

**AQUEOUS, EXTERNALLY EMULSIFIED ALKYD RESIN EMULSIONS FROM  
RENEWABLE RAW MATERIALS**

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The present invention relates to a process for the preparation of aqueous dispersions of alkyd resins from exclusively renewable raw materials.

10 Water-dilutable coating binders have increased constantly in importance in recent years. This trend will become substantially stronger in the future. Two principal factors are critical for this development: on the one hand, the environmental problems associated with the use  
15 of solvents, and on the other hand the shortage of raw materials, which may lead to supply difficulties. Binders which are produced exclusively from renewable raw materials and which are also free from conventional solvents constitute an ideal response to these concerns,  
20 since not only can they be prepared in a manner particularly compatible with the environment but they are also biodegradable and not dependent on petroleum as primary raw material.

25 Among the conceivable classes of binders, the alkyd resins appear best to meet the conditions mentioned above, since the alkyd resins which are common today on the one hand already consist to the extent of up to 80% of renewable raw materials, synthesis taking place  
30 without the use or emission of harmful by-products, and on the other hand can be transferred to the aqueous phase with relative simplicity with the aid of suitable emulsifiers.

35 Alkyd resins are predominantly hydrophobic substances which do not per se form stable dispersions in water. It is therefore necessary to add emulsifiers. Emulsifiers

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are, in general, substances having an amphipathic molecular structure, i.e. their molecule consists of a hydrophobic moiety and a hydrophilic moiety. As a result 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.

Numerous alkyd resin emulsions are already known, and differ essentially in the emulsifiers employed. Such systems are described in US Patents US-A 3 223 658, 3 269 967 and 3 440 193 and in the GDR Patent DD 88 833, and in German Patents DE-C 27 54 141, 27 54 092, 24 40 946 and 27 54 091. Such emulsifiers, added in quantities of from 5 to 15%, based on the mass of resin, give rise to dispersions of serviceable stability. DE-A-34 04 558 describes emulsifiers based on alkyl glycosides, which can be used in alkyd resin emulsions and consist predominantly of renewable raw materials.

All of the systems known from these documents have the common feature that, although the binders and emulsifiers can be prepared to a large extent from renewable raw materials, synthesis necessarily involves the use of raw materials based on petrochemicals.

The object of the present invention, therefore, was to develop an aqueous alkyd resin emulsion in which both the alkyd resin and the emulsifier are composed exclusively of renewable raw materials.

This object has been achieved with the provision of the alkyd resins and emulsifiers according to the invention and their use in accordance with the invention.

The invention therefore provides an aqueous alkyd resin emulsion comprising

(a) an alkyd resin prepared from

(a1) a fatty acid or an oil

5 (a2) at least one compound of relatively high functionality whose functional groups are selected from hydroxyl and carboxyl groups, and

(b) an emulsifier,

10

wherein all of the raw materials required for components (a) and (b) can be prepared exclusively from renewable starting substances.

15 The invention additionally provides a process for the preparation of coating compositions which consist of an aqueous alkyd resin emulsion and, if desired, of auxiliaries and additives which are known from coatings technology.

20

Finally, the invention also provides for the use of the binder combinations according to the invention as binders for paints, coating compositions and sealing compounds.

25 The alkyd resins (a) suitable in accordance with the invention are polyesters modified with fatty acids. The alkyd resins are prepared from saturated and/or unsaturated fatty acids or oils, polyalcohols, polycarboxylic acids or hydroxycarboxylic acids. The fatty acids can be  
30 replaced, at least in part, by other monocarboxylic acids.

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Fatty acids are generally understood as being linear or branched aliphatic monocarboxylic acids having 6 to 35 carbon atoms. The fatty acids may be nondrying or drying. Examples of suitable nondrying fatty acids are saturated and monounsaturated, linear or branched aliphatic mono-

carboxylic acids, in each case individually or as a mixture, preferably having from 6 to 18 carbon atoms.

5 Examples of suitable drying fatty acids are unsaturated fatty acids or fatty acid mixtures containing at least one polyunsaturated, linear or branched aliphatic mono-carboxylic acid having at least two isolated or conjugated double bonds and an iodine number of more than 125 g/(100 g). Preference is given to linear unsaturated  
10 fatty acids having 16 to 18 carbon atoms.

