

The present invention relates to a liquid, radiation-curable coating composition for coating glass surfaces and containing

- 5 A) 56 to 89% by weight, based on the coating composition, of at least one diethylenically unsaturated polyurethane optionally containing urea groups,
 - B) 10 to 30% by weight, based on the coating composition, of at least one ethylenically unsaturated monomer,
 - 10 C) 0.5 to 8% by weight, based on the coating composition, of at least one photoinitiator, and
 - D) 0.05 to 6% by weight, based on the coating composition, of an alkoxysilane,
- the sum of components (A) to (D) in each case being 100%
15 by weight.

The present invention also relates to a process for coating glass surfaces, in particular optical glass fibres, using these radiation-curable coating compositions.

Optical glass fibres have achieved constantly
20 increasing importance in the sector of communications as optical waveguide fibres. For this application, it is absolutely necessary to protect the glass surface against moisture and abrasion. The glass fibres are therefore provided, immediately after production, with a protecting
25 paint coat.

Thus, it is known, for example, from EP-B-114,982 to provide glass fibres firstly with a buffer coating (primer) which is elastic, but not very hard and not very tough, and then to apply a radiation-curable top coat
30 which has high hardness and toughness. The two-layered construction is intended to ensure good protection of the optical fibres under mechanical load, even at low temperatures. As the top coat, radiation-curable coating compositions based on a polyurethane containing diethy-
35 lenic end groups, a diethylenically unsaturated ester of a diglycidyl ether of a bisphenol, and a monoethylenically unsaturated monomer, the glass transition temperature of the homopolymer prepared from this monomer being above

55°C, are employed in EP-B-114,982.

However, glass fibre coatings of this type have the considerable disadvantage of only poor adhesion to the glass surface. In particular on exposure to moisture, this adhesion is further impaired, under certain circumstances even so greatly that full loss of adhesion on the glass surface occurs. The problem of poor adhesion of the coating compositions to the glass surface is known. In order to improve the adhesion, organosilanes, as adhesion promoters, are therefore frequently added to the coating compositions. Thus, it is known, for example, from EP-B-33,043 to add organosilanes, as adhesion promoters, to radiation-curable coating agents based on vinyl monomers and reactive polymers (not polyurethanes), it being essential to the invention that either the vinyl monomers or the polymers have a thirane ring. Examples mentioned of suitable compounds are γ -aminopropyltriethoxysilane, N, β -aminoethyl- γ -aminopropyltrimethoxysilane and γ -glycidyloxypropyltrimethoxysilane. There is no mention in this application of the loss in adhesion of the glass fibre coatings on exposure to moisture.

It is also known, from Japanese Patent 45,138/85 of 8 October 1985 (corresponds to Japanese Preliminary Published Specification 42,244/80 of 25 March 1980), to employ organosilanes as adhesion promoters in radiation-curable glass fibre coating agents. The film-forming components employed are polymers having azide groups. γ -methacryloxypropyltrimethoxysilanes, γ -aminopropyltrimethoxysilane and γ -glycidyloxypropyltrimethoxysilane are mentioned as suitable silanes. However, it is essential to Japanese Patent 45,138 that the azide groups are incorporated into the polymers in order to increase the curing rate. This publication too does not therefore mention the problem of the effect of moisture on the adhesion of the glass fibre coating.

Finally, EP-A-149,741 discloses liquid, radiation-curable glass fibre coating agents which contain, besides a radiation-curable, polyethylenically

unsaturated polymeric compound, 0.5 to 5%, based on the coating composition, of a polyalkoxysilane. Polyalkoxysilanes which carry an organic substituent which carries a single active amino or mercaptyl hydrogen atom which is able to react with the ethylenically unsaturated bonds in a Michael addition are suitable. An example mentioned of suitable silanes is γ -mercaptopropyltrimethoxysilane. According to the teaching of EP-A-149,741, it is only possible to improve the adhesion even on exposure to moisture by using silanes of this type. By contrast, compounds usually employed as adhesion promoters, such as, for example, γ -aminopropyltriethoxysilane and N- β -(N-vinylbenzylaminopropyl)trimethoxysilane prove, according to EP-A-149,741, to be unsuitable for improving the adhesion on exposure to moisture.

