

Hydroxy-functional polyurethane-polyureas and their use as dispersants

5 The present invention relates to emulsifiers, to a process for their preparation and to their use in aqueous dispersions of synthetic resins.

The range of water-dilutable binder systems is as yet still incomplete, so that the replacement of all conventional coating materials is currently still not possible.
10 In particular, the alkyd resins for the two-component coating and stoving enamel sectors, which are generally employed in the form of solutions in aliphatic or aromatic hydrocarbons, cannot at present be replaced by systems of equal quality. The low solids contents and the
15 poor shelf life of aqueous self-emulsifying alkyd resins, in addition to the no more than moderate water resistance of the films, are the main points of criticism by users.

In contrast, externally emulsified aqueous dispersions of synthetic resins (e.g. alkyd resins) should enable an
20 ideal solution of the problem: in this case, organic solvents can in general be dispensed with, and the use of emulsifiers permits a very good shelf life and high solids contents to be obtained despite the high molar mass of the synthetic resins. Despite this, even these
25 synthetic-resin dispersions have not acquired any great importance to date, since no-one has as yet come up with an optimum solution to the problem of stabilizing the dispersions without impairing the other properties.

Synthetic resins, such as alkyd resins and polyester
30 resins, are predominantly hydrophobic substances which do not per se form stable dispersions in water. It is therefore necessary to add emulsifiers. In general,

emulsifiers are substances with an amphipathic structure, i.e. their molecule consists of a hydrophobic and a hydrophilic moiety. As a consequence of this structure, the emulsifier molecules accumulate at the water-resin interface, reduce the interfacial tension, and thus enable the formation of very fine resin droplets in the aqueous phase.

The object of the invention was therefore to develop emulsifiers which are able in particular to stabilize dispersions in water of synthetic resins crosslinkable by melamine resin and isocyanate, and which do not adversely affect the film properties, especially in relation to gloss, reactivity and resistance to chemicals, weather and water.

Surprisingly, this object has been found to be achievable using polyurethane-polyurea emulsifiers bearing hydroxy-functional polyesters as their hydrophobic moiety.

The synthesis of high molecular weight polyurethane-polyureas by chain extension in the aqueous phase is known and is described, for example, in DE-A 26 24 442 and in EP-A 0 089 497. The suitability of particular polyurethane-polyureas as emulsifiers, however, was not known.

In the case of alkyd resin dispersions, the most favorable results achieved up to now have been with nonionic emulsifiers formed by condensation of ethylene oxide with octyl- or nonylphenol, i.e. in which the hydrophobic moiety is composed of the alkylphenol radical and the hydrophilic moiety of the polyethylene glycol chain. Systems of this type are described in the Patent Documents US-A 3 223 658, US-A 3 269 967 and US-A 3 440 193 and in the Laid-Open Specifications DD 88 833 and DE-A 27 54 091. Emulsifiers of this kind, added in quantities of from 5 to 10%, give alkyd resin dispersions of serviceable stability. The disadvantage is that these emulsifiers are of relatively low molecular

weight and consequently function as "internal plasticizers" in the alkyd resin film.

German Laid-Open Specifications DE-A 27 54 141, 27 54 092 and 24 40 946 describe alkyd resin dispersions which are
5 stabilized in the aqueous phase with the aid of emulsifiers comprising polyethylene glycols, fatty acids and/or allyl ethers.

EP-A 0 501 247 describes olefinically unsaturated polyurethanes comprising a β,γ -ethylenically unsaturated
10 ether alcohol component and their use as reactive emulsifiers. They are principally employed as emulsifiers for unsaturated polyester resins, but are unsuitable for alkyd resins.

Because of their double bonds, these emulsifiers can be
15 incorporated into the film during oxidative drying, thereby making it possible to obtain films of enhanced water resistance. Owing to a lack of reactive groups, they are unsuitable for stoving and for two-component applications. In addition, the low molar mass of these
20 emulsifiers permits limited migration of the emulsifiers in the film, impairing the properties of the film formed.

A further problem of these alkyd resin emulsions, in addition to their slow drying, is poor pigmentability: it is not possible by the methods described above to obtain
25 glossy highly pigmented films.

The object of the present invention, therefore, was to find aqueous coating systems which stand out from the known prior art by improved properties, especially in respect of reactivity, film hardness, pigmentability and
30 shelf life.

