that Bakelite 100 is replaced by
PHENODUR PR 217.

30 Properties . stable

. VOC = 250 gr/kg solids

. D_n = 0.65 nm. D_w = 1.15 nm

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EXAMPLE 13

Exactly the same as Example 8 but E 1055 is replaced by E 1007 and N-ethyl-Morpholine is replaced with dimethylethanol amine.

5 Example: EPIKOTE 1007 : 70 parts solids
 EPIKURE DX 200-MN-70 : 30 parts solids
 NIS-Q : 7 parts solids
 AIS B : 6 parts solids
 dimethylethanolamine : 0.76 parts
10 + water.

Properties: . stable
 . VOC: 158 gr/kg solids
 . $D_n = 1.22$ nm
 . $D_w = 2.77$ nm

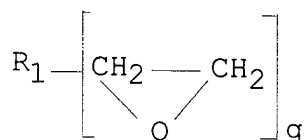
- 25 -

C L A I M S

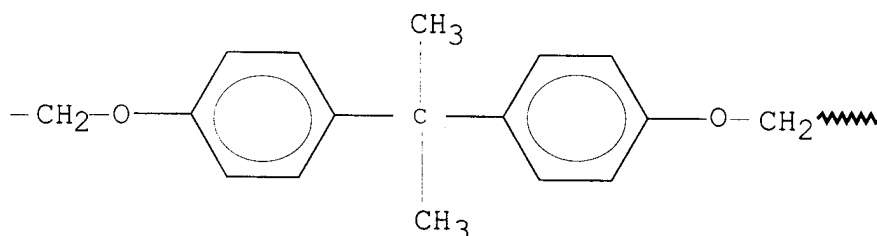
1. Stable aqueous coating dispersions, comprising a codispersion of at least a curable epoxy resin and a co-curable phenolic resin, and a combination of a non-ionic surfactant, comprising at least a reaction product of
5 poly(ethylene oxide)polymer alcohols and a diglycidylether of a dihydric phenol having an epoxy group content in the range of from 1000 to 6000 mmol/kg, or a block copolymer of ethylene oxide and propylene oxide alcohol, and an anionic surfactant, comprising a
10 random copolymer of at least one monovinyl arene, an alkyl acrylate, containing from 2 to 6 in the alkyl group, and acrylic acid, the copolymer having a weight average molecular weight in the range of from 3000 to 30.000, said composition partly neutralized by an amine
15 to a neutralization degree of from 25% to 95%.
2. Stable aqueous coating dispersions according to claim 1, characterized in that the anionic surfactant comprises a random copolymer of at least one monovinyl arene, an alkyl acrylate containing from 2 to 4 carbon
20 atoms in the alkyl group and acrylic acid.
3. Stable aqueous coating dispersions according to claims 1-2, characterized in that the composition is neutralised by a tertiary amine to a degree of from 35 to 85%.
- 25 4. Stable aqueous coating dispersions according to claims 1-3, characterized in that the non-ionic surfactant is a reaction product of poly(ethylene oxide) alcohol having an apparent molecular weight from 5000 to 10.000, and a diglycidyl ether of a dihydric phenol.

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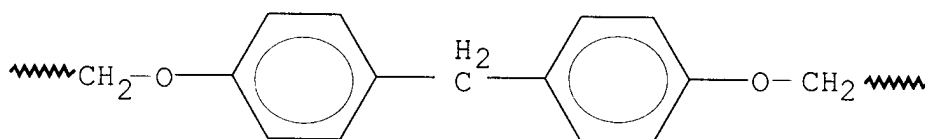
5. Stable aqueous coating dispersions according to claims 1-4, characterized in that epoxy resins have been dispersed, comprising one or more polyglycidyl ethers of polyhydric phenols having two or more epoxide groups and one or more six carbon aromatic rings present in the molecule, as represented by the structural formula



wherein R_1 represents a group



or a group



, and wherein g is an equal to or greater than 2, but less than or equal to 6.

6. Stable aqueous coating dispersions according to claims 1-5 characterized in that a phenolic resin component has been derived from bisphenol A and formaldehyde.

7. Stable aqueous coating dispersions according to claims 1-6, characterized in that the weight ratio between the dispersed epoxy resin and the curable phenolic resins is in the range of from 85/15 to 65/35.