The present invention therefore had the object of providing radiation-curable coating compositions for coating glass surfaces, in particular optical glass fibres, in which the resultant coating, after exposure to moisture, had only slight loss in adhesion, or none at all, compared with the corresponding freshly prepared coating examined immediately after curing.

The object underlying the invention is achieved by a liquid, radiation-curable coating composition for coating glass surfaces which contains

- A) 56 to 89% by weight, based on the coating composition, of at least one diethylenically unsaturated polyurethane optionally containing urea groups,
- B) 10 to 30% by weight, based on the coating composition, of at least one ethylenically unsaturated monomer,
- C) 0.5 to 8% by weight, based on the coating composition, of at least one photoinitiator,
- D) 0.05 to 6% by weight, based on the coating composition, of an alkoxysilane,

the sum of components (A) to (D) in each case being 100% by weight.

The coating composition is characterised in that component (D) is N- β -aminoethyl- γ -aminopropyltrimethoxysilane or γ -aminopropyltrimethoxysilane or N-methyl- γ -aminopropyltrimethoxysilane or triamino-modified propyltrimethoxysilane.

In view of the large number of organosilicon compounds known as adhesion promoters, it was surprising and not foreseeable that the use of N- β -aminoethyl- γ -aminopropyltrimethoxysilane, γ -aminopropyltrimethoxysilane, N-methyl- γ -aminopropyltrimethoxysilane and triamino-modified propyltrimethoxysilane (for example DYNASYLAN[®] adhesion promoters, type "TRIAMO", commercial product from Dynamit-Nobel Chemie) impairs the adhesion of radiation-curable coating agents based on unsaturated polyurethanes on glass surfaces on exposure to moisture only insignificantly or not at all, while considerable impairment in adhesion occurs on exposure to moisture when other known adhesion promoters, such as, for example, γ -glycidyloxytrimethoxysilane and the monohydrochloride of N- β -(N-vinylbenzylamino)ethyl- γ -aminopropyltrimethoxysilane, are used.

The coating composition according to the invention is described below in greater detail:

The diethylenically unsaturated polyurethanes (A) employed as the film-forming component can be obtained by reacting a diisocyanate or polyisocyanate with a chain extender from the group comprising diols/polyols and/or diamines/polyamines and/or dithiols/polythiols and/or alkanolamines and subsequently reacting the free isocyanate groups which remain with at least one hydroxyalkyl acrylate or hydroxyalkyl ester of other ethylenically unsaturated carboxylic acids.

The amounts of chain extenders, diisocyanate or polyisocyanate and hydroxyalkyl esters of an ethylenically unsaturated carboxylic acid are selected here so that

- 1.) the equivalent ratio between the NCO groups and the reactive groups of the chain extender (hydroxyl, amino or mercaptyl groups) is between 3:1 and 1:2,

and is preferably 2:1, and

2.) the OH groups of the hydroxyalkyl esters of ethylenically unsaturated carboxylic acids are present in a stoichiometric amount relative to the still-free isocyanate groups of the prepolymer made from isocyanate and chain extender.

In addition, it is possible to prepare the polyurethanes (A) by firstly reacting some of the isocyanate groups of a diisocyanate or polyisocyanate with at least one hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid, and subsequently reacting the remaining isocyanate groups with a chain extender. In this case too, the amounts of chain extender, isocyanate and hydroxyalkyl esters of unsaturated carboxylic acids are selected so that the equivalent ratio between the NCO groups and the reactive groups of the chain extender is between 3:1 and 1:2, and is preferably 2:1, and the equivalent ratio between the remaining NCO groups and the OH groups of the hydroxyalkyl ester is 1:1.

It is of course possible to use all intermediate forms of these two processes. For example, some of the isocyanate groups of a diisocyanate can firstly be reacted with a diol, more of the isocyanate groups can subsequently be reacted with the hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid, and the remaining isocyanate groups can then be reacted with a diamine.