It has been possible to achieve this object by the provision of the hydrophilic polyurethane-polyureas.

described in more detail below and by their use, which is likewise described in more detail below.

The invention provides aqueous polyurethane-polyureas which are obtainable by reaction of:

- 5 a) a polyisocyanate component, consisting of at least one organic polyisocyanate, with
- b) at least one isocyanate-reactive polyesterpolyol which can be prepared from
 - i one or more dicarboxylic acids
 - 10 ii one or more diols and
 - iii if desired, one or more polyfunctional components whose functional groups are selected from hydroxyl and carboxyl groups, and
 - 15 iv if desired, a monofunctional carboxylic acid,
- c) if desired, an isocyanate-reactive fatty acid derivative,
- d) if desired, a compound of relatively high
20 functionality (functionality greater than 2) whose functional groups are selected from hydroxyl and carboxyl groups, and
- e) a polyalkylene glycol component having a number-average molar mass of from 750 to 10,000 g/mol and
- 25 f) a compound which contains active hydrogen atoms and in which the active hydrogen reacts with the NCO groups more quickly than water,

while maintaining a ratio of the number of isocyanate groups to the number of isocyanate-reactive hydrogen
30 atoms, based on all of the starting components a) to f), of from 0.6:1 to 1:1, wherein the proportion by mass of polyester-derived structural units in the emulsifier resin is from 10 to 60%, preferably from 12 to 40% and

particularly preferably from 18 to 30% and the proportion by mass of polyalkylene glycol-derived structural units in the emulsifier resin is from 25 to 75%, preferably from 30 to 60%.

- 5 The invention also provides for the use of these polyurethane-polyureas as reactive emulsifiers for curable synthetic resins, which are not per se dispersible in water, in the preparation of aqueous synthetic-resin dispersions.
- 10 As synthetic resins it is possible to use polyesters, polyurethanes, alkyd resins and other commercially available resins; the polyurethane-polyureas of the invention are particularly suitable as emulsifiers for alkyd resins.
- 15 As alkyd resins, it is preferred to employ commercially available types, which in certain cases are modified slightly in order to increase the shelf life. In preparing the dispersions, the resins are generally employed in the solvent-free state, although it is also possible to
- 20 add small quantities of solvent. In order to increase the shelf life, the alkyd resin can be modified such that its acid number is as low as possible. This modification can either be carried out during the preparation of the alkyd resin, by esterification with further alcohols, or the
- 25 acid groups can also be esterified subsequently, using an epoxide. Suitable epoxide compounds are all monoepoxides, which are described, for example, in the handbook "Epoxidverbindungen und Epoxidharze" [Epoxide Compounds and Epoxy Resins] by A.M. Paquin, Springer Verlag, Berlin
- 30 1958, Chapter IV, and in the "Handbook of Epoxy Resins" by Lee and Neville, 1967, Chapter 2. Particularly suitable are epoxidized fatty acids and, for example, *Cardura E10 (*Versatic acid glycidyl ester from Shell Chemical).

The polyurethane-polyureas according to the invention are essentially reaction products of the abovementioned starting components (a) to (f), preferably prepared using, per mole of component (a), from 0.05 to 0.4 mol of component (b), from 0 to 0.3 mol of component (c), from 0 to 0.6 mol of component (d), from 0.1 to 0.8 mol of component (e) and from 0.01 to 0.3 mol of component (f). Particular preference is given to the use, per mole of component (a), of from 0.05 to 0.25 mol of component (b), from 0.05 to 0.25 mol of component (c), from 0.05 to 0.4 mol of component (d), from 0.2 to 0.6 mol of component (e) and from 0.02 to 0.25 mol of component (f).

Component (a) comprises at least one organic polyisocyanate. Suitable polyisocyanates are any organic polyisocyanates known per se from polyurethane chemistry which contain isocyanate groups attached to aliphatic, cycloaliphatic and/or aromatic structures and which preferably have a molar mass of from 168 to 1,000 g/mol, preferably from 168 to 300 g/mol. Diisocyanates are preferably employed. However, it is also possible to replace up to 10% of the diisocyanates by isocyanates with a functionality of three or more. Preference is given to those isocyanate compounds in which the isocyanate groups are attached to aliphatic carbon atoms. Suitable examples are 1,6-diisocyanatohexane (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (IPDI), m-tetramethylxylylene diisocyanate (TMXDI), 4,4'-diisocyanatodicyclohexylmethane, and also 4,4'-diisocyanatodiphenylmethane, its technical-grade mixtures with 2,4'-diisocyanatodiphenylmethane and, if appropriate, oligomers of these diisocyanates, and 2,4-diisocyanatotoluene and its technical-grade mixtures with 2,6-diisocyanatotoluene. Diisocyanates of the type given as examples are preferred as component (a), but more highly functional polyisocyanates such as, for example, biuret-, isocyanurate- or urethane-modified polyisocyanates based on the simple diisocyanates mentioned by way of example

are also suitable in principle. These derivatives generally have a molar mass of up to 1,000 g/mol.