8. Stable aqueous coating dispersions according to the claims 1-7, characterized in that the non-ionic

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surfactant has been derived from poly(ethoxy)polymers of the formula

$G-O-[C_2H_4-O]_x-H$, wherein G represents the residue of a polyalkylene glycol and wherein x has a value from 100 to 250 and preferably from 150 to 200.

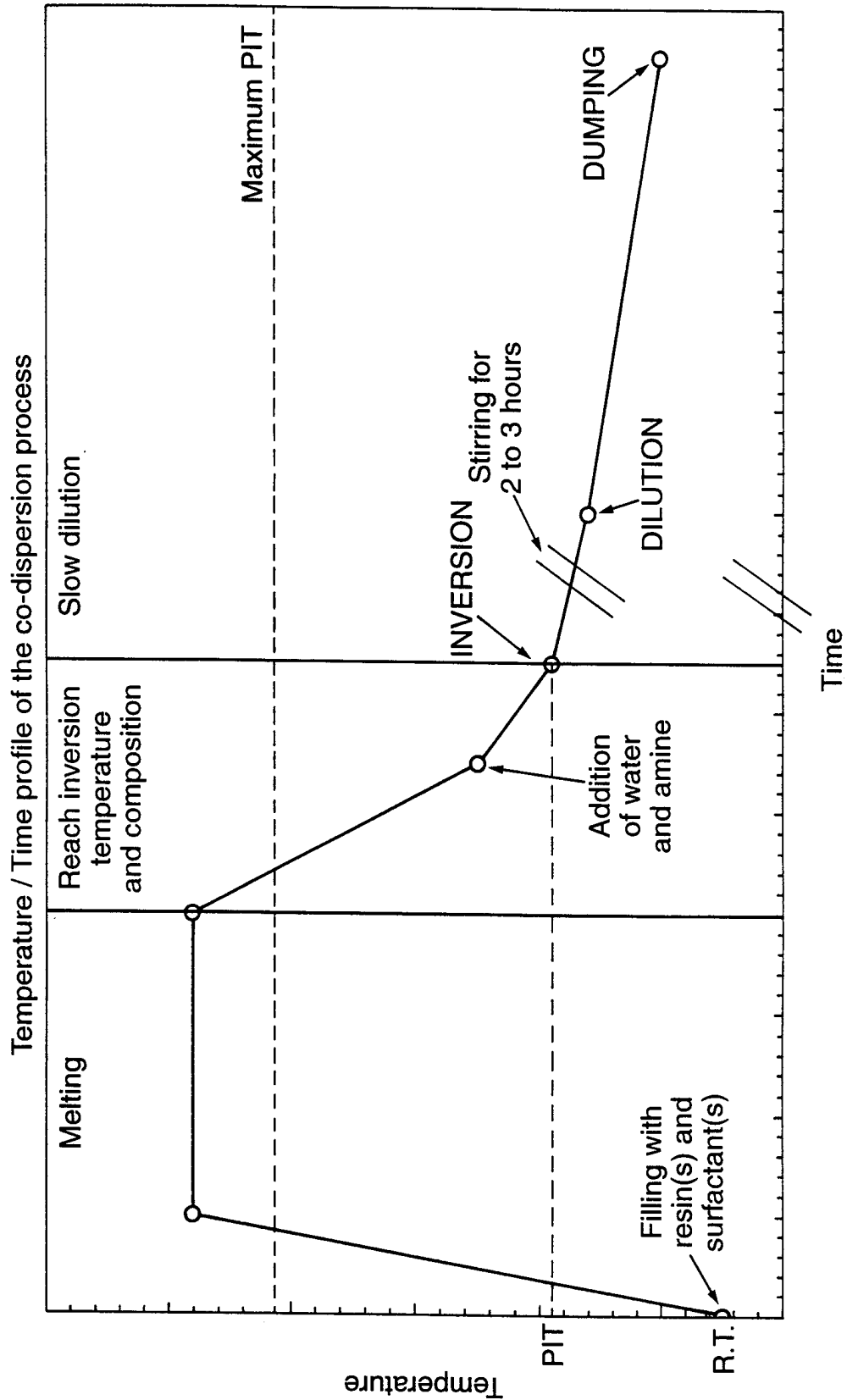
9. Stable aqueous coating compositions according to claim 8, characterized in that the dihydric alcohols to be used for the preparation of poly(ethylene oxide) alcohol or poly(propylene oxide) alcohol or combinations thereof, are polyethylene glycol, polypropylene glycols or a mixture thereof.