These various preparation processes for polyurethanes are known (cf., for example, EP-A-204,161) and do not therefore require more detailed description.

Isocyanates which are suitable for preparation of the polyurethanes (A) are aromatic, aliphatic and cycloaliphatic diisocyanates and polyisocyanates, such as, for example, 2,4- and 2,6-toluylene diisocyanates and mixtures thereof, 4,4'-diphenylmethane diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 1,4-naphthalene diisocyanate, 4,4'-toluidine diisocyanate,

xylylene diisocyanate and substituted aromatic systems, such as, for example dianisidine diisocyanates, 4,4'-diphenyl ether diisocyanates or chlorodiphenylene [sic] diisocyanates, and higher-functional aromatic isocyanates, such as, for example, 1,3,5-triisocyanatobenzene, 4,4',4"-triisocyanatetriphenylmethane [sic], 2,4,6-triisocyanatotoluene and 4,4'-diphenyldimethylmethane 2,2',5,5'-tetra-
isocyanate; cycloaliphatic isocyanates, such as, for example, 1,3-cyclopentane diisocyanate, 1,4-cyclohexane diisocyanate, 1,2-cyclohexane diisocyanate, 4,4'-methylene bis(cyclohexyl isocyanate) and isophorone diisocyanate; aliphatic isocyanates, such as, for example, tri-methylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, trimethylhexamethylene 1,6-diisocyanate and tris-hexamethylene triisocyanate, and the diisocyanates derived from dimeric fatty acids described in EP-A-204,161, column 4, lines 42 to 49.

2,4- and 2,6-toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate and 4,4'-methylene bis-(cyclohexyl isocyanate) are preferably employed.

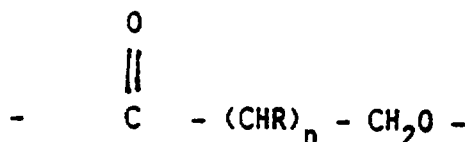
Examples of suitable diols and polyols are, for example, ethylene glycol, propylene 1,2-glycol and 1,3-glycol, butanediols, pentanediols, neopentyl glycol, hexanediols, 2-methylpentane-1,5-diol, 2-ethylbutane-1,4-diol, dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane and trimethylolbutane, erythritol, mesoerythritol, arabitol, adonitol, xylitol, mannitol, sorbitol, dulcitol, hexanetriol, (poly)-pentaerythritol; further monoethers, such as diethylene glycol and dipropylene glycol, and polyethers, the adducts of the polyols mentioned and alkylene oxides. Examples of alkylene oxides they [sic] are suitable for polyaddition to these polyols to form polyethers are ethylene oxide, propylene oxide, butylene oxide and styrene oxide. These polyaddition products are generally called polyethers having terminal hydroxyl groups. They may be linear or branched.

Examples of polyethers of this type are polyoxyethylene glycols having a molecular weight of from 200 to 4,000, polyoxypropylene glycols having a molecular weight of from 200 to 4,000, polyoxytetramethylene glycol, polyoxy-
5 hexamethylene glycol, polyoxynonamethylene glycol, polyoxydecamethylene glycol, polyoxydodecamethylene glycol and mixtures thereof. Other types of polyoxyalkylene glycol ethers may also be used. Suitable polyether polyols are also those which are obtained by reacting
10 polyols of this type, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,4-butanediol, 1,3-butanediol, 1,6-hexanediol and mixtures thereof; glycerol trimethylolethane, trimethylolpropane 1,2,6-hexanetriol, dipentaerythritol, tripentaerythritol, polypentaeryth-
15 ritol, methyl glycosides and sucrose, with alkylene oxides, such as ethylene oxide, propylene oxide or mixtures thereof.

Examples of suitable polyether diols are also the polymerisation products of tetrahydrofuran or of butylene
20 oxide. It is also possible to use polyester polyols, preferably polyester diols, which can be prepared, for example, by reacting the abovementioned glycols with dicarboxylic acids, such as, for example, phthalic acid, isophthalic acid, hexahydrophthalic acid, adipic acid,
25 azelaic acid, sebacic acid, maleic acid, glutaric acid, tetrachlorophthalic acid and hexachloroheptanedicarboxylic acid. Instead of these acids, it is also possible to use their anhydrides if they exist.