The preparation of such derivatives is described, for example, in US-A 3 124 605, US-A 3 183 112,
5 US-A 3 919 218 and US-A 4 324 879.

The hydroxy-functional polyesters (b) are linear or branched polyesters having a hydroxyl number (OHN) of from 30 to 180 mg/g and an acid number (AN) of from 1 to 15 mg/g. They are built up by customary polycondensation
10 methods from dicarboxylic acids, dioles and, if desired, compounds of higher functionality, the dicarboxylic acid component (i) being selected from saturated and unsaturated aliphatic, aromatic and cycloaliphatic dicarboxylic acids, dimeric fatty acids, and mixtures of two or more
15 of these dicarboxylic acids. Examples of such dicarboxylic acids are oxalic, malonic, glutaric, pimelic, adipic, azelaic, sebacic, succinic, fumaric, maleic and itaconic acid, 1,3-cyclopentanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, phthalic, terephthalic and
20 isophthalic acid, tetrahydrophthalic acid, 2,5-norbornanedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-sulfonyldibenzoic acid and 2,5-naphthalenedicarboxylic acid, and the esters
25 and anhydrides thereof.

Preferred dicarboxylic acids (i) are phthalic, isophthalic and terephthalic acid, tetrahydrophthalic acid, adipic acid, succinic acid, succinic anhydride, dimeric fatty acids, sebacic and azelaic acid, 1,3- and 1,4-cyclohexanedicarboxylic and glutaric acid, and the esters and
30 anhydrides thereof.

The glycol component (ii) can comprise low molecular weight aliphatic, cycloaliphatic or aromatic glycols. Examples of the glycols are ethylene glycol, 1,2-propanediol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-
35 diol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-

butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, perhydrobisphenol A, p-xylylenediol, 2-ethyl-
5 and 2-butylpropanediol.

As the polyfunctional component (iii), which preferably contains from 3 to 6 hydroxyl and/or carboxyl groups, preference is given to polyols such as trimethylolpropane, trimethylolethane, glycerol, ditrimethylolpropane, pentaerythritol and dipentaerythritol; polycarboxylic acids such as trimellitic acid (anhydride), pyromellitic acid (anhydride) and benzophenonetetracarboxylic acid; hydroxycarboxylic acids, such as
10 dimethylolpropionic acid, dihydroxypropionic acid, dihydroxysuccinic acid, malic acid, tartaric acid,
15 mesotartaric acid and dihydroxyhexanoic acid; and polyanhydrides, as described in DE-A 28 11 913, or mixtures of two or more of these compounds, the proportion of the polyfunctional component (iii) being preferably from 0 to
20 30 mol per 100 mol of all of components (i) to (iv).

Particular preference is given to the use of trimethylolpropane as branching agent (iii).

The monofunctional carboxylic acid component (iv) can comprise aliphatic saturated and unsaturated monocarboxylic acids. Linear unsaturated monocarboxylic acids having
25 10 to 22 carbon atoms are particularly preferred, such as occur, for example, in natural fats and oils. Specific examples of suitable saturated fatty acids are 2-ethylhexanoic acid, isononanoic acid, lauric acid, *Versatic
30 acid or coconut fatty acid.

Examples of suitable unsaturated fatty acids are oleic acid, linoleic acid and linolenic acid. Particular preference attaches to unsaturated monocarboxylic acids having an iodine number of more than 125 g/(100 g) and
35 from 16 to 20 carbon atoms. These include, in particular,

fatty acids containing isolated unsaturation, having two or three isolated double bonds of different steric configuration, or corresponding fatty acids with conjugated double bonds. Such fatty acids are present, for example, in natural oils, such as linseed oil, soya oil, safflower oil, cottonseed oil or castor oil, sunflower oil, groundnut oil, wood oil and ricinene oil. The unsaturated fatty acids obtained from these oils are linseed oil fatty acid, safflower oil fatty acid, tall oil fatty acid, cottonseed fatty acid, groundnut oil fatty acid, wood oil fatty acid, ricinenic fatty acid or sunflower oil fatty acid.