Specific examples of suitable nondrying fatty acids are 2-ethylhexanoic acid, isononanoic acid, Versatic acid or coconut fatty acid and also oleic acid. Preferred  
15 examples of drying fatty acids are unsaturated monocarboxylic acids having an iodine number of more than 125 g/(100 g) and 18 carbon atoms. These include, in particular, unsaturated fatty acids having two or three isolated double bonds and various steric configurations,  
20 and the corresponding "conjuene acids", i.e. unsaturated fatty acids having conjugated double bonds. Such fatty acids are present, for example, in natural oils such as linseed oil, soya oil, safflower oil, cottonseed oil, castor oil, sunflower oil, groundnut oil, wood oil and  
25 dehydrated castor oil. The unsaturated fatty acids obtained therefrom are, for example, 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  
30 acid.

In order to incorporate the fatty acids into the alkyd resins it is possible either to esterify the fatty acids with the alcohol components or to introduce them into the  
35 alkyd resin by transesterification reactions of the oils.

It is also possible to employ so-called technical-grade oils as fatty acids, these oils generally being mixtures of cis-linolenic acid, linoleic acid, oleic acid and stearic acid. The technical-grade oils or fatty acids can  
5 be employed as such or are incorporated into the alkyd resin by transesterification reactions or after dehydration reactions (ricinenic fatty acids).

Where polyunsaturated fatty acids are used, it is particularly preferred to employ mixtures of fatty acids  
10 containing isolated and conjugated unsaturation, for example mixtures containing from 10 to 80 % by mass of fatty acids containing conjugated unsaturation.

15 The content by mass of saturated and unsaturated fatty acids incorporated is preferably from 20 to 80 %, based on the resin solids. This saturated and unsaturated fatty acid component comprises, with particular preference, from 10 to 60 % of unsaturated fatty acids having conjugated double bonds. For nonyellowing resins, preference is  
20 given to saturated monocarboxylic acids or fatty acids having one or two isolated double bonds. The fatty acids obtained can be chemically optimized by fractional distillation, isomerization or conjugation. In order to  
25 modify the properties of the alkyd resins it is possible for up to 15 % by mass of the unsaturated fatty acids to be replaced by other monocarboxylic acids, such as benzoic acid, benzoylglycine (hippuric acid), mandelic acid, cinnamic acid or abietic acid.

30 The naturally occurring compounds (a2) of relatively high functionality contain in each case at least two functional groups selected from hydroxyl and carboxyl groups. This class includes dicarboxylic acids, polycarboxylic acids, (poly)hydroxy(poly)carboxylic acids and polyols  
35 having from at least two up to six hydroxyl groups. The aliphatic or aromatic (poly)hydroxy(poly)carboxylic acids

contain at least one carboxyl group and at least two, preferably two or three, hydroxyl groups, or at least two carboxyl groups and at least one, preferably one to three, hydroxyl groups. It is also possible to use some  
5 or all of the carboxylic acids in the form of their anhydrides. The individual compounds of component (a2) and their amounts are chosen such that their mean functionality in the mixture is greater than 2.

10 As dicarboxylic acids from renewable raw materials it is possible on the one hand to use saturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid, as well as unsaturated carboxylic acids, for example fumaric acid.

15 Hydroxycarboxylic acids mentioned are glycolic acid, lactic acid, ricinoleic acid, gluconic acid and glucuronic acid, salicylic acid and gallic acid; also particularly suitable are hydroxypolycarboxylic acids, for  
20 example malic acid, citric acid, tartaric acid, saccharic acid and mucic acid.

Examples of polyols which can be employed are glycerol and carbohydrates or derivatives thereof, such as adoni-  
25 tol, arabitol, sorbitol, mannitol, glucose and fructose.

As emulsifiers it is possible to use fatty acid derivatives, derivatives of carbohydrates (sugars) and polypeptides, and derivatives thereof. Examples of suitable  
30 emulsifiers are alkali metal salts or amine salts of fatty acids, alkylglycosides, for example as described in DE-A 34 04 558, alkyl polysaccharides, sorbitol mono- and diesters, ethoxylated sorbitol esters, sorbitol hexa-  
esters, fatty acid gluconamides, fatty acid taurides,  
35 glycolipids, lipopeptides, phospholipids and polymeric biosurfactants, for example lecithin, casein or "Emul-  
san", a complex of a protein and a lipopolyhetero-

saccharide. It is also possible to employ mixtures of these surfactants.

5 The alkyd resins can be prepared by polycondensation in accordance with known methods, as described for example in S. Paul, Surface Coatings, pp. 70 to 139, John Wiley & Sons, New York, 1985.