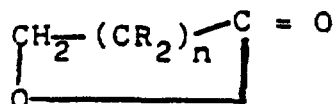
It is also possible to use polycaprolactone diols
30 and triols. These products are obtained, for example, by reacting an ϵ -caprolactone with a diol. Such products are described in US Patent 3,169,945.

The polylactone polyols obtained by this reaction are distinguished by the presence of a terminal hydroxyl
35 group and by recurring polyester units derived from the lactone. These recurring molecular units may conform to the formula



in which n is preferably 4 to 6, and the substituent is hydrogen, an alkyl radical, a cycloalkyl radical or an alkoxy radical, no substituent containing more than 12 carbon atoms and the total number of carbon atoms in the substituent in the lactone ring not exceeding 12.

The lactone used as starting material can be any lactone or any combination of lactones, but this lactone should contain at least 6 carbon atoms in the ring, for example 6 to 8 carbon atoms, and at least 2 hydrogen substituents should be present on the carbon atom bonded to the oxygen group of the ring. The lactone used as starting material may be represented by the general formula below.



in which n and R are as already defined above. The lactones which are preferred in the invention for the preparation of the polyester diols are caprolactones in which n has the value 4. The most-preferred lactone is substituted ε-caprolactone in which n has the value 4 and all R substituents are hydrogen. This lactone is particularly preferred since it is available in large amounts and gives coatings having excellent properties. In addition, various other lactones can be used individually or in combination.

Examples of aliphatic diols which are suitable for the reaction with the lactone are the diols already mentioned above for the reaction with the carboxylic acids.

Examples of suitable amines are ethylenediamine, tri-, tetra-, penta- hexa-, hepta-, nona-, deca- and dodecamethylenediamine, 2,2,4- and 2,4,4-trimethylhexamethylenediamine, propylenediamine and the corresponding polyalkylenediamines, such as, for example, polypropylenediamine, polyether diamines having a molecular weight

of from 200 to 4,000, for example polyoxylethylenediamine [sic], polyoxypropylenediamine, polyoxytetramethylenediamine, 1,3- and 1,4-butylenediamine, isophoronediamine, 1,2- and 1,4-diaminocyclohexane, 4,4'-diaminodicyclohexylmethane, bis-(3-methyl-4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane, 4,7-dioxadecane-1,10-diamine, 4,9-dioxadodecane-1,12-diamine, 7-methyl-4,10-dioxatridecane-1,13-diamine [sic], nitrilotris(ethanamine) [sic], ethanolamine, propanolamine, N-(2-aminoethyl)ethanol, polyether polyamines, bis-(3-aminopropyl)methylamine, 3-amino-1-(methylamino)propane, 3-amino-1-(cyclohexylamino)propane, N-(2-hydroxyethyl)ethylenediamine, tris-(2-aminoethyl)amine, and polyamines of the formula $H_2N-(R_2-NH)_n-R_1-NH_2$. n is an integer between 1 and 6, preferably 1-3. R_1 and R_2 are identical or different alkylene groups or cycloalkylene groups or alkylene groups containing ether groups, in each case having 2-6, preferably 2-4, C atoms. Examples of polyalkylenepolyamines of this type are diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, tripropylenetetramine, tetrapropylenepentamine and dibutylenetriamine.

Chain extenders which can be employed are also dithiols and polythiols, such as, for example, dithioethylene glycol, 1,2- and 1,3-propanedithiol, butanedithiols, pentanedithiols, hexanedithiols and the other S-H analogous compounds of the diols and polyols mentioned.

Suitable for introducing the ethylenically unsaturated groups into the polyurethane are hydroxyalkyl esters of ethylenically unsaturated carboxylic acids, such as, for example, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyamyl acrylate, hydroxyhexyl acrylate, hydroxyoctyl acrylate and the corresponding hydroxyalkyl esters of methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, and isocrotonic acid.

