

The present invention relates to radiation-curable oligomers having a plurality of ethylenically unsaturated end groups and a plurality of urethane and/or urea groups per molecule, which oligomers can be prepared from

- a) at least one hydroxy- and/or aminofunctional compound having a functionality between 3 and 4 and a number-average molecular weight of more than 750 to 4000, polyesterpolyols being excepted,
- b) at least one compound having 2 hydroxyl and/or amino groups per molecule and a number-average molecular weight between 200 and 4000, polyesterdiols being excepted,
- c) at least one monoethylenically unsaturated compound having a group containing one active hydrogen atom per molecule and having a number-average molecular weight between 116 and 1000, and
- d) at least one aliphatic and/or cycloaliphatic diisocyanate.

The present invention also relates to radiation-curable coating compositions containing these radiation-curable oligomers, and to processes for the coating of glass surfaces, in particular optical glass fibres, in which these coating compositions are used.

Optical glass fibres have acquired constantly increasing importance in the communications sector as light waveguide fibres. For this particular application, it is absolutely necessary to protect their glass surface from moisture and wear. Accordingly, directly after their manufacture, the glass fibres are provided with at least one protective surface coating.

Thus it is known, for example from EP-B-114,982, to provide glass fibres first with a buffer layer (primer) which is elastic but has low hardness and low toughness and then to apply a radiation-curable top coat which has high hardness and toughness. The two-layered structure is intended to ensure good protection of the glass fibres

upon exposure to mechanical stress even at low temperatures.

According to EP-B-114,982, radiation-curable coating agents based on linear urethane acrylates are used as the primer. Radiation-curable coating agents based on a linear urethane acrylate, a diethylenically unsaturated ester, 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, can be used as the top coat.

EP-A-223,086 furthermore discloses radiation-curable coating agents for the coating of optical glass fibres. These coating agents contain radiation-curable oligomers according to the preamble of the main claim as the binder.

These radiation-curable coating agents described in EP-A-223,086 are used either as top coat or as single-layer coating. However, they are not suitable as primer due to the excessively high modulus of elasticity value of the cured coatings.

Radiation-curable coating compositions for the coating of optical glass fibres are also described in EP-A-209,641. These coating compositions contain a polyurethane oligomer containing acrylate end groups and based on a polyfunctional core as the binder. These coating compositions can be used not only as primer but also as top coat. Single-layer processing is also possible.

Furthermore, US-A-4,131,602 discloses radiation-curable coating compositions which contain radiation-curable urethane acrylate oligomers which are prepared either by reacting a diisocyanate with a polyester-triol or -tetraol and a polyetherdiol or by reacting a diisocyanate with a polyether-triol or -tetraol and a polyesterdiol and subsequent addition of hydroxyethyl acrylate. The use of the coating compositions for the coating of optical glass fibres, however, is not described in US-A-4,131,602.

Furthermore, EP-A-228 854 discloses radiation-curable coating compositions which contain a mixture of a linear and a branched urethane acrylate oligomer. The branched urethane acrylate oligomer is prepared by reacting a diisocyanate with a polyethertriol having a molecular weight of 300 to 750 and hydroxyalkyl acrylate. The use of the coating compositions for the coating of optical glass fibres is not described in EP-A-228 854.

EP-A-323 546 discloses buffer coating compositions for the coating of glass fibres, which contain essentially linear, radiation-curable urethane acrylate oligomers which are prepared by reacting a diisocyanate with the reaction product of polyoxytetramethylene glycol and a dicarboxylic acid having long-chain side chains.

EP-A-207 257 discloses radiation-curable (meth)acryloyl-functional polyesters which have a substantially linear basic structure with alkyl side chains. These polyesters are used in particular as adhesives, while a use in coating compositions for the coating of glass fibres is not described.

Finally, for example EP-A-208,845, EP-A167,199, EP-A-204,161, EP-A-204,160 and EP-A-250,631 disclose radiation-curable coating compositions for the coating of optical glass fibres which contain linear urethane acrylates as binders.

These coating compositions have the disadvantage of unsatisfactory ageing behaviour. Furthermore, the mechanical properties of the coatings, in particular elasticity, still need to be improved upon long-term exposure.

The object of the present invention is to provide radiation-curable coating compositions for the coating of glass surfaces, in particular of optical glass fibres, which, compared with the known coating compositions, lead to coatings having improved properties. In particular, the cured coatings should have improved ageing behaviour and correspondingly increased storage stability of the coated glass fibres. Furthermore, the cured coatings should have

improved behaviour in the absorption and desorption of water.

5 This is of particular importance for the optical damping of the coated fibres. Moreover, the cured coatings should have a good buffer effect even at low temperature. This means that the mechanical properties of the coating should deteriorate only as little as possible with decreasing temperature. In particular, the increase in the modulus of elasticity value with decreasing temperature
10 should be only minimal. On the other hand, the coating compositions should cure as quickly as possible. Moreover, the resulting coatings should have only very slight evolution of hydrogen upon storage and ageing and show good adhesion on the glass surface.

15 Surprisingly, the object is achieved by radiation-curable oligomers having a plurality of ethylenically unsaturated end groups and a plurality of urethane and/or urea groups per molecule in dissolved form, which oligomers can be prepared from

- 20 a) at least one hydroxy- and/or aminofunctional compound having a functionality between 3 and 4 and a number-average molecular weight of more than 750 to 4000, polyesterpolyols being excepted,
- 25 b) at least one compound having 2 hydroxyl and/or amino groups per molecule and a number-average molecular weight between 200 and 4000, polyesterdiols being excepted,
- 30 c) at least one monoethylenically unsaturated compound having a group containing one active hydrogen atom per molecule and having a number-average molecular weight between 116 and 1000, and
- d) at least one aliphatic and/or cycloaliphatic diisocyanate.

35 The radiation-curable oligomers are characterized in that components a to d are used in amounts such that

1. the molar ratio of component a to component b is between 0.1 : 1 and 1.1 : 1, preferably between 0.1 and 0.8,

2. the molar ratio of component c to component a is between 2.0 : 1 and 10 : 1, preferably between 2.5 and 10, and

3. the equivalent ratio of the isocyanate groups of component d to the hydroxyl and/or amino groups of the sum of components a to c is between 0.9 and 1.0.

The present invention furthermore relates to radiation-curable coating compositions containing these radiation-curable oligomers and to processes for the coating of glass surfaces, in particular optical glass fibres, in which these coating compositions are used.

It is surprising and was not foreseeable that radiation-curable coating compositions based on the oligomers according to the invention give coatings having improved ageing behaviour compared with conventional coatings, as a result of which the glass fibres coated with these coating compositions have increased long-term stability. Moreover, the coatings prepared from the coating compositions according to the invention have improved behaviour, compared with conventional coatings, in the absorption and desorption of water. Another advantage is the good buffer effect of the coatings even at low temperatures, thus solving the problem of the so-called microbends. Furthermore, the coatings according to the invention are distinguished by good mechanical properties, such as, for example, tensile strength and elongation adapted to the particular application, and by only minimal evolution of hydrogen upon storage or ageing. Finally, they have good adhesion on the glass surface.