10. Process for the manufacture of stable aqueous coating dispersions comprising heating of a curable epoxy resin and a co-curable phenolic resin to be dispersed, and a combination of a non-ionic surfactant, comprising at least a reaction product of poly(ethylene oxide)polymer alcohols and a diglycidylether of a dihydric phenol having an epoxy group content in the range of from 1000 to 6000 mmol/kg, or a block copolymer of ethylene oxide and propylene oxide alcohol, and an anionic surfactant, comprising a random copolymer of at least one monovinyl arene, an alkyl acrylate, containing from 2 to 6 in the alkyl group, and acrylic acid, the copolymer having a weight average molecular weight in the range of from 3000 to 30.000, stirring until a homogeneous liquid mixture at a stirring speed in the range of from 50 to 150 RPM, adjusting the temperature to the desired Phase Inversion Temperature (PIT) and adding water dropwise and an aqueous solution of the neutralizing amine just before inversion occurs, to reach a neutralization degree of from 35% to 95% of the composition, continuation of adding water dropwise to avoid back inversion and stirring the obtained aqueous dispersion at a few degrees below the PIT for an extra one to four hours, optionally

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further dilution of the obtained aqueous dispersion and cooling.

Fig.1.



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Fig.2.

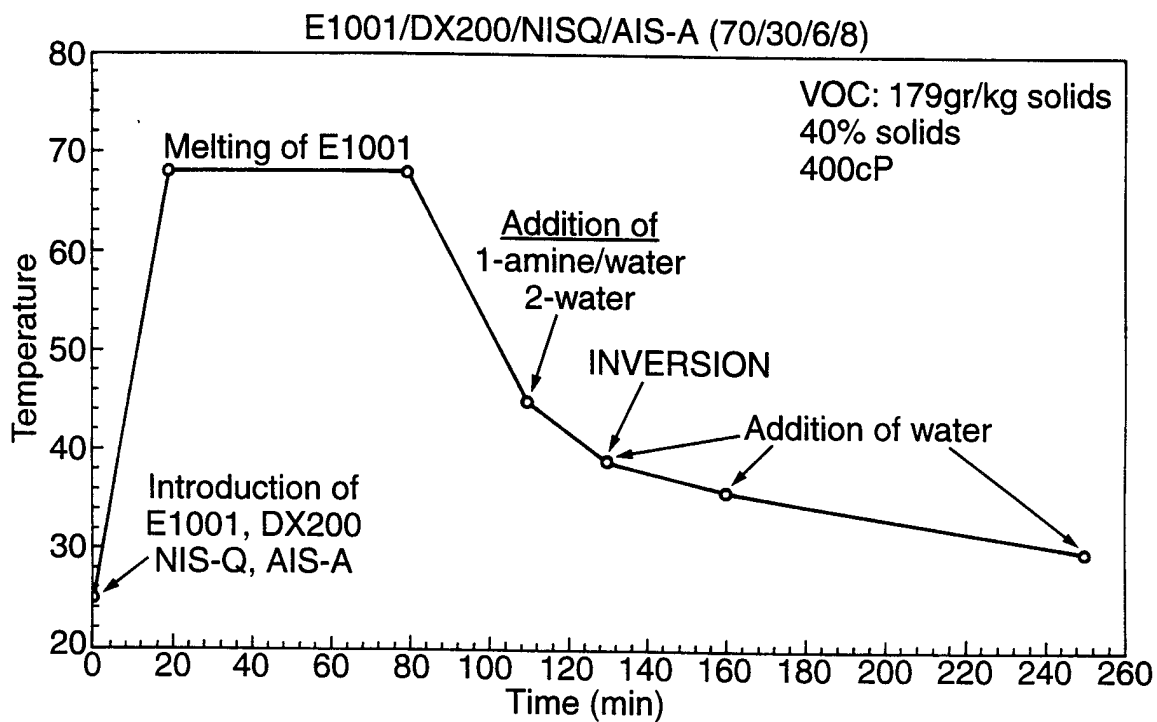
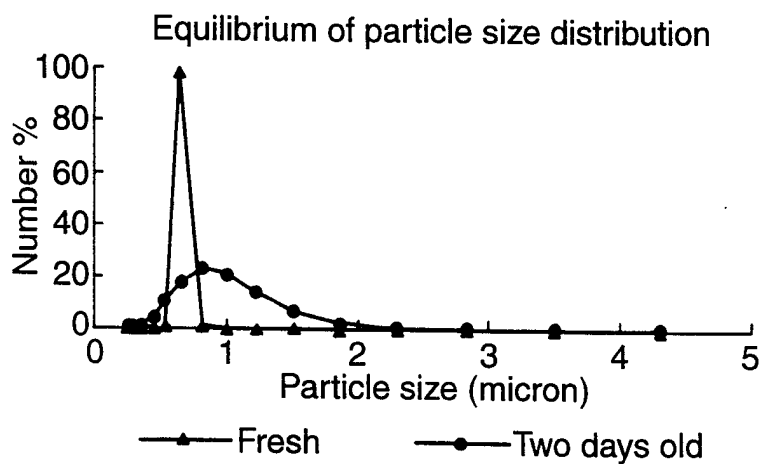