The fatty acids can also be introduced into the polyester during synthesis by transesterification from the respective oils.

The isocyanate-reactive fatty acid derivative (c) contains from 10 to 40 carbon atoms, at least one hydroxyl or amino group and if appropriate at least one, or two or more, C=C double bonds. Examples of these fatty acid derivatives are fatty alcohols, such as lauryl alcohol, stearyl alcohol, oleyl alcohol, linoleyl alcohol or linolenyl alcohol. It is also possible to employ ethoxylated fatty alcohols containing from 1 to 30, preferably 1 to 20, ethylene oxide units, for example *Genapol O-020 (Hoechst AG). Other alcohols which can be mentioned are those obtained by reaction from an unsaturated acid and an epoxide, for example by reaction of a fatty acid, such as linseed oil fatty acid or soya oil fatty acid, with an epoxide, such as *Cardura E10 or other epoxides. It is also possible to employ partial esters of polyhydroxy compounds such as glycerol, trimethylolpropane or pentaerythritol and also partially hydrolyzed fats, for example *Ligalub 40/1 (fatty acid glycerol monoester from P. Graeven Fettchemie). Also suitable, furthermore, are the fatty amines, for example *Genamin grades (Hoechst AG).

The polyfunctional component (d) used, which preferably contains 3 to 6 hydroxyl and/or carboxyl groups, can for example be trimethylolpropane, trimethylolethane, glycerol, ditrimethylolpropane, pentaerythritol or
5 dipentaerythritol. Hydroxyalkanecarboxylic acids are similarly preferred, especially bishydroxyalkanecarboxylic acids, such as dimethylolpropionic acid, for example, with the use of glycolic acid, malic acid, tartaric acid or 2,6-dihydroxybenzoic acid also being possible. Other
10 possibilities are the mixtures of two or more of these compounds.

Component (e) comprises linear polyoxyalkylene glycols (polyether glycols) having a number-average molar mass of from 750 to 10,000 g/mol, preferably from 1,000 to
15 6,000 g/mol, in which at least 80 mol and preferably 100 mol of each 100 mol of alkylene oxide units are ethylene oxide units.

The term polyethylene glycols is thus intended to comprise not only actual polyethylene glycols whose alkylene
20 oxide units are exclusively ethylene oxide units but also polyalkylene glycols whose alkylene oxide units are predominantly, i.e. to the extent of at least 80 mol per 100 mol, ethylene oxide units. "Mixed" polyalkylene glycols of this kind are formed, for example, by using
25 mixtures of different alkylene oxides, for example ethylene oxide and propylene oxide in a quantitative ratio of about 8:2, in the preparation of the polyether glycols by alkoxylation of suitable divalent starter molecules, for example water, ethylene glycol or
30 propylene glycol.

The compounds employed as component (f) are also referred to as chain extenders. Examples which may be mentioned are polyfunctional primary and secondary amines, hydrazine, and substituted hydrazines.

Particular preference is given to di- and polyamines such as ethylenediamine, butylenediamine, tolylenediamine, isophoronediamine, 3,3'-dichlorobenzidine; polyalkylene-polyamines, such as triethylenetetramine, diethylenetri-
5 amine, hydrazine and substituted hydrazines, such as dimethylhydrazine. Also suitable are those chain extenders which carry additional functional groups, for example alkanolamines such as N-aminoethylethanolamine, ethanolamine and diethanolamine. It is also possible to
10 use carboxyl-containing amines or hydrazides, for example lysine, glutamic acid and adipic monohydrazide.

The hydrophilic polyurethanes of the invention which are to be used as emulsifiers are prepared in two stages. First of all, a hydrophilic isocyanate-functional pre-
15 polymer is synthesized from components (a) to (e) and then, after dispersion in water, is reacted with the chain extenders described under (f).

The preparation of the prepolymer by reacting the above-mentioned starting components (a) to (e) can be carried
20 out in bulk or in solvents which are inert with respect to isocyanate groups, such as ketones, tertiary alcohols, (substituted) aromatic compounds, ethers or esters, examples being acetone, methyl ethyl ketone, ethyl acetate, butyl acetate, N-methylpyrrolidone, toluene and
25 mixtures of such solvents, preferably keeping to reaction temperatures of from 20 to 200°C, in particular from 50 to 150°C.