Hereinafter, first the radiation-curable oligomers according to the invention will be defined in more detail: suitable components a for the preparation of the oligomers are hydroxy- and/or aminofunctional compounds having a functionality of 3 to 4, preferably 3. These compounds have number-average molecular weights of 500 to 4000, preferably 750 to 2000.

Examples of suitable compounds are polyalkoxylated triols, such as, for example, ethoxylated and propoxylated

triols, preferably ethoxylated triols, particularly preferably having a number-average molecular weight of greater than or equal to 1000. Examples of the triols used are glycerol and trimethylolpropane.

5 The corresponding aminofunctional compounds such as, for example, aminofunctional compounds derived from polyalkoxylated triols, are also suitable. Examples of such products are obtainable from Texaco under the name JEFFAMIN^(R), for example JEFFAMIN^(R) T 403, T 3000, T 10 5000, C 346, DU 700 and BuD 2000.

These aminofunctional compounds can contain both primary and secondary amino groups.

In addition, compounds containing both amino and hydroxyl groups are also suitable.

15 Suitable components b are compounds containing two hydroxyl and/or amino groups per molecule. These compounds have number-average molecular weights of 200 to 4000, preferably 600 to 2000.

20 Examples of suitable compounds b are polyoxyalkylene glycols and polyoxyalkylenediamines, alkylene groups of 1 to 6 C atoms being preferred. Thus, for example, polyoxyethylene glycols having a number-average molecular weight of 1000, 1500, 2000 or 2500 and polyoxypropylene glycols having corresponding molecular weights 25 and polytetramethylene glycols are suitable. Polyethoxylated and polypropoxylated diols can also be used, such as, for example, ethoxylated and propoxylated derivatives of butanediol, hexanediol, and the like.

30 It is of course also possible to use the corresponding diamines and compounds having an OH and an amino group as component b. Examples of suitable compounds are the products available from Texaco under the name JEFFAMIN[®] D 230, D 400, D 2000, D 4000, ED 600, ED 900, ED 2001 and ED 4000.

35 A mixture comprising

b₁) 0 to 90 mol % of at least one polyetherdiol and

b₂) 10 to 100 mol % of at least one modified polyetherdiol composed of

b₂₁) at least one polyetherdiol

b₂₂) at least one aliphatic and/or cycloaliphatic dicarboxylic acid and

b₂₃) at least one aliphatic, saturated compound having an

5 epoxy group and 8 to 21 C atoms per molecule, in which the sum of the amounts of components b₁ and b₂ and the sum of the amounts of components b₂₁ to b₂₃ is in each case 100 mol %, is preferably used as component b.

10 For preparing the modified polyetherdiols by conventional methods, components b₂₁ to b₂₃ are used in amounts such that the equivalent ratio of the OH groups of component b₂₁ to the carboxyl groups of component b₂₂ is between 0.45 and 0.55, preferably 0.5, and that the
15 the equivalent ratio of the epoxy groups of component b₂₃ to the carboxyl groups of component b₂₂ is between 0.45 and 0.55 and preferably 0.5.

Examples of suitable polyetherdiols b₁ and b₂₁ are the polyoxyalkylene glycols already listed in which the
20 alkylene groups have 1 to 6 C atoms. Polyoxypropylene glycols having a number-average molecular weight between 600 and 2000 are preferably used as component b₁. Polyoxybutylene glycols (poly-THF) having a number-average molecular weight of > 1000 are preferably used as component b₂₁.

25 Aliphatic and cycloaliphatic dicarboxylic acids having 8 to 36 C atoms per molecule, such as, for example, hexahydrophthalic acid, are preferably used as component b₂₂. Examples of suitable components b₂₃ are epoxidized vinylcyclohexane compounds, epoxidized, monoolefinically
30 unsaturated fatty acids and/or polybutadienes.

Glycidyl esters of branched monocarboxylic acids, such as, for example, the glycidyl ester of Versatic Acid, are preferably used as component b₂₃.

35 For introducing the ethylenically unsaturated groups into the polyurethane oligomer, monoethylenically unsaturated compounds having a group containing an active hydrogen atom and having a number-average molecular weight of 116 to 1000, preferably 116 to 400, are used. Examples

of suitable components c are, for example, hydroxyalkyl esters of ethylenically unsaturated carboxylic acids, such as, for example, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyamyl acrylate, 5 hydroxyhexyl acrylate, hydroxyoctyl acrylate, and the corresponding hydroxalkyl esters of methacrylic, fumaric, maleic, itaconic, crotonic and isocrotonic acid, the hydroxyalkyl esters of acrylic acid being, however, preferred.

10 Furthermore, adducts of caprolactone with one of the abovementioned hydroxyalkyl esters of ethylenically unsaturated carboxylic acids are suitable as component c. Adducts of the hydroxyalkyl esters of acrylic acid having a number-average molecular weight of 300 to 1000 are 15 preferably used.

Suitable components d for the preparation of the oligomers according to the invention are aliphatic and/or cycloaliphatic diisocyanates, such as, for example, 1,3-cyclopentane diisocyanate, 1,4-cyclohexane diisocyanate, 20 1,2-cyclohexane diisocyanate, 4,4'-methylenebis(cyclohexane isocyanate) and isophorone diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate and trimethyl-1,6-hexamethylene diisocyanate and the 25 diisocyanates derived from dimeric fatty acids and described in EP-A-204,161, column 4, lines 42 to 49.

Isophorone diisocyanate and trimethyl-1,6-hexamethylene diisocyanate are preferably used.

30 It is essential to the invention that components a to d for preparing the oligomers are used in amounts such that

1. the molar ratio of component a to component b is between 0.1 : 1 and 1.1 : 1, preferably between 0.1 and 0.8,
- 35 2. the molar ratio of component c to component a is between 2:1 and 10:1, preferably between 2.5 and 10, and

3. the equivalent ratio of the isocyanate groups of component d to the active hydrogen atoms from components a plus b plus c is between 0.9 and 1.0.

5 The oligomers according to the invention can be prepared by various methods. Thus, for example, it is possible first to react diisocyanate d with chain-lengthening agents a and b and then to react the remaining free isocyanate groups with the ethylenically unsaturated compound c.

10 It is also possible to prepare the oligomers by first reacting a portion of the isocyanate groups of component b with the ethylenically unsaturated compound c and then reacting the remaining free isocyanate groups with chain-lengthening agents a and b.

15 Furthermore, it is possible to prepare the polyurethane oligomers by the process described in EP-A-223,086 on page 5.

20 The polyurethane oligomers are preferably prepared by a two-step process by first carrying out the stoichiometric polyaddition reaction of components a to d until more than 85 % of the NCO groups of component d have been converted. In this first process step, components a to d are used in amounts such that the equivalent ratio of the NCO groups of component d to the active hydrogen atoms of
25 components a to c is 1:1.

In a second process step, the remainder of the other components (in accordance with the desired NCO:OH ratio) is then added, and the reaction is continued up to an NCO group conversion of > 99 %. In this second process
30 step, it is preferred to add more of component c and to achieve the desired NCO: OH equivalent ratio by adding this component c.

