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(71) **Demandeur/Applicant:**
BAYER MATERIALSCIENCE LLC, US

(72) **Inventeurs/Inventors:**
ROESLER, RICHARD R., US;
GARRETT, JAMES T., US;
LOCKHART, AARON, US;
KINNEY, CAROL L., US

(74) **Agent:** OGILVY RENAULT LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : POLYISOCYANATES A FAIBLE ENERGIE SUPERFICIELLE ET UTILISATION CONNEXE POUR PRODUIRE
DES COMPOSITIONS DE REVETEMENT A UN OU DEUX CONSTITUANTS

(54) Title: LOW SURFACE ENERGY POLYISOCYANATES AND THEIR USE IN ONE- OR TWO- COMPONENT
COATING COMPOSITIONS

(57) **Abrégé/Abstract:**

The present invention is directed to a polyisocyanate mixture i) having an NCO content of 5 to 35% by weight and a monomeric diisocyanate content of less than 3% by weight, and prepared from a polyisocyanate adduct, ii) containing allophanate groups in an amount such that there are more equivalents of allophanate groups than urethane groups and iii) containing fluorine (calculated as F, AW 19) in an amount of 0.001 to 50% by weight, wherein the preceding percentages are based on the solids content of the polyisocyanate mixture and wherein fluorine is incorporated by reacting an isocyanate group with a compound containing two or more carbon atoms, one or more hydroxyl groups and one or more fluorine atoms. The present invention is also directed to a process for the production of this polyisocyanate mixture and to its use, optionally in blocked form, as an isocyanate component in one- or two-component coating compositions.



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MD-05-06

LOW SURFACE ENERGY POLYISOCYANATES AND THEIR
USE IN ONE- OR TWO-COMPONENT COATING COMPOSITIONS

ABSTRACT OF THE DISCLOSURE

The present invention is directed to a polyisocyanate mixture

- i) having an NCO content of 5 to 35% by weight and a monomeric diisocyanate content of less than 3% by weight, and prepared from a polyisocyanate adduct,
- ii) containing allophanate groups in an amount such that there are more equivalents of allophanate groups than urethane groups and
- iii) containing fluorine (calculated as F, AW 19) in an amount of 0.001 to 50% by weight,

wherein the preceding percentages are based on the solids content of the polyisocyanate mixture and wherein fluorine is incorporated by reacting an isocyanate group with a compound containing two or more carbon atoms, one or more hydroxyl groups and one or more fluorine atoms.

The present invention is also directed to a process for the production of this polyisocyanate mixture and to its use, optionally in blocked form, as an isocyanate component in one- or two-component coating compositions.

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**LOW SURFACE ENERGY POLYISOCYANATES AND THEIR
USE IN ONE- OR TWO-COMPONENT COATING COMPOSITIONS**

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention is directed to low surface energy polyisocyanates which contain allophanate groups and fluorine, to a process for their preparation by allophanatizing the isocyanate groups of polyisocyanate adducts in the presence of compounds containing hydroxyl groups and fluorine, and to their use in one- and two-component coating compositions.

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Description of the Prior Art

Polyurethane coating compositions containing a polyisocyanate component, in either blocked or unblocked form and an isocyanate-reactive component, generally a high molecular weight polyol, are well known.

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Although coatings prepared from these compositions possess many valuable properties, one property, in particular, which needs to be improved is the surface quality. It can be difficult to formulate coating compositions to obtain a coating having a smooth surface as opposed to one containing surface defects such as craters, etc.

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It is believed that these difficulties are related to the high surface tension of the two-component coating compositions. Another problem caused by the high surface tension is the difficulty in cleaning the coatings. Regardless of their potential application area, there is a high likelihood that the coatings will be subjected to stains, graffiti, etc.

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The incorporation of either fluorine or siloxane groups into polyisocyanates via allophanate groups in order to reduce the surface tension of the polyisocyanates and the surface energy of the resulting polyurethane coatings is disclosed in U.S. Patents 5,541,281; 5,574,122; 25 5,576,411; 5,646,227; 5,691,439; and 5,747,629. A disadvantage of the

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polyisocyanates disclosed in these patents is that they are prepared by reacting an excess of monomeric diisocyanates with the compounds containing either fluorine or siloxane groups. After the reaction is terminated the unreacted monomeric diisocyanates must be removed by

5 an expensive thin film distillation process. In addition, it is important to avoid the use of any unnecessary apparatus, such as distillation apparatus, when preparing the low surface energy polyisocyanates because fluorine and the siloxane groups can contaminate the production apparatus requiring extensive cleaning before the apparatus can be used

10 to prepare other products.