The unsaturated polyurethane is employed in the coating compositions in an amount of from 56 to 89% by weight, based on the coating composition.

Besides the polyurethane (A) just described, the coating agent according to the invention also contains 10 to 30% by weight, based on the coating composition, of at least one ethylenically unsaturated monomer (B). Examples of suitable monomers are ethoxyethoxyethyl acrylate, N-vinylpyrrolidone, phenoxy-ethyl [sic] acrylate, dimethyl-aminoethyl acrylate, hydroxyethyl acrylate, butoxyethyl acrylate, isobornyl acrylate, dimethylacrylamide and dicyclopentyl acrylate. Also suitable are diacrylates and polyacrylates, such as, for example, butanediol diacrylate, trimethylolpropane diacrylate and triacrylate, pentaerythritol diacrylate and the long-chain linear diacrylates having a molecular weight of from 400 to 4,000, preferably 600 to 2,500, which are described in EP-A-250,631. For example, the two acrylate groups may be separated by a polyoxybutylene structure. It is also possible to employ 1,12-dodecyl diacrylate and the product of the reaction of 2 moles of acrylic acid with one mole of a dimeric fatty alcohol, which generally has 36 C atoms.

Mixtures of the monomers just described are also suitable.

Preferably employed are N-vinylpyrrolidone, phenoxyethyl acrylate, isobornyl acrylate and mixtures of these monomers.

The photoinitiator employed in the coating compositions according to the invention in an amount of from 0.5 to 8% by weight, preferably 2 to 5% by weight, based on the coating composition, varies with the radiation employed to cure the coating agents (UV radiation, electron radiation, visible light). The coating compositions according to the invention are preferably cured by means of UV radiation. In this case, ketone-based photoinitiators are usually employed, for example acetophenone, benzophenone, diethoxyacetophenone,

m-chloroacetophenone, propiophenone, benzoin, benzil, benzil dimethyl ketal, anthraquinone, thioxanthone [sic] and thioxanthone derivatives, and mixtures of different photoinitiators.

5 Together with the photoinitiators mentioned, various amines, for example diethylamine and triethanolamine, can be employed, if appropriate, in amounts of up to 4% by weight, based on the coating composition, and act as synergists.

10 As the component essential to the invention, the coating compositions contain 0.05 to 6% by weight, based on the coating composition, of N, β -aminoethyl- γ -aminopropyltrimethoxysilane, γ -aminopropyltrimethoxysilane, N-methyl- γ -aminopropyltrimethoxysilane or triamino-modified
15 propyltrimethoxysilane (for example DYNASYLAN[®] adhesion promoters, "type TRIAMO", commercial product from Dynamit Nobel Chemie). These alkoxysilanes are commercially available products and therefore need not be described in greater detail. Preferred coating agents are obtained by
20 employing either 0.5 to 2% by weight, based on the coating composition, of N, β -aminoethyl- γ -aminopropyltrimethoxysilane or 2 to 4% by weight, based on the coating composition, of γ -aminopropyltrimethoxysilane or 3 to 5%
25 by weight, based on the coating composition, of N-methyl- γ -aminopropyltrimethoxysilane or 4 to 6% by weight, based on the coating composition, of triamino-modified propyltrimethoxysilane (for example DYNASYLAN[®] adhesion promoters, "type TRIAMO", commercial product from Dynamit Nobel Chemie) as component (D).

30 The coating compositions according to the invention may, if appropriate, additionally contain customary auxiliaries and additives in customary amounts, preferably 0.05 to 10% by weight, based on the coating composition. Examples of substances of this type are flow agents
35 and plasticisers. The coating compositions may be applied to the glass surface by means of known methods of application, such as, for example, spraying, rolling, flow-coating, dipping, knife coating or brushing.

The paint films are cured by means of radiation, preferably by means of UV radiation. The equipment and conditions for these methods of curing are known from the literature (cf., for example, R. Holmes, U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints, SITA Technology, Academic Press, London, United Kingdom 1984) and require no further description.