The urethane oligomers according to the invention usually have number-average molecular weights of 2500 to
35 10000, preferably 3000 to 6000 (measured by GPC against a polystyrene standard), weight-average molecular weights of 5000 to 50000, preferably 7000 to 20000 (measured by GPC against a polystyrene standard), double-bond contents of

0.45 to 1.5, preferably 0.45 to 0.9, mol/kg and particularly preferably 0.45 to 0.63, and very particularly preferably 0.5 to 0.63 mol/kg, and a functionality of >2 to 3.5, preferably 2.2 to 2.8, in each case per statistically average polymer molecule.

The oligomers according to the invention are used in radiation-curable coating compositions as film-forming component A. The coating compositions usually contain 10 to 78 % by weight, preferably at least 15 % by weight, and particularly preferably 63 to 73 % by weight, in each case relative to the total weight of the coating composition, of these oligomers according to the invention.

As further component, the coating compositions can contain 0 to 60 % by weight, preferably 0 to 50 % by weight, in each case relative to the total weight of the coating composition, of at least one further ethylenically unsaturated oligomer B. Apart from unsaturated polyesters, polyester acrylates and acrylate copolymers, in particular urethane acrylate oligomers, with the exception of the urethane acrylate oligomers used as component A, are used. The properties of the completely cured coating can be selectively adjusted by means of the type and amount of this component B. The higher the amount of this component B, the higher in general the modulus of elasticity value of the completely cured coating. Component B is therefore added to the coating composition especially if the coating compositions are used as top coat. However, the effect of this component B on the properties of the resulting coating is known to one skilled in the art. The most favorable amount to be used in each case can therefore be simply determined by a few routine experiments. These ethylenically unsaturated polyurethanes used as component B are known. They can be obtained by reacting a di- or polyisocyanate with a chain-lengthening agent from the group of diols/polyols and/or diamines/polyamines, followed by reaction of the remaining free isocyanate groups with at least one hydroxyalkyl

acrylate or hydroxyalkyl ester of other ethylenically unsaturated carboxylic acids.

5 The amounts of chain-lengthening agent, di- or polyisocyanate and hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid are selected in such a manner that

- 10 1. the equivalent ratio of the NCO groups to the reactive groups of the chain-lengthening agent (hydroxyl, amino or mercapto groups) is between 3:1 and 1:2, preferably 2:1, and
2. the OH groups of the hydroxyalkyl esters of the ethylenically unsaturated carboxylic acids are present in a stoichiometric amount with respect to the still free isocyanate groups of the prepolymer
15 composed of isocyanate and chain-lengthening agents.

Furthermore, it is possible to prepare the polyurethanes B by first reacting a portion of the isocyanate groups of a di- or polyisocyanate with at least one hydroxyalkyl ester of an ethylenically unsaturated
20 carboxylic acid and then reacting the remaining isocyanate groups with a chain-lengthening agent. In this case too, the amounts of chain-lengthening agent, isocyanate and hydroxyalkyl ester of unsaturated carboxylic acids are selected in such a manner that the equivalent ratio of the
25 NCO groups to the reactive group of the chain-lengthening agent is between 3:1 and 1:2, preferably 2:1, and the equivalent ratio of the remaining NCO groups to the OH groups of the hydroxyalkyl ester is 1:1.

All intermediate forms of these two processes are
30 of course also possible. For example, a portion of the isocyanate groups of a diisocyanate can first be reacted with a diol, a further portion of the isocyanate groups can then be reacted with the hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid, and this can be
35 followed by reacting the remaining isocyanate groups with a diamine.

These various preparation processes for polyurethanes are known (cf. for example, EP-A-204,161) and therefore need not be described in more detail.

Compounds which are suitable for the preparation of these urethane-acrylate oligomers B are the compounds already used in the preparation of component A and further the compounds mentioned in German Offenlegungsschrift 3,840,644.

Especially when the coating compositions according to the invention are used as top coat, aromatic structural components are preferably used for preparing the urethane-acrylate oligomers B. In this case, 2,4- and 2,6-toluylene diisocyanate are preferably used as isocyanate components and aromatic polyester polyols based on phthalic acid and isophthalic acid and/or polypropylene glycol, ethylene glycol and diethylene glycol as chain-lengthening agents.

As further component, the radiation-curable coating compositions additionally contain at least one ethylenically unsaturated monomeric compound C, usually in an amount of 20 to 50 % by weight, preferably 22 to 35 % by weight, in each case relative to the total weight of the coating composition.

By adding this ethylenically unsaturated compound C, the viscosity and the curing rate of the coating compositions and the mechanical properties of the resulting coating are controlled, as is known to one skilled in the art and described, for example, in EP-A-223,086 and which should be consulted for further details.

Examples of monomers which can be used are ethoxyethoxyethyl acrylate, N-vinylpyrrolidone, phenoxyethyl acrylate, dimethylaminoethyl acrylate, hydroxyethyl acrylate, butoxyethyl acrylate, isobornyl acrylate, dimethylacrylamide and dicyclopentyl acrylate. Di- and polyacrylates, such as, for example, butanediol diacrylate, hexanediol diacrylate, trimethylolpropane di- and triacrylate, pentaerythritol diacrylate and the long-chain linear diacrylates having a molecular weight of 400 to 4000 or preferably 600 to 2500, and described in

EP-A-250,631, are also suitable. The two acrylate groups can be, for example, separated by a polyoxybutylene structure. Furthermore, 1,12-dodecyl diacrylate and the reaction product of 2 mol of acrylic acid with one mol of
5 a dimeric fatty alcohol, which in general has 36 C atoms, can also be used.

Mixtures of the monomers just described are also suitable. Phenoxyethyl acrylate, hexanediol diacrylate, N-vinylpyrrolidone and tripropylene glycol diacrylate are
10 preferably used.

The photoinitiator usually used in the coating compositions according to the invention in an amount of 2 to 8 % by weight, preferably 3 to 5 % by weight, relative to the total weight of the coating composition, varies
15 with the radiation used for curing 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 used, for example aceto-
20 phenone, benzophenone, diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenyl-1-propanone, hydroxypropyl phenyl ketone, m-chloroacetophenone, propiophenone, benzoin, benzil, benzil dimethyl ketal, anthraquinone, thioxanthone and thioxanthone derivatives and triphenylphosphine and
25 the like, as well as mixtures of various photoinitiators.

Furthermore, the coating compositions can additionally contain, if desired, customary auxiliaries and additives. These are usually used in an amount of 0 to 4 % by weight, preferably 0.5 to 2.0 % by weight, in each case
30 relative to the total weight of the coating composition. Examples of substances of this type are flow-improving agents, plasticizers and in particular adhesion promoters. Adhesion promoters used for this are alkoxysilanes, such as, for example, N- β -aminoethyl- γ -aminopropyltrimethoxy-
35 silane, γ -aminopropyltrimethoxysilane, N-methyl- γ -aminopropyltrimethoxysilane or triamino-modified propyltrimethoxysilane (for example adhesion promoter DYNASYLAN® of

"TRIAMO type", commercial product from Dynamit Nobel Chemie).

5 The coating compositions can be applied to the substrate by means of known application methods, such as, for example, spraying, rolling, flooding, dipping, knife- or brush-application.

10 The coating films are cured by means of radiation, preferably by means of UV radiation. Apparatuses and conditions for these curing methods 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 Kindom [sic] 1984) and need no further description.

15 The coating compositions are suitable for the coating of a wide range of substrates, for example glass, wood, metal and plastic surfaces. However, they are in particular used for the coating of glass surfaces, particularly preferably of optical glass fibres.