Accordingly, it is an object of the present invention to provide coating compositions which have reduced surface tension and, thus, are suitable for the production of coatings which have lower surface energies, improved surfaces and improved cleanability and which also possess the

15 other valuable properties of the known polyurethane coatings. It is an additional object of the present invention to provide polyisocyanates that attain the preceding objective and can be prepared without the need for the expensive and difficult removal of excess, unreacted monomeric diisocyanates.

20 Surprisingly, these objectives may be achieved with the polyisocyanate mixtures according to the present invention containing allophanate groups and fluorine which are described hereinafter. These polyisocyanate mixtures are prepared from polyisocyanate adducts instead of monomeric diisocyanates. While it would be expected that the

25 use of higher molecular weight and optionally higher functionality polyisocyanate adducts as starting materials would result in insoluble, high viscosity or gel-like products, this is not the case.

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SUMMARY OF THE INVENTION

The present invention is directed to a polyisocyanate mixture

5 i) having an NCO content of 5 to 35% by weight and a monomeric diisocyanate content of less than 3% by weight, and prepared from a polyisocyanate adduct,

10 ii) containing allophanate groups in an amount such that there are more equivalents of allophanate groups than urethane groups and

15 iii) containing fluorine (calculated as F, AW 19) in an amount of 0.001 to 50% by weight,

20 wherein the preceding percentages are based on the solids content of the polyisocyanate mixture and wherein fluorine is incorporated by reacting an isocyanate group with a compound containing two or more carbon atoms, one or more hydroxyl groups and one or more fluorine atoms.

The present invention is also directed to a process for the

15 production of a polyisocyanate mixture

20 i) having an NCO content of 5 to 35% by weight and a monomeric diisocyanate content of less than 3% by weight, and prepared from a polyisocyanate adduct,

25 ii) containing allophanate groups in an amount such that there are more equivalents of allophanate groups than urethane groups and

30 iii) containing fluorine (calculated as F, AW 19) in an amount of 0.001 to 50% by weight,

wherein the preceding percentages are based on the solids content of the polyisocyanate mixture,

25 by

30 a) reacting a portion of the isocyanate groups of a polyisocyanate adduct with 0.01 to 500 millimoles, per mole of polyisocyanate adduct, of a compound containing two or more carbon atoms, one or more hydroxyl groups and one or more fluorine atoms to form urethane groups,

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- b) adding an allophanatization catalyst prior to, during or after step a),
- c) converting a sufficient amount of the urethane groups formed in step a) to allophanate groups to satisfy the requirements of ii) and
- d) terminating the allophanatization reaction at the desired NCO

5 content by adding a catalyst poison and/or by thermally deactivating the catalyst and recovering the polyisocyanate mixture without removing monomeric diisocyanates.

10 The present invention also relates to the use of the polyisocyanate mixture, optionally in blocked form, as an isocyanate component in one- or two-component coating compositions.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention the term "(cyclo)aliphatically bound isocyanate groups" means aliphatically and/or cycloaliphatically bound isocyanate groups.

15 In accordance with the present invention the polyisocyanate mixtures are prepared from polyisocyanate adducts which are prepared from monomeric polyisocyanates and contain isocyanurate, uretdione, biuret, urethane, allophanate, iminoxadiazine dione, carbodiimide, acylurea and/or oxadiazinetrione groups. The polyisocyanate adducts, 20 which preferably have an NCO content of 5 to 30% by weight, include:

- 1) Isocyanurate group-containing polyisocyanates which may be prepared as set forth in DE-PS 2,616,416, EP-OS 3,765, EP-OS 10,589, EP-OS 47,452, US-PS 4,288,586 and US-PS 4,324,879.

The isocyanato-isocyanurates generally have an average NCO

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functionality of 3 to 4.5 and an NCO content of 5 to 30%, preferably 10 to 25% and most preferably 15 to 25% by weight.