In this procedure, components (b) to (e) can be reacted with component (a) simultaneously or in steps.

30 In practice, therefore, one example of a possible procedure is to introduce components (b) to (e) as initial charge and to react this charge, within the abovementioned temperature ranges, with the isocyanate (a) until the NCO content has fallen to a specific value, which
35 must be calculated.

This prepolymer is then dispersed in water and reacted with component (f) at temperatures from 40 to 100°C, resulting in chain extension. After a reaction time of from 1 to 5 hours, the aqueous dispersion of the emulsifier is then obtained following, if appropriate, further addition of ammonia or amines.

In this context, in principle, the nature and proportions of the starting components are chosen within the specified ranges such that, based on all components (a) to (f), a ratio of the number of isocyanate groups to the number of reactive hydrogen atoms of from 0.6:1 to 1:1 is ensured.

The reactions of urethane formation can be catalyzed in a manner known per se, for example with tin octoate, dibutyltin dilaurate or tertiary amines. Similarly, the polyurethane can be protected against premature and unwanted polymerization or oxidation by the addition of suitable inhibitors and antioxidants in respective amounts of from 0.001 to 0.3%, based on the mass of the overall mixture.

The hydrophilic polyurethane-polyureas obtained in this way, which comprise unsaturated groups, have a number-average molar mass (gel permeation chromatography, polystyrene as standard) M_n of from 2 to 40 kg/mol; preferably from 2 to 20 kg/mol, a content by mass of olefinic double bonds (calculated as $-C=C-$, molar mass = 24 g/mol) of from 0 to 6%, preferably from 0.1 to 4%, a content by mass of polyester units of from 15 to 60%, preferably from 18 to 40%, and a content by mass of ethylene oxide units $-CH_2-CH_2-O-$, incorporated via polyethylene glycol, of from 25 to 75%, preferably from 30 to 60%.

The hydrophilic polyurethane-polyureas represent valuable emulsifiers for hydrophobic synthetic resins which are not dispersible in water. These synthetic resins

generally have a number-average molar mass (M_n ; gel permeation chromatography, polystyrene as standard) of from 500 to 10,000, preferably from 500 to 5,000, g/mol. They are particularly suitable as an emulsifier for alkyd
5 resins and oil-free polyesters, and preferably for polyesters modified with unsaturated fatty acids.

Synthetic-resin dispersions of this kind are prepared by first mixing these synthetic resins with the above-described polyurethane-polyurea dispersions, in the
10 presence if desired of the inert solvents described above. Heating of the mixture to temperatures of from about 30 to about 100°C may be necessary here.

The mixtures comprise from 40 to 97, preferably from 50 to 95, parts by weight of the said hydrophobic synthetic
15 resins in a blend with from 3 to 60, preferably from 5 to 50, parts by weight of the said hydrophilic polyurethane-polyurea dispersions, which act as emulsifiers. However, it is important to select the nature and proportions of the individual components, within the scope of the
20 comments made, such that the content by mass in the water-dispersible mixtures of ethylene oxide units originating from component (e) is not more than 20%, preferably not more than 15%.

The mixtures of synthetic resins and emulsifier dispersion are then dispersed in water, which can be done
25 either by simply stirring water into the initial mixture of the synthetic resins with the emulsifier emulsion, using conventional dissolvers or stirrers, or else by pouring the mixture into water with vigorous stirring. If
30 desired, it is possible initially to add part of the water to the mixture described above and then to pour this mixture, with stirring, into the residual quantity of water. In this way, stable oil-in-water emulsions can be obtained.

The aqueous dispersions obtained in this way are valuable aqueous binders for coating compositions. They can be used as they are or in combination with the auxiliaries and additives known from coatings technology, such as, 5 for example, fillers, pigments, solvents, leveling assistants, for producing coatings on any desired substrates.

Suitable substrates are paper, cardboard packaging, leather, wood, plastics, nonwovens, films, textiles, 10 ceramic materials, mineral materials, glass, metal, coated metal, synthetic leather and photographic materials, for example paper provided with a photographic coat.