20 Accordingly, the present invention also relates to a process for the coating of a glass surface, in which a radiation-curable coating composition is applied and cured by means of UV or electron radiation, which process comprises using the coating compositions according to the invention as the radiation-curable coating compositions.

25 The process according to the invention is particularly suitable for the coating of optical glass fibres. For this purpose, the coating compositions according to the invention can be applied to the glass fibres as a primer and/or top coat of a two-layer coat.
30 When the coating compositions are used as a primer, the completely cured coatings usually have a modulus of elasticity value (at 2.5 % elongation and room temperature) of less than 10 MPa.

35 When the coating compositions are used as top coat, the completely cured coatings usually have a modulus of elasticity value (at 2.5 % elongation and room temperature) of 500 to 1000 MPa.

The invention will be illustrated in more detail in the examples which follow. All parts and percentages given are by weight, unless expressly stated otherwise.

Preparation of a modified polyetherdiol

5 In a boiler equipped with stirrer, inert gas inlet and temperature sensor, 51.1 parts of polytetrahydrofuran having a number-average molecular weight of 1000 and an OH number of 118 mg of KOH/g and 19.1 parts of hexahydrophthalic anhydride are heated to 120°C and maintained
10 at this temperature until an acid number of 102 mg of KOH/g has been reached. 0.02 % of chromium octoate, relative to the weight of the mixture composed of poly-THF, hexahydrophthalic acid and glycidyl ester of Versatic Acid, and 29.7 parts of the glycidyl ester of Versatic
15 Acid having an epoxy equivalent weight of 266 are then added. The mixture is heated at 120°C until the reaction product has an epoxy equivalent weight of > 20,000, an acid number of 4 mg of KOH/g and an OH number of 60 mg of KOH/g.

20 The modified polyether diol has an average molecular weight M_n of 1860 (calculated from the OH number), an $M_n \approx 1500$ determined by GPC and an $M_w/M_n = 1.67$. The viscosity of an 80 % strength solution in butyl acetate is 3.8 dPas (measured at 23°C with the plate/cone
25 viscometer).

Example 1

In a boiler equipped with stirrer, inlet means, temperature sensor and air inlet, 0.35 mol of a commercially available ethoxylated trimethylolpropane having
30 a number-average molecular weight of 1000, 0.65 mol of a commercially available polyoxypropylene glycol having a number-average molecular weight of 600, 0.65 mol of the modified polyetherdiol described above, 1.75 mol of hydroxyethyl acrylate, 0.05 % of dibutyltin dilaurate
35 (relative to the total weight of the sum of components a, b, c and d), 0.1 % of 2,6-ditert.-butylcresol (relative to the total weight of the sum of components a, b, c and d) and 30 ppm of phenothiazine (relative to the total weight

of the sum of components a, b, c and d) are initially introduced, and the mixture is heated to 60°C. 2.70 mol of isophorone diisocyanate are then metered in at 50°C over a period of 2.5 h. The mixture is then diluted with phenoxyethyl acrylate to a theoretical solids content of 90 % (sum of components a to d), and the temperature is maintained at 60°C until an NCO value of 1 % has been reached. 0.05 % of dibutyltin dilaurate and 0.51 mol of a commercially available hydroxyethyl acrylate/caprolactone oligomer having a number-average molecular weight of 344 (commercial product TONE M 100 from Union Carbide) are added at a temperature of 80°C, and the temperature is maintained at 80°C until an NCO value of < 0.1 % has been reached. The oligomer thus obtained has a double-bond content of 0.6 mol/kg and a functionality of 2.5.

A 40 % solution (relative to the theoretical solids content) of the oligomer 1 obtained in phenoxyethyl acrylate has a viscosity of 4.9 d Pas (measured at 23°C with the plate/cone viscometer).

78.1 parts of the 90 % strength solution of the urethane oligomer 1 described above, 12.1 parts of phenoxyethyl acrylate, 6.2 parts of N-vinylpyrrolidone, 1.6 parts of N- β -aminoethyl- γ -aminopropyl-trimethoxysilane and 2.0 parts of diethoxyacetophenone are used to prepare a radiation-curable coating composition 1 by mixing. Thoroughly cleaned (in particular grease-free) glass plates (width x length = 98 x 161 mm) are covered at the edge with Tesakrepp[®] adhesive tape No. 4432 (width 19 mm), and the coating composition 1 is applied by means of a knife (dry-film thickness 180 μ m).

The curing is carried out using a UV radiation apparatus equipped with two Hg medium-pressure lamps each of 80 W/cm lamp power at a belt rate of 40 m/minute in two runs at half-load operation (= 40 W/cm).

The dose of this incoming radiation was 0.08 J/cm² (measured with the UVICURE dosimeter, system EIT from Eltosch).

This gave completely cured coatings which have very good mechanical properties and furthermore are distinguished by good resistance to ageing, good low-temperature performance and improved performance in the absorption and desorption of water.

The results of the determination of the modulus of elasticity at 0.5 and 2.5 % elongation (according to DIN Standard 53 455) and the results of the elongation at break test are listed in Table 2. The results of the measurement of the modulus of elasticity values (2.5 % elongation) after various ageing treatments of the completely cured coatings are also shown in Table 2.

The dependence of the modulus of elasticity value on the temperature is shown in Figure 1. The measurements were carried out using the DMTA instrument from Polymer Laboratories Ltd.

The absorption and desorption performance of the completely cured coating in contact with water is shown in Figure 2.

Comparative Example 1

2.0 mol of isophorone diisocyanate and 0.05 % of dibutyltin dilaurate (relative to the total weight of the sum of components a to d) are initially introduced into a boiler equipped with stirrer, inlet means, temperature sensor and air inlet, and the mixture is heated to 60°C. 1.30 mol of commercially available polyoxypropylene glycol having a number-average molecular weight of 600 are then metered in at 60°C over a period of 120 to 180 minutes. The temperature is maintained at 60°C until an NCO value of 4.5 % has been reached. 0.1 % of 2,6-di-tert.-butylcresol (relative to the total weight of the sum of components a to d) and 40 ppm of phenothiazine (relative to the total weight of the sum of components a to d) are then added to the boiler. 1.54 mol of hydroxyethyl acrylate are then metered in at 60°C over a period of 30 minutes. Dissolution of the mixture is then started with phenoxyethyl acrylate until a theoretical solids content of 90 % (relative to the total weight of the sum of

components a to d) has been reached. The temperature is then maintained at 60°C until an NCO content of < 0.1 % has been reached.

5 The oligomer 2 thus obtained has a double-bond content of 1.01 mol/kg and a functionality of 2.0. A 50 % strength solution (relative to the theoretical solids content) of the oligomer 2 obtained in phenoxyethyl acrylate has a viscosity of 10 dPas (measured at 23°C with a plate/cone viscometer).

10 Analogously to Example 1, 78.1 parts of the 90 % strength solution of the urethane oligomer 2 described above, 12.1 parts of phenoxyethyl acrylate, 6.2 parts of N-vinylpyrrolidone, 1,6 parts of N- β -aminoethyl- γ -aminopropyltrimethoxysilane and 2.0 parts of diethoxyacetophen-
15 one are used to prepare a radiation-curable coating composition 2 by mixing. Application of this coating composition 2 and testing of the completely cured coating is carried out analogously to Example 1. The results are shown in Table 2 and in Figures 3 and 4.