The present invention also relates to a process for coating a glass surface, in which

- 10 I.) a radiation-curable coating composition is applied which contains
- A) 56 to 89% by weight, based on the coating composition, of at least one diethylenically unsaturated polyurethane optionally containing urea groups,
 - 15 B) 10 to 30% by weight, based on the coating composition, of at least one ethylenically unsaturated monomer,
 - C) 0.5 to 8% by weight, based on the coating composition, of at least one photoinitiator, and
 - 20 D) 0.05 to 6% by weight, based on the coating composition, of an alkoxysilane,
- the sum of components (A) to (D) in each case being 100% by weight, and
- 25 II.) the coating composition is cured by means of UV or electron radiation.

The process is characterised in that the coating composition contains, as component (D), N- β -aminoethyl- γ -aminopropyltrimethoxysilane or γ -aminopropyltrimethoxysilane or N-methyl- γ -aminopropyltrimethoxysilane or triamino-modified propyltrimethoxysilane.

For a more detailed description of the coating agent employed in the process according to the invention and of the way in which this process is carried out, reference is made to pages 5 to 13 of this description.

35 The process according to the invention is particularly suitable for coating optical glass fibres. In particular when optical glass fibres are used as optical waveguides, it is important that the coating compositions

applied to protect the surface have good adhesion to the glass surface even on exposure to moisture. Losses in adhesion of the coating after exposure to moisture - which cannot be avoided when glass fibres are used as optical waveguides - (for example glass fibres are exposed to the air at coupling stations), result in paint damage on the glass fibre surface. This surface, which is then unprotected, can very easily be damaged, for example by grains of dust, which results in a loss in optical properties. The process according to the invention and the coating compositions according to the invention, in particular, make it possible, however, to avoid these disadvantages and to provide coatings having very good adhesion, even after exposure to moisture.

The coating compositions according to the invention can be applied to the glass fibres either in the form of a single coat or as the primer of a two-coat system. Suitable top coats in the case of the two-coat system are described, for example, in EP-B-114,982.

The invention is described in greater detail in the examples below. All parts and percentages are by weight, unless expressly stated otherwise.

Example 1 (comparison)

A radiation-curable coating composition comprising 75.8 parts of unsaturated polyurethane, 9.2 parts of trimethylolpropane triacrylate, 12 parts of phenoxyethyl acrylate, 0.5 part of benzil dimethyl ketal and 2.5 parts of benzophenone is prepared by known methods (cf., for example, EP-B-114,982), by firstly reacting 4 moles of 4,4'-methylene bis-(cyclohexyl isocyanate) with 2 moles of polyoxypropylene glycol (molecular weight 1,000) in the presence of trimethylolpropane triacrylate and phenoxyethyl acrylate. This intermediate obtained is reacted with 2 moles of 2-hydroxyethyl acrylate and then with 1 mole of polyoxypropylenediamine (molecular weight 230). The photoinitiators are then added to the mixture.

Thoroughly purified (in particular grease-free) glass plates (width x length = 98 x 151 mm) are masked at

the edge with Tesakrepp® adhesive tape No. 4432 (width 19 mm), and the coating composition is applied by knife coating (dry film thickness 180 μm).

5 The curing is carried out using a UV irradiation apparatus equipped with two Hg medium-pressure lamps each with a lamp power of 80 W/cm, at a belt speed of 40 m/minute, in 2 passes at half power (= 40 W/cm).

The incident dose here is 0.08 J/cm² (measured using the dosimeter, UVICURE, system EIT from Eltosch).

10 The adhesion is tested immediately thereafter as follows:

- Carefully detach the beginning of the foil from the glass using a razor blade.
- Attach a wire hook to the detached part of the foil
15 using adhesive tape.
- Hook in a spring balance and remove at right angles at the most constant rate possible.
- Read off the removal force required in g from the measurement scale.

20 The adhesion test is evaluated by averaging the values obtained from a double determination and checking the reproducibility of good (= high) adhesion values by several repetitions.

The result of the adhesion test is shown in Table
25 1.

Besides this adhesion test, which was carried out, a roll peeling test in accordance with DIN 55 289 is also possible, but was not carried out.