10 The polycondensation can be carried out by heating in the melt, or by an azeotropic method with elimination of water. The desired number of hydroxyl and acid groups can be introduced by an appropriate choice of the ratios of equivalents, an appropriate reaction regime and, if desired, by working in steps. The appropriate process  
15 conditions and selection criteria are familiar to the person skilled in the art.

The alkyd resins according to the invention preferably have hydroxyl numbers of from 1 to 80 mg/g, acid numbers  
20 of from 1 to 20 mg/g or oil lengths of from 10 to 80 %.

Particular preference is given to alkyd resins having hydroxyl numbers of from 20 to 70 mg/g, acid numbers of from 2 to 15 mg/g or oil lengths of from 50 to 70 %.  
25

In order to prepare the alkyd resin emulsions, it is possible as a first step to mix these alkyd resins with the above-described emulsifiers or emulsifier dispersions. The mixtures comprise from 40 to 97 parts, preferably from 50 to 95 parts, by weight of the specified  
30 hydrophobic alkyd resins as a blend with from 3 to 60 parts, preferably from 5 to 50 parts, by weight of the specified emulsifiers. The mixtures can be prepared simply by blending the synthetic resins with the emul-  
35 sifiers.

In order to prepare the aqueous alkyd resin dispersions according to the invention, the mixtures of the invention are dispersed in water, which can be effected either simply by stirring water into the initially introduced mixture of the synthetic resins with the emulsifier, using customary dissolvers or stirrers, or else by pouring the mixture into water with vigorous stirring. If desired, part of the water can first be added to the mixture described above, and this mixture can then be poured with stirring into the residual quantity of water. In this way it is possible to obtain stable oil-in-water emulsions.

The alkyd resin emulsion can also be prepared by first preparing an aqueous solution of the emulsifier and then stirring the alkyd resin into this solution with severe shearing.

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

Suitable pigments are the customary pigments as described, for example, in DIN 55 944. Examples of those employed are carbon black, titanium dioxide, monodisperse silica, aluminum silicate, metal powders or flakes, organic and inorganic color pigments, anticorrosion pigments, such as lead compounds and chromate compounds, and metal-effect pigments. In addition to the pigments and fillers it is also possible, if desired, to employ customary organic dyes. It is likewise possible to add proportions of crosslinked organic microparticles.

The methods of preparing the coating compositions from the individual components are known. For example, it is possible to disperse these pigments in a particularly suitable grinding resin and, if desired, to mill the dispersion to the required particle size. An alternative procedure envisages the milling of the pigments in the aqueous dispersion of the binder component.

In this context it should be ensured that the stability of the aqueous dispersion is not affected during the milling process. Following the dispersing of the pigments it is possible to add further binder components. These may comprise the same one or another of the externally emulsified alkyd resin dispersions according to the invention. If appropriate, further coatings auxiliaries may be added in order to influence properties such as, for example, dispersibility.

In accordance with a further procedure, the externally emulsified alkyd resins or, if desired, other customary paste resins are first mixed with a little water, with or without the addition of fillers, pigments, dyes and the like, and this mixture is processed on a roller bed or in a ball mill, to form a paste. This paste can then be diluted with further water, with or without the addition of further resin emulsion and additives, to produce the ready-to-use coating formulation.

The coating compositions according to the invention can be applied to the materials to be coated using customary techniques, for example dipping, spraying or rolling. The applied film then crosslinks by oxidative drying.

The thicknesses of the coatings applied depend on the intended use of the coating composition. Clearcoats, for example, have a thickness of up to 60  $\mu\text{m}$ , pigmented basecoats or topcoats from 10 to 50  $\mu\text{m}$ , filler or stone-

chip resistance coatings a thickness of from 30 to 100  $\mu\text{m}$ , and anticorrosion primer coatings a thickness of from 20 to 70  $\mu\text{m}$ .

5     Suitable substrates are any substrates desired, for example metal substrates, for instance iron, aluminum or zinc, nonmetallic substrates, such as mineral substrates (e.g. concrete, glass), wood, paper, card, textiles, plastics substrates, such as polyolefins, polycarbonates  
10     and polyurethanes, and also substrates which have, if desired, been provided with preliminary coatings. Application may be made to an already coated substrate whose coating has been dried or crosslinked prior to the second application.