Table 1 : Composition of the urethane oligomers (in mol)

		Example 1	Comparison 1
5	a) Ethoxylated tri-methylolpropane ($M_n = 1000$)	0.35	-
10	b ₁) Polyoxypropylene glycol ($M_n = 600$)	0.65	1.30
	b ₂) Modified polyetherdiol ($M_n = 1860$)	0.65	-
15	c) Hydroxyethyl acrylate	1.75	1.54
	c) Hydroxyethyl acrylate-caprolactone oligomer	0.51	-
20	d) Isophorone diisocyanate	2.70	2.0
	Molar ratio a/b	0.27	0
	Molar ratio c/a	6.46	∞
25	Equivalent ratio NCO/OH	0.91	0.97

Table 2: Test results

		1	C1
5	Elongation at break in %	53.1	58
10	Modulus of elasticity 05 (0.5 % elongation) in MPa	3.1	2.75
15	Modulus of elasticity 25 (2.5 % elongation) in MPa	2.9	2.6
	E25 after 800 h, 55°C, in MPa	3	2.7
20	E25 after 800 h, 90°C, in MPa	4.2	7.5
	E25 after 800 h, 120°C, in MPa	7.3	18.3

25 Example 2

2 mol of isophorone diisocyanate are initially introduced into the boiler described in Example 1, and 0.05% of dibutyltin dilaurate and 30 ppm of phenothiazine are added, and the mixture is heated to 60°C. 2 mol of hydroxyethyl acrylate are then added dropwise at such a rate that the temperature does not exceed 60°C. 1 mol of ethoxylated trimethylolpropane [sic] (20 mol of ethylene oxide per mole of trimethylolpropane) are then added dropwise also at 60°C. The mixture is maintained at 60°C until an NCO content of 0% has been reached. The intermediate 1 thus obtained is then processed further. 2 mol of isophorone diisocyanate and dibutyltin dilaurate are initially introduced, and 0.65 mol of polyoxytetra-

methylene glycol having a number-average molecular weight of 1,000, and 0.65 mol of the modified polyether diol are then added as a mixture, and the temperature is maintained at 60°C until an NCO content of 2.7% has been reached.

5 Phenothiazine is then added as a stabilizer. A mixture of 1.05 mol of hydroxyethyl acrylate and 0.35 mol of the intermediate 1 described above is then metered in, and the temperature is maintained at 60°C until an NCO content of less than 0.1% has been reached.

10 The radiation-curable coating composition is prepared from 70 parts of the urethane oligomer described above, 20.0 parts of phenoxyethyl acrylate, 6.5 parts of N-vinylpyrrolidone, 1.5 parts of N- β -aminoethyl- γ -aminopropyltrimethoxysilane and 2.0 parts of diethoxy-
15 acetophenone by mixing. The chemical properties are listed in Table 4. Thoroughly clean (in particular grease-free) glass plates (width $\times$ length = 98 $\times$ 161 mm) are covered at the edge with Tesakrepp[®] adhesive tape No. 4432 (width 19 mm), and the coating composition is applied by means of
20 a knife (dry-film thickness 180 μ m).

Curing is carried out using a UV radiation apparatus equipped with two Hg medium-pressure lamps each of 80 W/cm lamp power at a belt rate of 40 m/minute in 2 runs at half-load operation (= 40 W/cm).

25 The dose of this incoming radiation was 0.08 J/cm² (measured with the UVICURE dosimeter, system EIT from Eltosch).

This gave completely cured coatings which have very good mechanical properties and furthermore are
30 distinguished by good resistance to ageing, good low-temperature performance and improved performance in the absorption and desorption of water.

The results of the determination of the modulus of elasticity at 0.5% and 2.5% elongation (according to DIN
35 Standard 53 455) and the results of the elongation at break test are listed in Table 5.

The dependence of the modulus of elasticity value on the temperature is shown in Table 6 and Figures 5 and 7. The

measurements were carried out using the DMTA instrument from Polymer Laboratories Ltd.

Example 3

5 The intermediate 1 is prepared analogously to Example 2.

2 mol of isophorone diisocyanate and dibutyltin dilaurate are initially introduced, and 0.65 mol of polyoxytetramethylene glycol having a number-average molecular weight of 1,000, and 0.65 mol of the modified polyether diol are added as a mixture, and the temperature is maintained at 60°C until an NCO content of 2.6% has been reached. Phenothiazine is then added as a stabilizer. A mixture of 0.35 mol of hydroxyethyl acrylate and 1.05 mol of the intermediate 1 described above is then metered in, and the temperature is maintained at 60°C until an NCO content of less than 0.1% has been reached.

Preparation, application and curing of the radiation-curable coating agent and testing of the coating were carried out analogously to Example 2. The test results are shown in Tables 5 and 6 and in Figures 5 and 8.

Example 4

The intermediate 1 is prepared analogously to Example 2.

25 2 mol of isophorone diisocyanate are initially introduced, and 1.3 mol of modified polyether diol are added. After addition is complete, the mixture is maintained at 60°C for another 6 hours. 1.4 mol of the intermediate described above are then metered in, and the temperature is maintained at 60°C until an NCO content of less than 0.1% has been reached.

Preparation, application and curing of the radiation-curable coating agent and testing of the coating were carried out analogously to Example 2.

35 The test results are shown in Tables 5 and 6 and in Figures 5 and 9.

Comparative Examples 2 and 3

Analogously to Example 2, polyurethane acrylate oligomers were prepared from the components listed in Table 3.

5 These urethane acrylate oligomers were used to prepare radiation-curable coating compositions analogously to Example 2. Application, curing and testing of the coatings were also carried out analogously to Example 2. The results of the determination of the modulus of elasticity at 0.5% and 2.5% elongation (according to DIN Standard 10 53 455) and the results of the elongation at break test are listed in Table 5.

The dependence of the modulus of elasticity value on the temperature is shown in Figure 5 and in Table 8. The measurements were carried out using the DMTA instrument 15 from Polymer Laboratories Ltd.