- 2) Uretdione diisocyanates which may be prepared by oligomerizing a portion of the isocyanate groups of a diisocyanate in the presence of a suitable catalyst, e.g., a trialkyl phosphine catalyst, and which may be used in admixture with other aliphatic and/or cycloaliphatic polyisocyanates, particularly the isocyanurate group-containing polyisocyanates set forth under (1) above.
- 3) Biuret group-containing polyisocyanates which may be prepared according to the processes disclosed in U.S. Patent Nos. 3,124,605; 3,358,010; 3,644,490; 3,862,973; 3,906,126; 3,903,127; 4,051,165; 4,147,714; or 4,220,749 by using co-reactants such as water, tertiary alcohols, primary and secondary monoamines, and primary and/or secondary diamines. These polyisocyanates preferably have an NCO content of 18 to 22% by weight.
- 4) Iminooxadiazine dione and optionally isocyanurate group-containing polyisocyanates which may be prepared in the presence of special fluorine-containing catalysts as described in DE-A 19611849. These polyisocyanates generally have an average NCO functionality of 3 to 3.5 and an NCO content of 5 to 30%, preferably 10 to 25% and most preferably 15 to 25% by weight.
- 5) Carbodiimide group-containing polyisocyanates which may be prepared by oligomerizing di- or polyisocyanates in the presence of known carbodiimidization catalysts as described in DE-PS 1,092,007, US-PS 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350.
- 6) Polyisocyanates containing oxadiazinetrione groups and containing the reaction product of two moles of a diisocyanate and one mole of carbon dioxide.

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Preferred polyisocyanate adducts are the polyisocyanates containing isocyanurate, uretdione, biuret, and/or iminoxadiazine dione groups, especially polyisocyanate containing isocyanurate groups and optionally uretdione or iminoxadiazine dione groups.

5 Suitable monomeric diisocyanates for preparing the polyisocyanate adducts include those represented by the formula



in which R represents an organic group obtained by removing the isocyanate groups from an organic diisocyanate having a molecular weight 10 of about 140 to 400. Preferred diisocyanates are those in which R represents a divalent aliphatic hydrocarbon group having 4 to 40, preferably 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon group having 7 to 15 carbon atoms or a divalent aromatic hydrocarbon 15 group having 6 to 15 carbon atoms.

Examples of the suitable organic diisocyanates include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)-methane, 2,4'-dicyclohexyl-methane diisocyanate, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diisocyanate, 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, 2,4- and/or 4,4'-diphenyl-methane diisocyanate, 1,5-diisocyanato naphthalene and mixtures thereof.

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Polyisocyanates containing 3 or more isocyanate groups such as 4-isocyanantomethyl-1,8-octamethylene diisocyanate and aromatic polyisocyanates such as 4,4',4"-triphenylmethane triisocyanate and polyphenyl polymethylene polyisocyanates obtained by phosgenating 5 aniline/formaldehyde condensates may also be used.

Preferred organic diisocyanates include 1,6-hexamethylene diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanato-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene 10 diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, and 2,4- and/or 4,4'-diphenylmethane diisocyanate.

In accordance with the present invention urethane groups and preferably allophanate groups are incorporated into the polyisocyanate mixtures by the use of compounds containing two or more carbon atoms, 15 one or more hydroxyl groups (preferably one or two hydroxyl groups, more preferably one) and one or more fluorine atoms (preferably in the form of fluoroalkyl groups such as $-CF_2-$). Examples of these compounds include aliphatic, cycloaliphatic, araliphatic or aromatic hydroxyl group-containing compounds, which contain two or more carbon atoms and also contain 20 fluorine atoms, preferably fluoroalkyl groups. The compounds may be linear, branched or cyclic and have a molecular weight (number average molecular weight as determined by gel permeation chromatography using polystyrene as standard) of up to 50,000, preferably up to 10,000, more preferably up to 6000 and most preferably up to 2000. These compounds 25 generally have OH numbers of greater than 5, preferably greater than 25 and more preferably greater than 35. The hydroxyl group-containing compounds may optionally contain other hetero atoms in the form of, e.g., ether groups, ester groups, carbonate groups, acrylic groups, etc.