15     The coating composition according to the invention is also suitable for use in any multicoat system. In this context it is possible, depending on pigmentation, to produce clearcoat compositions, basecoat or topcoat  
20     compositions and also stone-chip resistance coatings, fillers or primers, for example. The preferred use is as a clearcoat composition applied to a basecoat based on an aqueous or solvent-containing coating composition. Use as a pigmented topcoat is particularly preferred. The  
25     coatings obtained in this way are distinguished by high mar resistance, high gloss retention capacity and enhanced resistance properties.

30     After evaporation of the water, the crosslinking and curing of the coatings can take place by atmospheric oxygen or (hydro)peroxides, catalyzed with metal salts of siccative acids or other siccatives, at temperatures between room temperature and 250°C.

35     The examples which follow illustrate the invention. Parts and percentages are by mass unless otherwise specified.

## Examples

### Alkyd resins

#### 5 A1

600 g of soya oil and 170 g of glycerol together with 0.05 g of LiOH and 0.3 g of triphenylphosphite are stirred at 250°C under nitrogen for 3 hours, until a 1:1 sample with ethanol forms a clear solution. Then, at 10 250°C with stirring, 105 g of succinic anhydride are added. After an acid number below 5 mg/g has been reached, a further 110 g of succinic anhydride are added. When an acid number of below 5 mg/g has again been reached, the mixture is cooled to 160°C and 100 g of 15 rosin are added. After about 4 hours at 250°C, with a quantity of distillate of about 41 g and an acid number of from 3 to 5 mg/g, boiling is ended. A 100 % alkyd resin is obtained with an oil length of 60 % and a theoretical OH number of 60 mg/g.

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#### A2

600 g of soya oil and 150 g of glycerol together with 0.05 g of LiOH and 0.3 g of triphenylphosphite are stirred at 250°C under nitrogen for 3 hours, until a 1:1 25 sample with ethanol forms a clear solution. Then, at 250°C with stirring, 105 g of succinic anhydride are added. After an acid number below 5 mg/g has been reached, a further 110 g of succinic anhydride are added. The mixture is then heated slowly to 270°C. After about 30 5 hours, with a quantity of distillate of about 38 g and an acid number of from 6 to 8 mg/g having been reached, boiling is ended. A 100 % alkyd resin is obtained with an oil length of 67 % and a theoretical OH number of 42 mg/g.

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**A3**

600 g of soya oil, 143 g of glycerol and 150 g of a 70% strength aqueous sorbitol solution together with 0.05 g of LiOH and 0.3 g of triphenyl phosphite are stirred at 250°C under nitrogen for 3 hours. Then 40 g of succinic anhydride are added in portions at 270°C, with stirring, until the batch is a single phase. At this point, 100 g of succinic anhydride are added and stirring is continued at 270°C. After an acid number of below 5 mg/g has been reached, a further 75 g of succinic anhydride are added. After about 6 hours, with a quantity of distillate of about 82 g and an acid number of from 8 to 10 mg/g having been reached, boiling is ended. A 100% alkyd resin is obtained with an oil length of 63 %.

**A4**

600 g of soya oil and 160 g of glycerol together with 0.05 g of LiOH and 0.3 g of triphenyl phosphite are stirred at 250°C under nitrogen for 3 hours, until a 1:1 sample with ethanol forms a clear solution. Then 105 g of succinic anhydride are added with stirring at 250°C. After an acid number of below 5 mg/g has been reached the mixture is heated to 160°C and 140 g of malic acid are then added. After 3 hours at 160°C, the mixture is heated slowly to 240°C. After about 5 hours, boiling is ended on reaching an acid number of from 6 to 8 mg/g. A 100 % alkyd resin is obtained with an oil length of 65 %.

**A5**

600 g of soya oil, 520 g of 70% pure sorbitol and 100 g of succinic anhydride together with 0.05 g of LiOH and 0.3 g of triphenyl phosphite are heated under nitrogen. Condensation is then carried out at temperatures of up to 230°C, with distillation of 245 g of water of reaction. After an acid number of below 5 mg/g has been reached, a further 150 g of succinic anhydride and 155 g of

\*Ocenol HD (unsaturated fatty alcohol) are added. By further condensation to an acid number of 5 mg/g at temperatures of up to 220°C, with distillation of a further 27 g of water of reaction, a 100% alkyd resin is obtained.

#### Alkyd resin emulsions

##### E1

10 16 g of soya oil fatty acid and 3 g of 25% strength ammonia water are added to 200 g of the alkyd resin from Example A1 and the mixture is stirred at 70°C for about 60 minutes until it is homogeneous.