Table 3: Composition of the polyurethane acrylate oligomers in mol

Example	2	3	4	C2	C3
5 p-THF 1000	0.65	0.65	-	0.65	-
p 600	-	-	-	-	-
mod. PE	0.65	0.65	1.30	0.65	1.30
eth. TMP 7	-	-	-	0.70	0.70
eth. TMP 20	0.35	1.05	1.40	-	-
10 HEA	1.75	2.45	2.80	2.10	2.10
IPDI	2.70	4.10	4.80	3.40	3.40

The following abbreviations were used in Table 3:

15 p-THF 1000: polyoxytetramethylene glycol having a number-average molecular weight of 1,000

p 600: polyoxypropylene glycol having a number-average molecular weight of 600

mod. PE: modified polyether diol

20 eth. TMP 7: ethoxylated trimethylolpropane having 7 ethylene oxide units per trimethylolpropane ($M_n = 414$)

eth. TMP 20: ethoxylated trimethylolpropane having 20 ethylene oxide units per trimethylolpropane

HEA: 2-hydroxyethyl acrylate

25 IPDI: isophorone diisocyanate

Table 4: Chemical properties of the liquid coating agents

	1	2	3	4	C1	C2	C3
Oligomer	1	3	4	5	2	6	7
5 DBC (coating a.)	2.07	2.02	2.02	1.99	2.31	1.91	2.01
DBC (oligomer)	0.67	0.6	0.61	0.56		0.69	0.6
C = C - R	3.39	3.78	3.73	4.07	2.25	2.80	3.80
Funct.. 2.5	2.5	3.5	4	2	3	3	
10 DBC (coating a.):	concentration of acrylic groups in mol/kg in the coating agent						
DBC (oligomer):	concentration of acrylic groups in mol/kg in the oligomer						
C = C - R:	ratio of acrylic groups of the monomers to acrylic groups of the oligomer determined in the coating agent						
15 Funct.:	average acrylic group functionality of the polymer						

20 Table 5: Mechanical test values of the coatings

	1	2	3	4	C2	C3
Elongation at break (%)	53	48	44	42	56	62
Modulus of elasticity (0.5% elongation) in MPa	3.1	2.8	2.7	2.5	17	15
25 Modulus of elasticity (2.5% elongation) in MPa	2.9	2.6	2.5	2.2	15.7	13.5

Table 6

Example 2

Example 3

T[°C] ■ log E			T[°C] ■ log E		
-41	"	9.204	-39	"	9.174
-40	"	9.191	-38.5	"	9.161
-39	"	9.178	-37.5	"	9.148
-38.5	"	9.173	-36.5	"	9.132
-37.5	"	9.16	-35.5	"	9.122
-36.5	"	9.148	-35	"	9.107
-35.5	"	9.134	-34	"	9.092
-34.5	"	9.122	-32.5	"	9.074
-33.5	"	9.099	-32	"	9.054
-32.5	"	9.072	-31	"	9.043
-31	"	9.063	-30	"	9.032
-30.5	"	9.045	-29	"	9.011
-29.5	"	9.035	-28.5	"	8.996
-28.5	"	8.968	-27.5	"	8.977
-28	"	9.001	-26.5	"	8.957
-27	"	8.981	-26	"	8.945
-26	"	8.964	-25	"	8.921
-25	"	8.898	-24	"	8.899
-24.5	"	8.924	-23	"	8.883
-23.5	"	8.908	-22	"	8.862
-22.5	"	8.888	-21	"	8.779
-21.5	"	8.861	-20.5	"	8.818
-21	"	8.849	-19.5	"	8.792
-20	"	8.829	-18.5	"	8.714
-19	"	8.786	-18	"	8.745
-18	"	8.775	-17	"	8.721
-17.5	"	8.748	-16	"	8.613
-16.5	"	8.708	-15	"	8.656
-15.5	"	8.693	-14.5	"	8.636
-14.5	"	8.669	-13	"	8.587
-13.5	"	8.617	-12	"	8.556
-12.5	"	8.6	-11.5	"	8.528

Continuation of Table 6

Example 2

Example 3

T[°C] " log E	T[°C] " log E
-11.5 " 8.574	-10.5 " 8,48
-11 " 8.525	-9.5 " 8,417
-10 " 8.511	-8.5 " 8,415
-9.5 " 8.448	-7.5 " 8,382
-8.5 " 8.426	-7 " 8,327
-7.5 " 8.403	-6 " 8,299
-6.5 " 8.35	-5 " 8,153
-6 " 8.317	-4 " 8,205
-4.5 " 8,24	-3.5 "
-3.5 " 8.208	-3 " 8,034
-3 " 8.034	-2 " 8,109
-2 " 8.109	-1 " 8,076
-1 " 8.076	-,5 " 7,997
-.5 " 7.997	1 " 7,955
1 " 7.955	1,5 " 7,86
1.5 " 7.86	2,5 " 7,836
2.5 " 7.836	3 " 7,79
3 " 7.79	4 " 7,681
4 " 7.681	5 " 7,654
5 " 7.654	6 " 7,618
6 " 7.618	7,5 " 7,503
7.5 " 7.503	8 " 7,464
8 " 7.464	9 " 7,425
9 " 7.425	10 " 7,311
10 " 7.311	11 " 7,275
11 " 7.275	12 " 7,231
12 " 7.231	13 " 7,185
13 " 7.185	13,5 " 7,15
13.5 " 7.15	14,5 " 7,099
14.5 " 7.099	15,5 " 7,051
15.5 " 7.051	16 " 6,999
16 " 6.999	17,5 " 6,932
17.5 " 6.932	18 " 6,891

Example 3

[illegible]

Table 7

Example 4

Example 1

T[°C] " log E			T[°C] " log E		
-39	"	9.332	-39	"	9.395
-38	"	9.33	-38.5	"	9.394
-37	"	9.317	-38	"	9.393
-36	"	9.306	-36.5	"	9.39
-35	"	9.303	-35.5	"	9.378
-34	"	9.28	-35	"	9.378
-33.5	"	9.276	-34.5	"	9.377
-32.5	"	9.265	-33.5	"	9.378
-31.5	"	9.251	-32.5	"	9.363
-30.5	"	9.232	-31.5	"	9.356
-29.5	"	9.223	-31	"	9.357
-29	"	9.208	-29.5	"	9.35
-27.5	"	9.19	-28.5	"	9.337
-27	"	9.17	-28	"	9.334
-26	"	9.146	-27.5	"	9.332
-25	"	9.134	-26	"	9.32
-24	"	9.119	-25	"	9.279
-23.5	"	9.1	-24.5	"	9.305
-22.5	"	9.074	-24	"	9.303
-21.5	"	9.052	-22.5	"	9.295
-21	"	9.039	-21	"	9.267
-20	"	9.008	-20.5	"	9.263
-19	"	8.981	-20	"	9.261
-18	"	8.958	-19.5	"	9.256
-17.5	"	8.911	-18.5	"	9.241
-16.5	"	8.896	-17	"	9.205
-15	"	8.864	-16.5	"	9.202
-14.5	"	8.825	-16	"	9.199
-13.5	"	8.792	-15	"	9.192
-13	"	8.765	-13.5	"	9.136
-12	"	8.654	-13	"	9.129
-11	"	8.689	-12.5	"	9.125

Continuation of Table 7

Example 4

Example 1

T[°C] " log E	T[°C] " log E
-10 " 8.662	-11 " 9.103
-9.5 " 8.615	-10 " 9.044
-8.5 " 8.587	-9.5 " 9.041
-7.5 " 8.515	-9 " 9.037
-6.5 " 8.393	-6 " 8.892
-6 " 8.448	-5.5 " 8.921
-5 " 8.408	-5 " 8.919
-4 " 8.321	-5 " 8.64
-3 " 8.297	1 " 8.491
-2 " 8.22	1.5 " 8.528
-1 " 8.145	2 " 8.549
0 " 8.109	3 " 8.451
1 " 7.997	6 " 8.194
2 " 7.954	9.5 " 7.827
3 " 7.829	10 " 7.94
4 " 7.807	12.5 " 7.493
5.5 " 7.722	13.5 " 7.657
6 " 7.673	16.5 " 7.273
7 " 7.627	17 " 7.328
7.5 " 7.579	19 " 7.118
9 " 7.464	19.5 " 7.143
10.5 " 7.364	21.5 " 6.932
11 " 7.313	22.5 " 6.924
12 " 7.247	23 " 6.951
13 " 7.213	25 " 6.817
13.5 " 7.156	25.5 " 6.84
14.5 " 7.123	27.5 " 6.741
15.5 " 7.057	32 " 6.599
16 " 7.022	39 " 6.483
17 " 6.956	38.5 " 6.5
18 " 6.892	42 " 6.486
19 " 6.846	42.5 " 6.519
20 " 6.789	45.5 " 6.474