Fig.3.



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Fig.4.

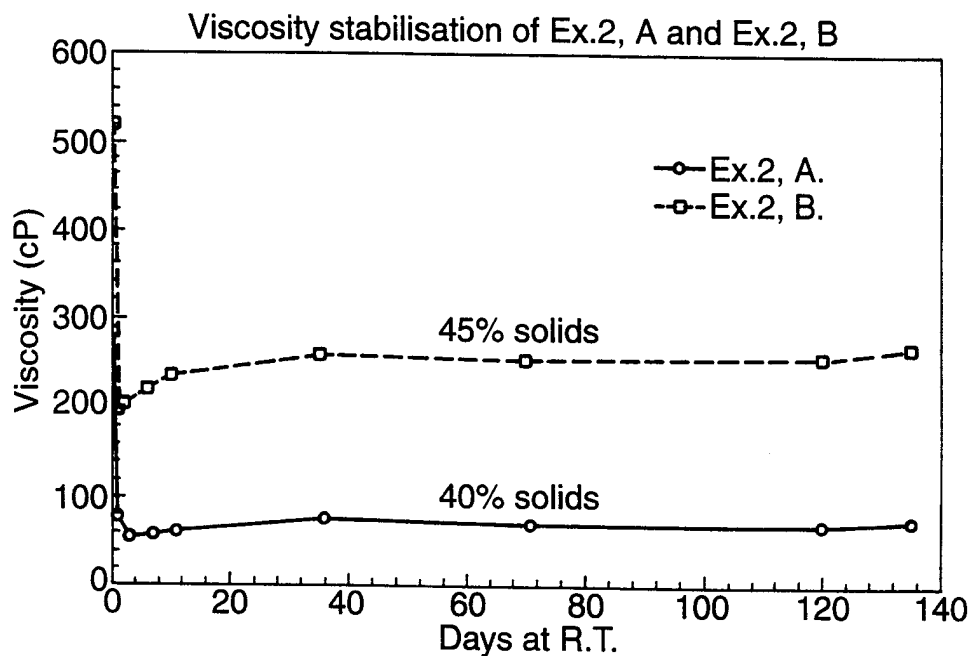
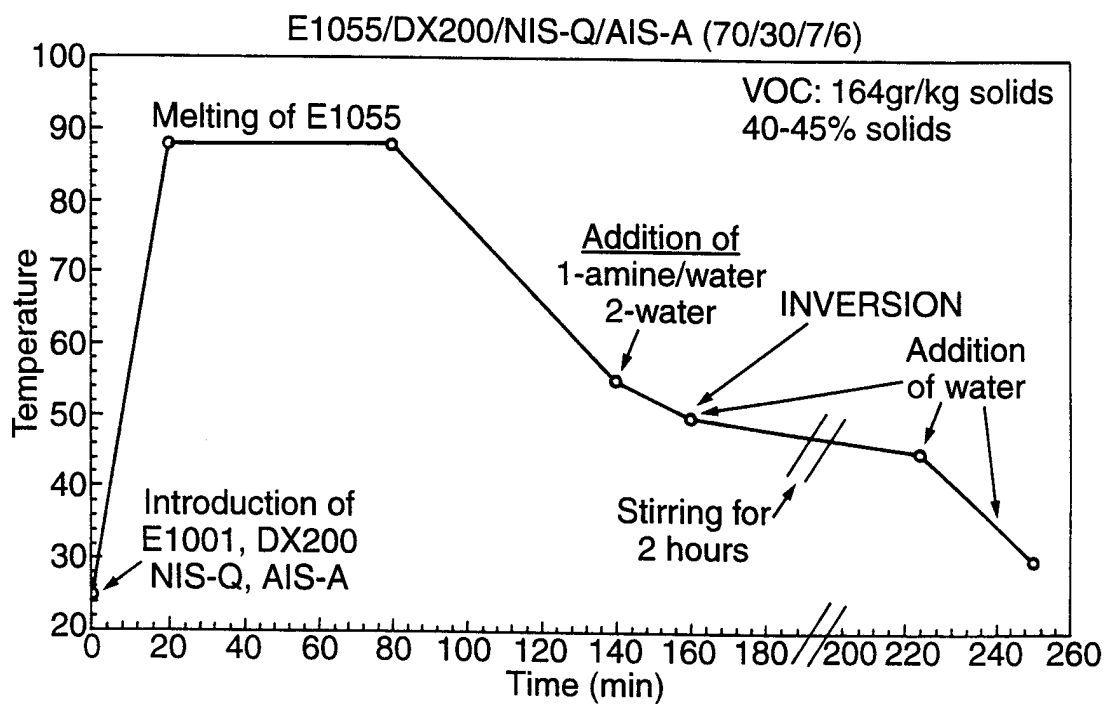