Thus, it is possible in accordance with the present invention to use 30 the known polyols from polyurethane chemistry, provided that they contain

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fluorine, e.g. by using fluorine-containing alcohols, acids, unsaturated monomers, etc. in the preparation of these polyols. Examples of these polyols, which may be prepared from fluorine-containing precursors and used in accordance with the present invention, are disclosed in U.S.

- 5 Patent 4,701,480, the disclosure of which is herein incorporated by reference. Additional examples of suitable fluorine-containing compounds are disclosed in U.S. Patents 5,294,662 and 5,254,660, the disclosures of which are herein incorporated by reference.

Preferred for use according to the invention are compounds

- 10 containing one or more hydroxyl groups, preferably one or two hydroxyl groups and more preferably one hydroxyl group; one or more fluoroalkyl groups; optionally one or more methylene groups; and optionally other hetero atoms such as ether groups. These compounds preferably have a molecular weight of less than 2000 or a hydroxyl number of greater
- 15 than 28.

To prepare the polyisocyanates mixtures according to the invention the minimum ratio of fluorine-containing compounds to polyisocyanate adduct is about 0.01 millimoles, preferably about 0.1 millimoles and more preferably about 1 millimole of fluorine-containing compounds for each

- 20 mole of polyisocyanates adduct. The maximum amount of fluorine-containing compounds to polyisocyanate adduct is about 500 millimoles, preferably about 100 millimoles and more preferably about 20 millimoles of fluorine-containing compounds for each mole of polyisocyanate adduct. The amount of fluorine is selected such that the resulting polyisocyanate
- 25 mixture contains a minimum of 0.001% by weight, preferably 0.01% by weight and more preferably 0.1% by weight, of fluorine (calculated as F, AW 19), based on solids, and a maximum of 50% by weight, preferably 10% by weight, more preferably 7% by weight and most preferably 3% by weight of fluorine, based on solids.

Suitable methods for preparing the polyisocyanate mixtures containing allophanate groups are known and described in U.S. Patents 3,769,318, 4,160,080 and 4,177,342 and 4,738,991, the disclosures of which are herein incorporated by reference. The allophanatization reaction

- 5 may be conducted at a temperature of 50 to 250°C, preferably 60 to 150°C and more preferably 70 to 120°C. The reaction may be terminated by reducing the reaction temperature, by removing the catalyst, e.g., by applying a vacuum, or by the addition of a catalyst poison. After the reaction is terminated, there is no need to remove unreacted monomeric
- 10 diisocyanates, e.g., by thin film evaporation, because polyisocyanate adducts having low monomeric diisocyanate contents are used as the starting material.

The allophanatization reaction may be carried out in the absence or in the presence of solvents which are inert to isocyanate groups, 15 preferably in the absence of solvents, especially when liquid starting materials are used. Depending on the area of application of the products according to the invention, low to medium-boiling solvents or high-boiling solvents can be used. Suitable solvents include esters such as ethyl acetate or butyl acetate; ketones such as acetone or butanone; aromatic 20 compounds such as toluene or xylene; halogenated hydrocarbons such as methylene chloride and trichloroethylene; ethers such as diisopropylether; and alkanes such as cyclohexane, petroleum ether or ligroin.

The process according to the invention may take place either batchwise or continuously, for example, as described below. The starting 25 polyisocyanate adduct is introduced with the exclusion of moisture and optionally with an inert gas into a suitable stirred vessel or tube and optionally mixed with a solvent which is inert to isocyanate groups such as toluene, butyl acetate, diisopropylether or cyclohexane. The previously described compounds containing fluorine and hydroxyl groups may be 30 introduced into the reaction vessel in accordance with several

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embodiments. They may be prereacted with the starting polyisocyanate adduct to form urethane and prior to introducing the polyisocyanate adducts into the reaction vessel; they may be mixed with the polyisocyanate adducts and introduced into the reaction vessel; they may

5 be separately added to the reaction vessel either before or after, preferably after, the polyisocyanate adducts are added; or the catalyst may be dissolved in these compounds prior to introducing the solution into the reaction vessel.