Continuation of Table 7

Example 4

Example 1

T[°C] = log E		T[°C] = log E	
20.5 "	6.759	45 "	6.477
23 "	6.617	47.5 "	6.522
24.5 "	6.566	48.5 "	6.489
25.5 "	6.518	51.5 "	6.536
26.5 "	6.506	54.5 "	6.472
27.5 "	6.491	57.5 "	6.542
28.5 "	6.452	58 "	6.52
29.5 "	6.439		
30.5 "	6.382		
31 "	6.366		
32 "	6.373		
33 "	6.302		
33.5 "	6.357		
34.5 "	6.329		
35.5 "	6.286		
36.5 "	6.283		
37 "	6.296		
38.5 "	6.269		
39 "	6.256		
40 "	6.137		
41 "	6.23		
42 "	6.247		
42.5 "	6.232		
43.5 "	6.181		
44 "	6.262		
45 "	6.215		
46 "	6.17		
46.5 "	6.158		
47.5 "	6.166		
48.5 "	6.067		
49.5 "	6.081		
50 "	6.154		
51 "	6.07		
53 "	6.025		
53.5 "	6.114		
54.5 "	6.185		
55.5 "	6.073		
56.5 "	6.083		
57 "	6.132		
58 "	6.105		
59 "	6.125		
59.5 "	6.142		
60.5 "	6.202		

Table 8

Comparative
Example 2

Comparative
Example 3

Comparative
Example 1

T [°C] * log E	T [°C] * log E	T [°C] * log E
-40.5 " 9.237	-38 " 9.363	-38.5 " 9.403
-41.5 " 9.264	-37.5 " 9.366	-38 " 9.408
-40 " 9.28	-37 " 9.37	-37.5 " 9.41
-37.5 " 9.223	-36.5 " 9.37	-37 " 9.409
-37 " 9.241	-36 " 9.368	-36.5 " 9.408
-37.5 " 9.257	-35.5 " 9.367	-36 " 9.406
-38 " 9.267	-34 " 9.341	-35 " 9.403
-35 " 9.24	-33 " 9.334	-33.5 " 9.384
-33.5 " 9.22	-32.5 " 9.333	-33 " 9.382
-33 " 9.229	-32 " 9.33	-32.5 " 9.382
-31 " 9.203	-30.5 " 9.312	-32 " 9.38
-30.5 " 9.2	-28.5 " 9.291	-31 " 9.376
-30 " 9.199	-28 " 9.294	-29.5 " 9.355
-29.5 " 9.203	-27.5 " 9.289	-28.5 " 9.353
-27.5 " 9.175	-27 " 9.287	-28 " 9.354
-26.5 " 9.157	-26 " 9.264	-27.5 " 9.351
-26 " 9.159	-25 " 9.255	-26 " 9.327
-25.5 " 9.158	-24.5 " 9.251	-24.5 " 9.317
-23.5 " 9.133	-23.5 " 9.251	-24 " 9.317
-22.5 " 9.116	-22 " 9.215	-23.5 " 9.317
-22 " 9.115	-21 " 9.207	-23 " 9.313
-21.5 " 9.117	-20.5 " 9.206	-22.5 " 9.313
-21 " 9.117	-20 " 9.202	-21 " 9.279
-19 " 9.075	-19 " 9.186	-20 " 9.274
-18.5 " 9.071	-17.5 " 9.156	-19.5 " 9.273
-18 " 9.071	-17 " 9.155	-19 " 9.271
-17.5 " 9.07	-16.5 " 9.153	-18 " 9.256
-16 " 9.047	-15 " 9.125	-16.5 " 9.226
-15 " 8.989	-14 " 9.1	-16 " 9.222
-14.5 " 9.02	-13.5 " 9.099	-15.5 " 9.22
-14 " 9.02	-13 " 9.096	-14.5 " 9.207
-13.5 " 9.02	-11.5 " 9.061	-13 " 9.165

Continuation of Table 8

Comparative
Example 2

Comparative
Example 3

Comparative
Example 1

T [°C] " log E	T [°C] " log E	T [°C] " log E
-11.5 " 8.967	-11 " 9.048	-12.5 " 9.162
-11 " 8.961	-10.5 " 9.045	-12 " 9.16
-10.5 " 8.96	-9 " 9.007	-11.5 " 9.157
-10 " 8.958	-8 " 8.99	-9.5 " 9.085
-8.5 " 8.917	-7.5 " 8.988	-8.5 " 9.081
-7.5 " 8.898	-7 " 8.987	-8 " 9.08
-7 " 8.894	-5.5 " 8.922	-7.5 " 9.079
-6.5 " 8.896	-5 " 8.917	-6 " 8.998
-5 " 8.846	-4.5 " 8.918	-5 " 8.982
-4 " 8.83	-3.5 " 8.91	-4.5 " 8.986
-3.5 " 8.798	-1.5 " 8.822	-4 " 8.985
-3 " 8.825	-1 " 8.83	-2 " 8.827
-1 " 8.741	-5 " 8.83	-1.5 " 8.886
-5 " 8.744	1 " 8.757	-1 " 8.888
0 " 8.747	2 " 8.717	5 " 8.703
1.5 " 8.708	2.5 " 8.725	1 " 8.761
3 " 8.62	3 " 8.728	1.5 " 8.768
3.5 " 8.635	5 " 8.531	2 " 8.767
4 " 8.643	6 " 8.556	5 " 8.573
6 " 8.508	6.5 " 8.577	7 " 8.422
6.5 " 8.501	7 " 8.591	9 " 8.372
7 " 8.52	7.5 " 8.597	12.5 " 8.297
7.5 " 8.524	10.5 " 8.266	16.5 " 7.757
10 " 8.245	11 " 8.41	19 " 7.359
10.5 " 8.331	12.5 " 8.04	20 " 7.414
11 " 8.363	14 " 8.164	20.5 " 7.468
10.5 " 8.389	14.5 " 8.209	23.5 " 7.158
12.5 " 8.101	16.5 " 7.791	23 " 7.209
14 " 8.132	17 " 7.982	23.5 " 7.244
14.5 " 8.165	17.5 " 8.023	26 " 6.909
14 " 8.196	20.5 " 7.679	26.5 " 6.989
16 " 8.067	21 " 7.806	28 " 6.911
17.5 " 7.908	23.5 " 7.476	29.5 " 6.844