Fig.5.



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Fig.6.

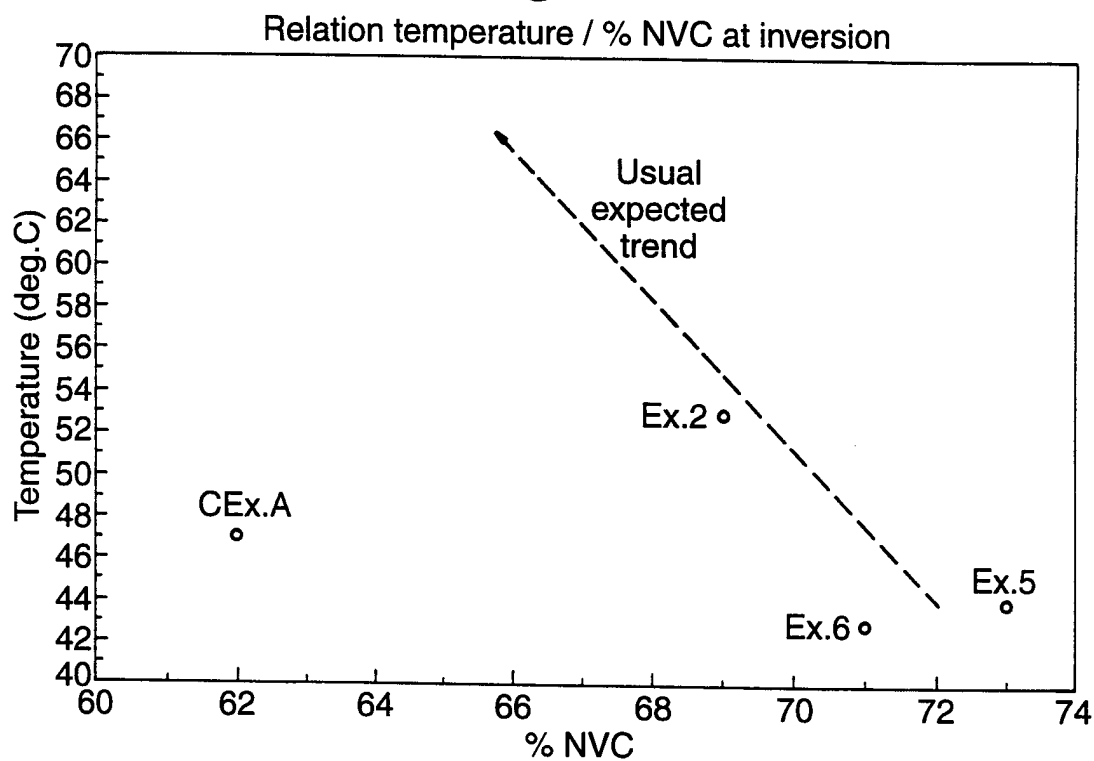
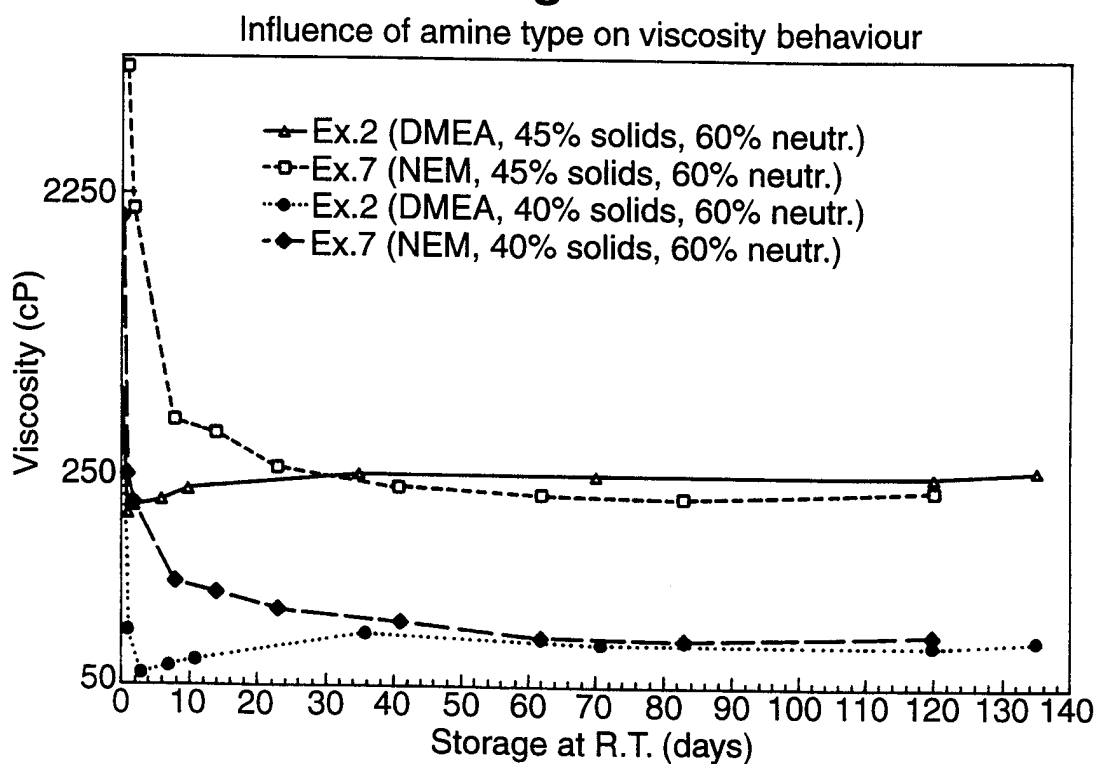


Fig.7.



INTERNATIONAL SEARCH REPORT

In ternational Application No

PCT/EP 98/01572

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D163/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 233 197 A (HOWELL, JR) 11 November 1980 see column 2, line 19 - column 4, line 47; claims 1,3 ---	1,8,9
A	WO 97 01609 A (BASF LACKE UND FARBEN) 16 January 1997 see page 3, line 28 - page 14, line 18; claim 1 ---	1
A	US 4 059 550 A (SHIMP) 22 November 1977 see column 1, line 38 - column 7, line 21; claim 1 ---	1
A	US 4 029 620 A (CHEN) 14 June 1977 see column 1, line 1 - column 2, line 68; claims 1-9 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 June 1998

Date of mailing of the international search report

02/07/1998

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INTERNATIONAL SEARCH REPORT

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PCT/EP 98/01572

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 204 511 A (CELANESE) 10 December 1986 see column 3, line 23 - column 7, line 4; claim 1 & US 4 623 680 A cited in the application -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/01572

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