These coating compositions can be applied in a known 15 manner by spraying, knife coating, roller coating, brush coating, dipping or casting. After the water and any inert solvents used have been evaporated, the coatings can be crosslinked by reaction with melamine resins or isocyanates at temperatures up to 250°C, or by oxidative 20 drying.

In the examples below, all percentages are by mass.

Examples

Preparation of the polyurethane-polyurea dispersions

Example E1

25 26.8 g of dimethylolpropionic acid are suspended at about 80°C in 100 g of polyethylene glycol 1000. Then, after heating to 70°C, 51 g of tetramethylxylylene diisocyanate (TMXDI) and 36.6 g of tolylene diisocyanate (TDI) are added dropwise at a rate such that the temperature does 30 not exceed 70°C (about 30 min). Once all of the isocyanate has been added, the mixture is stirred at the temperature for one hour and then the reaction temperature is raised to 90°C. The temperature is maintained until

the isocyanate content has fallen to 3.8%. Then 30 g of
•Genapol O-100 and 121 g of a polyester formed from
isophthalic acid, adipic acid, dimeric fatty acid and
hexanediol (OHN 46 mg/g, AN 2 mg/g) are added and the
5 mixture is stirred at 90°C until the NCO content has
fallen to 1.15%. Then 400 g of heated deionized water are
added with vigorous stirring over the course of 10 min-
utes. This is followed directly by the rapid (about
5 min) dropwise addition of 3.75 g of triethylenetetra-
10 mine dissolved in 37.5 g of water. After the addition of
4.5 g of triethylamine and after reaction at 80°C for
3 hours, a further 4.4 g of triethylamine and 1000 g of
deionized water are added and then the mixture is cooled.
A pastelike dispersion is obtained.

15 **Example E2**

26.8 g of dimethylolpropionic acid are suspended at about
80°C in 100 g of polyethylene glycol 1000. Then, after
heating to 70°C, 51 g of tetramethylxylylene diisocyanate
(TMXDI) and 36.6 g of tolylene diisocyanate (TDI) are
20 added dropwise at a rate such that the temperature does
not exceed 70°C (about 30 min). Once all of the isocyan-
ate has been added, the mixture is stirred at the tem-
perature for one hour and then the reaction temperature
is raised to 90°C. The temperature is maintained until
25 the isocyanate content has fallen to 3.8%. Then 30 g of
Genapol O-100 and 60 g of a polyester formed from iso-
phthalic acid, adipic acid, neopentyl glycol and tri-
methylolpropane (OHN 107 mg/g, AN 3 mg/g) are added and
the mixture is stirred at 90°C until the NCO content has
30 fallen to 1.4%. Then 400 g of heated deionized water are
added with vigorous stirring over the course of 10 min-
utes. This is followed directly by the rapid (about
5 min) dropwise addition of 3.75 g of triethylenetetrami-
ne dissolved in 37.5 g of water. After the addition of
35 4.5 g of triethylamine and after reaction at 80°C for
3 hours, a further 4.4 g of triethylamine and 1000 g of
deionized water are added and then the mixture is cooled.
A pastelike dispersion is obtained.

Example E3

26.8 g of dimethylolpropionic acid are suspended at about 80°C in 50 g of polyethylene glycol 1000 and 100 g of polyethylene glycol 2000. Then, after heating to 70°C, 51 g of tetramethylxylylene diisocyanate (TMXDI) and 36.6 g of tolylene diisocyanate (TDI) are added dropwise at a rate such that the temperature does not exceed 70°C (about 30 min). Once all of the isocyanate has been added, the mixture is stirred at the temperature for one hour and then the reaction temperature is raised to 90°C. The temperature is maintained until the isocyanate content has fallen to 3.2%. Then 117 g of a polyester formed from isophthalic acid, adipic acid and neopentyl glycol (OHN 95 mg/g, AN 4 mg/g) are added and the mixture is stirred at 90°C until the NCO content has fallen to 1.1%. Then 400 g of heated deionized water are added with vigorous stirring over the course of 10 minutes. This is followed directly by the rapid (about 5 min) dropwise addition of 3.75 g of triethylenetetramine dissolved in 37.5 g of water. After the addition of 4.5 g of triethylamine and after reaction at 80°C for 3 hours, a further 4.4 g of triethylamine and 1000 g of deionized water are added and then the mixture is cooled. A pastelike dispersion is obtained.