Continuation of Table 8

Comparative Example 2		Comparative Example 3		Comparative Example 1	
T [°C]	" log E	T [°C]	" log E	T [°C]	" log E
18	" 7.954	24	" 7.534	29	" 6.871
18.5	" 8.016	26	" 7.256	31.5	" 6.685
21	" 7.666	27	" 7.229	32.5	" 6.698
21.5	" 7.722	26.5	" 7.289	32	" 6.733
21	" 7.774	27.5	" 7.297	34.5	" 6.391
23.5	" 7.488	30.5	" 7.011	35	" 6.604
24.5	" 7.452	30	" 7.072	35.5	" 6.58
25	" 7.498	30.5	" 7.102	38	" 6.464
24.5	" 7.541	33.5	" 6.79	38.5	" 6.554
26.5	" 7.363	34	" 6.828	38	" 6.541
27.5	" 7.273	33.5	" 6.873	40.5	" 6.464
28	" 7.312	34	" 6.897	41.5	" 6.469
28.5	" 7.313	36	" 6.712	41	" 6.502
30.5	" 7.081	37	" 6.674	43	" 6.497
31	" 7.115	36.5	" 6.71	45	" 6.449
30.5	" 7.162	39	" 6.59	44.5	" 6.432
33	" 6.988	47.5	" 6.299	45	" 6.462
34.5	" 6.971	50.5	" 6.309	47.5	" 6.432
34	" 7.013	51	" 6.309	48.5	" 6.452
37	" 6.85	54.5	" 6.299	48	" 6.417
38	" 6.831	55	" 6.389	51.5	" 6.339
37.5	" 6.86	58	" 6.29	52	" 6.42
38.5	" 6.795	57.5	" 6.374	51	" 6.368
40.5	" 6.767	58.5	" 6.425	54	" 6.421
41	" 6.776			55	" 6.466
40.5	" 6.773			54.5	" 6.393
42.5	" 6.744			55	" 6.419
44	" 6.712			57	" 6.388
44.5	" 6.716			58	" 6.394
44	" 6.714			57.5	" 6.382
46	" 6.681			58.5	" 6.453
47.5	" 6.688				
47	" 6.668				
48	" 6.693				
50.5	" 6.657				
51	" 6.66				
50.5	" 6.641				
52	" 6.68				
54	" 6.646				
54.5	" 6.633				
53.5	" 6.637				
55.5	" 6.672				
57.5	" 6.644				
58	" 6.636				
57	" 6.651				
58.5	" 6.676				
60.5	" 6.648				



Patent claims

1. Radiation-curable oligomers having a plurality of ethylenically unsaturated end groups and a plurality of urethane and/or urea groups per molecule, which oligomers
5 can be prepared from
- a) at least one hydroxy- and/or aminofunctional compound having a functionality between 3 and 4 and a number-average molecular weight of more than 750 to 4000, polyesterpolyols being excepted,
 - 10 b) at least one compound having 2 hydroxyl and/or amino groups per molecule and a number-average molecular weight between 200 and 4000, polyesterdiols being excepted,
 - c) at least one monoethylenically unsaturated compound
15 having a group containing one active hydrogen atom per molecule and having a number-average molecular weight between 116 and 1000, and
 - d) at least one aliphatic and/or cycloaliphatic diisocyanate,
- 20 characterized in that components a to d are used in amounts such that
- 1) the molar ratio of component a to component b is between 0.1 : 1 and 1.1 : 1,
 - 2) the molar ratio of component c to component a is
25 between 2 : 1 and 10 : 1, and
 - 3) the equivalent ratio of the isocyanate groups of component d to the hydroxyl and/or amino groups of the sum of components a to c is between 0.9 and 1.0.
2. Radiation-curable oligomers according to Claim 1,
30 characterized in that compounds having a functionality of 3 have been used as component a.
3. Radiation-curable oligomers according to Claim 1 or 2, characterized in that compounds having a number-average molecular weight of more than 750 to 2000 have
35 been used as component a and/or compounds having a number-average molecular weight between 600 and 2000 as component b and/or compounds having a number-average molecular weight between 116 and 400 as component c.



4. Radiation-curable oligomers according to one of Claims 1 to 3, characterized in that components a to d have been used in amounts such that

- 1) the molar ratio of component a to component b is between 0.1 and 0.8 and/or
- 2) the molar ratio of component c to component a is between 2.5 and 10.

5. Radiation-curable oligomers according to Claim 4, characterized in that the oligomer has an acrylic group content of 0.45 to 0.63 mol/kg.

6. Radiation-curable oligomers according to one of Claims 1 to 5, characterized in that an ethoxylated triol having a number-average molecular weight of > 1000 has been used as component a.

7. Radiation-curable oligomers according to one of Claims 1 to 6, characterized in that a mixture comprising

- b₁) 0 to 90 mol % of a polyetherdiol and
- b₂) 100 to 10 mol % of a modified polyetherdiol composed of

b₂₁) at least one polyetherdiol

b₂₂) at least one aliphatic and/or cycloaliphatic dicarboxylic acid and

b₂₃) at least one aliphatic, saturated compound having an epoxy group and 8 to 21 C atoms per molecule,

in which the sum of the amounts of components b₁ and b₂ and the sum of the amounts of components b₂₁ to b₂₃ is in each case 100 mol %, has been used as component b.

8. Radiation-curable oligomers according to one of Claims 1 to 7, which have been prepared by

- 1) carrying out the polyaddition reaction of components a to d up to a conversion of more than 85 % of the NCO groups, in which components a to d have been used in amounts such that the equivalent ratio of the isocyanate groups of component a to the hydroxyl and/or amino groups of components a to c is 1:1 and
- 2) the polyaddition reaction of components a to d has been continued with addition of more of component c



up to a conversion of more than 99 % of the NCO groups.

9. Radiation-curable coating composition, which contains at least one radiation-curable oligomer according to one of Claims 1 to 8.

10. Radiation-curable coating composition according to Claim 9, in particular for the buffer coating of optical glass fibres, which contains

- A) 10 to 78 % of at least one radiation-curable oligomer according to one of Claims 1 to 8,
- B) 0 to 60 % by weight of at least one further ethylenically unsaturated oligomer,
- C) 20 to 50 % by weight of at least one ethylenically unsaturated monomeric compound,
- D) 2 to 8 % by weight of at least one photoinitiator and
- E) 0 to 4 % by weight of conventional auxiliaries and additives,

the % by weight given being in each case relative to the total weight of the coating composition.

11. Radiation-curable coating composition according to Claim 9, which contains

- A) at least 15 % of at least one radiation-curable oligomer according to one of Claims 1 to 8,
- B) 0 to 50 % by weight of at least one further ethylenically unsaturated oligomer,
- C) 22 to 35 % by weight of at least one ethylenically unsaturated monomeric compound,
- D) 3 to 5 % by weight of at least one photoinitiator and
- E) 0.5 to 2.0 % by weight of conventional auxiliaries and additives,

the % by weight given being in each case relative to the total weight of the coating composition.

12. Radiation-curable coating composition according to Claim 10 or 11, which contains a further ethylenically unsaturated polyurethane as component B.

13. Process for the coating of a glass surface, in particular a glass fibre, in which



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- 1) a radiation-curable primer is applied and cured by means of UV or electron radiation and
 - 2) a radiation-curable top coat is applied and cured by means of UV or electron radiation,
- 5 characterized in that a radiation-curable coating composition according to one of Claims 9 to 12 is used as primer and/or topcoat.
14. . . Optical glass fibre coated with a radiation-curable coating composition according to one of Claims 9
- 10 to 12.