30 In order to test the adhesion after exposure to moisture, the glass plates were additionally stored for 12 hours after curing in suitable climatic chambers having a defined atmospheric humidity of 90% relative atmospheric humidity (r.h.) (corresponding to DIN 50005) at room temperature (25°C).

35 Immediately after completion of exposure, the removal test using the spring balance was carried out analogously to the adhesion test immediately after irradiation.

In this case too, the adhesion test was evaluated by taking the average of a double determination. In the case of good (= high) adhesion values, at least two repeat measurements were carried out in order to check the reproducibility.

The result of this test is likewise shown in Table 1.

The test carried out for adhesion to window glass gives good, meaningful results as a laboratory method. This method is also carried out at glass fibre manufacturers since it gives values close to those in practice which agree very well with the adhesion values on optical glass fibres (typical fibre thickness 125 μm).

Example 2 (comparison)

A radiation-curable coating agent based on the unsaturated polyurethane is prepared analogously to Comparison Example 1. In contrast to Comparison Example 1, the coating agent additionally contains 2% by weight, based on the total composition, of γ -glycidyloxypropyltrimethoxysilane.

Analogously to Comparison Example 1, this coating agent is applied to glass plates by means of a knife coater (dry film thickness 180 μm) and cured using a mercury medium-pressure vapour lamp (dose likewise 0.08 J [sic]/ cm^2). The adhesion of the coating is measured, as described in Comparison Example 1, immediately after curing of the coating agent and after storage for 12 hours at 90% relative atmospheric humidity at room temperature. The results are shown in Table 1.

Examples 3 and 4 (comparison)

Glass coatings are prepared analogously to Example 2, but with the difference that the 2% by weight, based on the total composition, of γ -glycidyloxypropyltrimethoxysilane are now replaced by 2% by weight of 3-butenyltriethoxysilane (Example 3) or 2% by weight of the monohydrochloride of N- β -(N-vinylbenzylamino)ethyl- γ -aminopropyltrimethoxysilane (formula

$(\text{CH}_3\text{O})_3\text{Si} (\text{CH}_2)_3 \text{NH} (\text{CH}_2)_2 \text{NH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2 \cdot \text{HCl}$
(Example 4), in each case based on the total composition.

The results of the adhesion test are shown in Table 1.

5 Examples 5-7

Glass coatings are prepared analogously to Example 2, but with the difference that the 2% by weight of γ -glycidyloxypropyltrimethoxysilane are now replaced by 1 (Example 5) or 2 (Example 6) or 3 (Example 7) % by weight of N- β -aminoethyl- γ -aminopropyltrimethoxysilane, in each case based on the total composition.

The results of the adhesion test are shown in Table 1.

Example [sic] 8-9

15 Glass coatings are prepared analogously to Example 2, but with the difference that the 2% by weight of γ -glycidyloxypropyltrimethoxysilane are now replaced by 2 (Example 8) or 4 (Example 9) % by weight of N-methyl- γ -aminopropyltrimethoxysilane, in each case based on the total composition.

The results of the adhesion test are shown in Table 1.

Examples 10-11

25 Glass coatings are prepared analogously to Example 2, but with the difference that the 2% by weight of γ -glycidyloxypropyltrimethoxysilane are now replaced by 2% by weight of γ -aminopropyltrimethoxysilane (Example 10) or 2% by weight of triamino-modified propyltrimethoxysilane [sic] (DYNASYLAN[®] adhesion promoters, type "TRIAMO", commercial product from Dynamit-Nobel Chemie), in each case based on the total composition.