Example E4

400 g of polyethylene glycol 4000 are initially introduced into the flask. After heating to 70°C, 49 g of tetramethylxylylene diisocyanate (TMXDI) are added dropwise at a rate such that the temperature does not exceed 90°C (about 30 min). Once all of the isocyanate has been added stirring is continued at this temperature until the isocyanate content has fallen to 1.9%. Then 117 g of a polyester formed from isophthalic acid, adipic acid and neopentyl glycol (OHN 95 mg/g, AN 4 mg/g) are added and the mixture is stirred at 90°C until the NCO content has fallen to 0.75%. Then 400 g of heated deionized water are added with vigorous stirring over the course of 10 minutes. This is followed directly by the

rapid (about 5 min) dropwise addition of 3.75 g of triethylenetetramine dissolved in 37.5 g of water. After reaction at 80°C for 3 hours a further 1000 g of deionized water are added and then the mixture is cooled.

5 A pastelike dispersion is obtained.

Example E5

26.8 g of dimethylolpropionic acid are suspended at about 80°C in 100 g of polyethylene glycol 1000. Then, after heating to 70°C, 51 g of tetramethylxylylene diisocyanate (TMXDI) and 36.6 g of tolylene diisocyanate (TDI) are added dropwise at a rate such that the temperature does not exceed 70°C (about 30 min). Once all of the isocyanate has been added, the mixture is stirred at the temperature for one hour and then the reaction temperature is raised to 90°C. The temperature is maintained until the isocyanate content has fallen to 3.8%. Then 30 g of Genapol O-100 and 71 g of a polyester formed from isophthalic acid, adipic acid, soya oil fatty acid, neopentyl glycol and trimethylolpropane (OHN 90 mg/g, acid number 5 mg/g) are added and the mixture is stirred at 90°C until the NCO content has fallen to 1.3%. Then 400 g of heated deionized water are added with vigorous stirring over the course of 10 minutes. This is followed directly by the rapid (about 5 min) dropwise addition of 3.75 g of triethylenetetramine dissolved in 37.5 g of water. After the addition of 4.5 g of triethylamine and after reaction at 80°C for 3 hours, a further 4.4 g of triethylamine and 1000 g of deionized water are added and then the mixture is cooled. A pastelike dispersion is obtained.

Example E6

26.8 g of dimethylolpropionic acid are suspended at about 80°C in 150 g of polyethylene glycol 1500 and 27 g of Ocenol HD 150 (unsaturated fatty alcohol, iodine number 130). Then, after heating to 70°C, 49 g of tetramethylxylylene diisocyanate (TMXDI) and 35 g of tolylene diisocyanate (TDI) are added dropwise at a rate such that

the temperature does not exceed 70°C (about 30 min). Once all of the isocyanate has been added, the mixture is stirred at the temperature for one hour and then the reaction temperature is raised to 85°C. The temperature is maintained until the isocyanate content has fallen to about 1.5%. Then, with vigorous stirring, 475 g of heated deionized water to which 3.5 g of diethylenetriamine have been added are introduced over the course of 10 minutes. After reaction at 80°C for 3 hours, 7 g of 25% ammonia water, diluted with 64 g of deionized water, are added and the mixture is cooled. A pastelike dispersion is obtained.

Dispersions

Example D1

220 g of emulsifier E1 are added to 200 g of a commercial alkyd resin with an oil content of 34% (Alftalat AF 342 100%) and the mixture is stirred at 70°C for about 60 min until it is homogeneous.

Following the addition of 1 ml of ammonia water (25%), 70 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 2 hours). A milky, pseudoplastic dispersion is obtained.

Example D2

205 g of emulsifier E3 are added to 200 g of a commercial urethane group-containing oil-free polyester having an OHN of 120 mg/g and an AN of 3 mg/g and the mixture is stirred at 70°C for about 60 min until it is homogeneous. Following the addition of 1 ml of ammonia water (25%), 50 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 1 hour). A milky, pseudoplastic dispersion is obtained.

Example D3

140 g of emulsifier E3 are added to 200 g of a commercial oil-free polyester having an OHN of 115 mg/g and an AN of 5 mg/g (Alftalat AN 950) and the mixture is stirred at 70°C for about 60 min until it is homogeneous.

Following the addition of 1 ml of ammonia water (25%), 50 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 1 hour). A milky, pseudoplastic dispersion is obtained.