The progress of the reaction is followed by determining the NCO content by a suitable method such as titration, refractive index or IR analysis. Thus, the reaction may be terminated at the desired degree of allophanatization. The termination of the allophanatization reaction can take place, for example, after the NCO content has fallen by 5 to 80% by weight, preferably 10 to 60% by weight and more preferably 20 to 50% by

10 weight, based on the initial isocyanate group content of the polyisocyanate adduct starting material.

The polyisocyanate mixtures obtained in accordance with the present invention have an average functionality of about 2 to 7, preferably 2 to 4; an NCO content of 10 to 35% by weight, preferably 10 to 30% by weight and more preferably 15 to 30% by weight; and a monomeric diisocyanate content of less than 3% by weight, preferably less than 2% by weight and more preferably less than 1% by weight. The polyisocyanate mixtures have an allophanate group content (calculated as $N_2C_2H_4O_3$, MW 101) of preferably at least 0.001% by weight, more preferably at least 0.01% by weight and most preferably at least 0.5% by weight. The upper limit for the allophanate group content is preferably 20%, preferably 10% by weight and most preferably 5% by weight. The preceding percentages are based on the solids content of the polyisocyanate mixtures.

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The products according to the present invention are polyisocyanate mixtures containing allophanate groups and fluorine. The products may also contain residual urethane groups which are not converted to allophanate groups depending upon the temperature maintained during the reaction and the degree of isocyanate group consumption. While it is preferred to convert at least 50%, more preferably at least 70% and most preferably at least 90% of the urethane groups formed from the fluorine-containing hydroxyl compounds to allophanate groups, it is not necessary provided that the number of equivalents of allophanate groups exceeds the number of equivalents of urethane groups. Preferably, the polyisocyanate mixture contains sufficient allophanate groups to ensure that the polyisocyanate mixture remains stable and homogeneous in storage for 1 month at 25°C, more preferably for 3 months at 25°C. If the polyisocyanate mixture contains an insufficient number of allophanate groups, the mixture may be cloudy and a gradual settling of insoluble constituents may take place during storage.

The products according to the invention are valuable starting materials for the production of polyisocyanate polyaddition products by reaction with compounds containing at least two isocyanate reactive groups. The products according to the invention may also be moisture-cured to form coatings. Preferred products are one or two-component coating compositions, more preferably polyurethane coating compositions. When the polyisocyanates are unblocked, two-component compositions are obtained. To the contrary when the polyisocyanates are blocked, one-component compositions are obtained.

Prior to their use in coating compositions, the polyisocyanate mixtures according to the invention may be blended with other known polyisocyanates, e.g., polyisocyanate adducts containing biuret, isocyanurate, allophanate, urethane, urea, carbodiimide, and/or uretdione groups. The amount of the polyisocyanates mixtures according to the

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invention that must be blended with these other polyisocyanates is dependent upon the fluorine content of the polyisocyanate mixtures according to the invention, the intended application of the resulting coating compositions and the amount of low surface energy properties which are 5 desired for this application.

To obtain low surface energy properties the resulting polyisocyanate blends should contain a minimum of 0.001% by weight, preferably 0.01% by weight and more preferably 0.1% by weight, of fluorine (AW 19), based on solids, and a maximum of 10% by weight, 10 preferably 7% by weight and more preferably 3% by weight of fluorine (AW 19), based on solids. While fluorine contents of greater than 10% by weight are also suitable for providing low surface energy coatings, there are no further improvements to be obtained by using higher quantities. By knowing the fluorine content of the polyisocyanate mixtures according to 15 the invention and the desired fluorine content of the resulting polyisocyanate blends, the relative amounts of the polyisocyanate mixtures and the other polyisocyanates may be readily determined.

In accordance with the present invention any of the polyisocyanate mixtures according to the invention can be blended with other polyisocyanates, provided that the resulting blends have the minimum fluorine content required for the polyisocyanate mixtures of the present invention. However, the polyisocyanate mixtures to be blended preferably have a minimum fluorine content of 5% by weight, more preferably 10% by weight, and preferably have a maximum fluorine content of 50% by 20 weight, more preferably 40% by weight and most preferably 30% by weight. These so-called "concentrates" may then be blended with other polyisocyanates to form polyisocyanate blends that may be used to prepare coatings having low surface energy characteristics.