30 The results of the adhesion test are shown in Table 1.

Table 1

Example	Adhesion promoter (D)	Amount of (D) (% by weight)	Adhesion after curing (kg)	Adhesion after 12 hours at 90% r.h. (kg)
5	1 -	-	1,000-1,100	25
	2 γ -Glycidyloxypropyltrimethoxysilane	2	1,000-1,100	50- 100
10	3 3-Butenyltriethoxysilane	2	900-1,000	25- 50
	4 Monohydrochloride of N- β -(N-vinylbenzylamino)ethyl- γ -aminopropyltrimethoxysilane	2	750-1,000	150
15	5 N- β -Aminoethyl- γ -aminopropyltrimethoxysilane	1	1,000-1,100	900-1,000
	6 N- β -Aminoethyl- γ -aminopropyltrimethoxysilane	2	1,000-1,100	900-1,000
	7 N- β -Aminoethyl- γ -aminopropyltrimethoxysilane	3	900-1,000	800- 900
20	8 N-Methyl- γ -aminopropyltrimethoxysilane	2	850- 950	850- 950
	9 N-Methyl- γ -aminopropyltrimethoxysilane	4	1,200-1,400	1,000-1,100
	10 γ -Aminopropyltrimethoxysilane	2	1,000-1,150	750- 850
25	11 Triamino-modified propyltrimethoxysilane ("TRIAMO")	2	1,000-1,100	500

Examples 1-11 show that only very low loss in adhesion, if any, occurs after exposure to moisture due to the addition of N- β -aminoethyl- γ -aminopropyltrimethoxysilane, N-methyl- γ -aminopropyltrimethoxysilane, γ -aminopropyltrimethoxysilane and triamino-modified propyltrimethoxysilane (DYNASYLAN[®] adhesion promoters, type "TRIAMO", from Dynamit Nobel Chemie), while considerable loss in adhesion is observed on exposure to moisture when other, known silane adhesion promoters, such as, for example, γ -glycidyloxypropyltrimethoxysilane, 3-butenyltriethoxysilane and the monohydrochloride of N- β -(N-vinylbenzylamino)ethyl- γ -aminopropyltrimethoxysilane, are added.



Patent claims:

1. Liquid, radiation-curable coating composition for coating glass surfaces and containing
 - A) 56 to 89% by weight, based on the coating composition, of at least one diethylenically unsaturated polyurethane optionally containing urea groups,
 - B) 10 to 30% by weight, based on the coating composition, of at least one ethylenically unsaturated monomer,
 - 10 C) 0.5 to 8% by weight, based on the coating composition, of at least one photoinitiator, and
 - D) 0.05 to 6% by weight, based on the coating composition, of an alkoxysilane,the sum of components (A) to (D) in each case being 100%
15 by weight,
characterised in that component (D) is N- β -aminoethyl- γ -aminopropyltrimethoxysilane or γ -aminopropyltrimethoxysilane or N-methyl- γ -aminopropyltrimethoxysilane or triamino-modified propyltrimethoxysilane.
- 20 2. Coating composition according to Claim 1, characterised in that it contains 0.5 to 2% by weight, based on the coating composition, of N- β -aminoethyl- γ -aminopropyltrimethoxysilane as component (D).
3. Coating composition according to Claim 1,
25 characterised in that it contains 2 to 4% by weight, based on the coating composition, of γ -aminopropyltrimethoxysilane as component (D).
4. Coating composition according to Claim 1, characterised in that it contains 3 to 5% by weight of
30 N-methyl- γ -aminopropyltrimethoxysilane as component (D).
5. Coating composition according to Claim 1, characterised in that it contains 4 to 6% by weight of triamino-modified propyltrimethoxysilane as component (D).
6. Coating composition according to any of Claims 1
35 to 5, characterised in that monomer (B) is N-vinylpyrrolidone and/or phenoxyethyl acrylate and/or isobornyl acrylate.



7. Coating composition according to any of Claims 1 to 6, characterised in that it additionally contains at least one synergist and/or customary auxiliaries and additives.
- 5 8. Process for coating a glass surface, in which
- I) a radiation-curable coating composition is applied, and
- II) the coating composition is cured by means of UV or electron radiation,
- 10 characterised in that a coating composition according to any of Claims 1 to 7 is applied.
9. Process according to Claim 8, characterised in that the glass surface is the surface of an optical glass fibre.
- 15 10. Optical glass fibre characterised in that it is coated with a coating composition according to any of Claims 1 to 7.
11. Use of an optical glass fibre according to Claim 10 as an optical waveguide.
- 20 12. Use of a radiation-curable coating composition according to any of Claims 1 to 7 for coating optical glass fibres.