5 **Example D4**

230 g of emulsifier E5 are added to 200 g of a commercial alkyd resin with an oil content of 62% (e.g. Alftalat AS 632 100%) and the mixture is stirred at 50°C for about 60 min until it is homogeneous.

- 10 Following the addition of 1 ml of ammonia water (25%), 70 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 2 hours). A milky, pseudoplastic dispersion is obtained.

- 15 All of the other emulsifiers listed are processed to give dispersions in accordance with the examples described above.



Patent claims

1. A water-dispersible polyurethane-polyurea which is obtainable by reaction of:
 - 5 a) a polyisocyanate component, consisting of at least one organic polyisocyanate, with
 - b) at least one isocyanate-reactive polyesterpolyol which can be prepared from
 - i one or more dicarboxylic acids
 - 10 ii one or more diols and
 - iii if desired, one or more polyfunctional components whose functional groups are selected from hydroxyl and carboxyl groups, and
 - 15 iv if desired, a monofunctional carboxylic acid,
 - c) if desired, an isocyanate-reactive fatty acid derivative,
 - d) if desired, a compound of relatively high
 - 20 functionality (functionality greater than 2) whose functional groups are selected from hydroxyl and carboxyl groups, and
 - e) a polyalkylene glycol component having a molar mass of from 750 to 10,000 g/mol and
 - 25 f) a compound which contains active hydrogen atoms and in which the active hydrogen reacts with the NCO groups more quickly than water,
- while maintaining a ratio of the number of isocyanate groups to the number of isocyanate-reactive
- 30 hydrogen atoms, based on all of the starting components a) to f), of from 0.6:1 to 1:1, wherein the proportion by mass of polyester-derived structural



units in the polyurethane-polyurea is from 10 to 60% and the proportion by mass of polyalkylene glycol-derived structural units is from 25 to 75%.

- 5 2. The use of a polyurethane-polyurea as claimed in claim 1 as an emulsifier in synthetic resins which cannot be dispersed alone in water, in the preparation of aqueous synthetic-resin dispersions, with or without the use of further emulsifiers.
- 10 3. A polyurethane-polyurea as claimed in claim 1, wherein the proportion by mass of structural units derived from polyester is from 18 to 30%.
4. A polyurethane-polyurea as claimed in claim 1, wherein the proportion by mass of structural units derived from polyalkylene glycol is from 30 to 60%.
- 15 5. A polyurethane-polyurea as claimed in claim 1, wherein the polyisocyanates a) are diisocyanates of which up to 10% are replaced by isocyanates with a functionality of three or more.
6. A polyurethane-polyurea as claimed in claim 1, wherein component b) is a linear polyesterpolyol.
- 20 7. A polyurethane-polyurea as claimed in claim 1, wherein component b) has an acid number of from 1 to 15 mg/g and a hydroxyl number of from 30 to 180 mg/g.
- 25 8. A polyurethane-polyurea as claimed in claim 1, wherein component b) is a polyesterpolyol branched via trimethylolpropane.
9. A polyurethane-polyurea as claimed in claim 1, wherein component c) has olefinic double bonds.



10. A polyurethane-polyurea as claimed in claim 1,
wherein component c) is a fatty alcohol and/or a
fatty amine and/or an ethoxylated fatty alcoholfatty
amine having on average from 1 to 30 ethylene oxide
units per molecule.
11. A polyurethane-polyurea as claimed in claim 1,
wherein component c) is an ethoxylated fatty alcohol
having on average from 1 to 20 ethylene oxide units
per molecule.
12. A polyurethane-polyurea wherein component d) is a
bishydroxyalkanecarboxylic acid.
13. A polyurethane-polyurea wherein component d) is
dimethylolpropionic acid.
14. A polyurethane-polyurea wherein component e) is a
polyoxyalkylene glycol having a number-average molar
mass of from 750 to 10,000 g/mol and wherein at
least 80 out of 100 mol of the oxyalkylene groups
are oxyethylene groups.
15. A polyurethane-polyurea wherein component f) is a
polyalkylenepolyamine.
16. A polyurethane-polyurea wherein component f) is
triethylenetetramine.
17. The use of a hydrophilic polyurethane-polyurea as
claimed in claim 1 as an emulsifier for alkyd
resins.
18. The use of a hydrophilic polyurethane-polyurea as an
emulsifier for oil-free polyesters.
19. A polyurethane-polyurea as claimed in claim 1,
wherein component b) is a polyester modified with
unsaturated fatty acids.