15 Then 175 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 4 hours). A milky, viscous dispersion is obtained with a solids content of 55 % by mass.

##### 20 E2

30 g of C-12 glucamide and 0.5 g of 25% strength ammonia water are added to 200 g of the alkyd resin from Example A2 and the mixture is stirred at 70°C for about 60 minutes until it is homogeneous.

##### 25

Then 210 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 4 hours). A milky, viscous dispersion is obtained with a solids content of 52 % by mass.

##### 30

##### E3

20 g of soya oil fatty acid, 6 g of soya glucamide and 19 g of 25% strength ammonia water are added to 200 g of the alkyd resin from Example A3 and the mixture is stirred at 70°C for about 60 minutes until it is homogeneous.

Then 257 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 4 hours). A milky, viscous dispersion is obtained with a solids content of 45 % by mass.

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**E4**

16 g of linseed oil fatty acid tauride and 0.5 g of 25% strength ammonia water are added to 200 g of the alkyd resin from Example A4 and the mixture is stirred at 70°C for about 60 minutes until it is homogeneous.

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Then 200 g of deionized water heated at 70°C is added dropwise very slowly with vigorous stirring (about 4 hours). A milky, viscous dispersion is obtained with a solids content of 52 % by mass.

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### Patent Claims

- 5     1.     An aqueous alkyd resin emulsion comprising
- (a)   an alkyd resin prepared from
- (a1) a fatty acid or an oil
- (a2) at least one compound of relatively high
- 10               functionality whose functional groups are
- selected from hydroxyl and carboxyl
- groups, and
- (b) an emulsifier,
- wherein all of the raw materials required for components
- 15     (a) and (b) can be prepared exclusively from renewable
- starting substances.
2.     An aqueous alkyd resin emulsion as claimed in claim
- 1, wherein saturated or monounsaturated, linear or
- 20     branched aliphatic monocarboxylic acids, in each case
- individually or in a mixture, are used as component (a1)
- to prepare the alkyd resin.
3.     An aqueous alkyd resin emulsion as claimed in claim
- 25     2, wherein monocarboxylic acids having 6 to 18 carbon
- atoms are employed.
4.     An aqueous alkyd resin emulsion as claimed in claim
- 1, wherein polyunsaturated, linear or branched aliphatic
- 30     monocarboxylic acids having at least two isolated or
- conjugated double bonds, in each case individually or in
- a mixture, are used as component (a1) to prepare the
- alkyd resin.
- 35     5.     An aqueous alkyd resin emulsion as claimed in claim
- 4, wherein polyunsaturated fatty acids having 16 to 18



carbon atoms are used as component (a1) to prepare the alkyd resin.

5 6. An aqueous alkyd resin emulsion as claimed in claim 1, wherein fatty acid mixtures in the form of natural oils are employed as component (a1) to prepare the alkyd resin.

10 7. An aqueous alkyd resin emulsion as claimed in claim 1, wherein the compounds according to (a2) are selected from the group consisting of polyfunctional aliphatic hydroxy compounds having from at least two up to six hydroxyl groups, aliphatic saturated and unsaturated and aromatic dicarboxylic acids, and hydroxycarboxylic acids  
15 having in each case at least one hydroxyl group and one carboxyl group, the mean functionality of component (a2) being greater than 2.

20 8. An aqueous alkyd resin emulsion as claimed in claim 7, wherein component (a2) comprises aliphatic or aromatic hydroxycarboxylic acids which contain either one carboxyl group and at least two hydroxyl groups or two or more carboxyl groups and at least one hydroxyl group.

25 9. An aqueous alkyd resin emulsion as claimed in claim 1, wherein the emulsifiers are selected from the group consisting of fatty acid derivatives, derivatives of carbohydrates and polypeptides.

30 10. An aqueous alkyd resin emulsion as claimed in claim 1, wherein the alkyd resin has an OH number of from 1 to 80 mg/g.

35 11. An aqueous alkyd resin emulsion as claimed in claim 1, wherein the alkyd resin has an acid number of from 1 to 20 mg/g.



- 17 -

12. An aqueous alkyd resin emulsion as claimed in claim 1, wherein the alkyd resin has an oil length of from 40 to 80 %.

5 13. A coating composition comprising an aqueous alkyd resin emulsion as claimed in claim 1.

14. The use of a coating composition as claimed in claim 13 for producing single-coat finishes or topcoats.

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15. The use of a coating composition as claimed in claim 13 for producing primers.