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Several advantages are obtained by preparing concentrates with high fluorine contents and subsequently blending them with non-fluorine-containing polyisocyanates. Initially, it is possible to convert many products to low surface energy polyisocyanates while only producing one

5 concentrate. By forming such low surface energy polyisocyanates by blending commercially available polyisocyanates with concentrates, it is not necessary to separately prepare each of the products in both a fluorine-containing and a non-fluorine-containing form. One possible disadvantage of the highest fluorine contents is that all of the isocyanate

10 groups of a small portion of the starting polyisocyanate adducts may be reacted. These molecules that do not contain isocyanate groups cannot react into the resulting coating and, thus, may adversely affect the properties of the final coating.

Preferred reaction partners for the products according to the

15 invention are the polyhydroxy polyesters, polyhydroxy polyethers, polyhydroxy polyacrylates, polyhydroxy polylactones, polyhydroxy polyurethanes, polyhydroxy polyepoxides and optionally low molecular weight, polyhydric alcohols known from polyurethane coatings technology. Polyamines, particularly in blocked form, for example as polyketimines,

20 oxazolidines or polyaldimines are also suitable reaction partners for the products according to the invention. Also suitable are polyaspartic acid derivatives (aspartates) containing secondary amino groups, which also function as reactive diluents.

To prepare the coating compositions the amount of the

25 polyisocyanate component and the isocyanate reactive component are selected to provide equivalent ratios of isocyanate groups (whether present in blocked or unblocked form) to isocyanate-reactive groups of about 0.8 to 3, preferably about 0.9 to 1.5. The coating compositions may be cured either at ambient temperature or at elevated temperature.

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To accelerate hardening, the coating compositions may contain known polyurethane catalysts, e.g., tertiary amines such as triethylamine, pyridine, methyl pyridine, benzyl dimethylamine, N,N-dimethylamino cyclohexane, N-methyl-piperidine, pentamethyl diethylene triamine, 1,4-5 diazabicyclo[2.2.2]-octane and N,N'-dimethyl piperazine; or metal salts such as iron(III)-chloride, zinc chloride, zinc-2-ethyl caproate, tin(II)-ethyl caproate, dibutyltin(IV)-dilaurate and molybdenum glycolate.

The products according to the invention are also valuable starting materials for one-component coating compositions, preferably poly-10 urethane coating compositions, in which the isocyanate groups are used in a form blocked by known blocking agents. The blocking reaction is carried out in known manner by reacting the isocyanate groups with suitable blocking agents, preferably at an elevated temperature (e.g. about 40 to 160°C), and optionally in the presence of a suitable catalyst, for 15 example, the previously described tertiary amines or metal salts.

Suitable blocking agents include monophenols such as phenol, the cresols, the trimethylphenols and the tert. butyl phenols; tertiary alcohols such as tert. butanol, tert. amyl alcohol and dimethylphenyl carbinol; compounds which easily form enols such as acetoacetic ester, acetyl 20 acetone and malonic acid derivatives, e.g. malonic acid diethylester; secondary aromatic amines such as N-methyl aniline, the N-methyl toluidine, N-phenyl toluidine and N-phenyl xylidine; imides such as succinimide; lactams such as ϵ -caprolactam and δ -valerolactam; pyrazoles such as 3,5-dimethyl pyrazole; oximes such as butanone oxime, 25 methyl amyl ketoxime and cyclohexanone oxime; mercaptans such as methyl mercaptan, ethyl mercaptan, butyl mercaptan, 2-mercaptobenz-thiazole, α -naphthyl mercaptan and dodecyl mercaptan; and triazoles such as 1H-1,2,4-triazole.

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The polyisocyanate mixtures according to the invention may also be used as the polyisocyanate component in two-component water borne coating compositions. To be useful in these compositions the polyisocyanate mixtures may be rendered hydrophilic either by blending

- 5 with external emulsifiers or by a reaction with compounds containing cationic, anionic or non-ionic groups. The reaction with the hydrophilic compound may be carried out either before, during or after the allophanatization reaction to incorporate the fluorine-containing compound. Methods for rendering the polyisocyanates hydrophilic are
- 10 disclosed in copending application, U.S. Patents 5,194,487 and 5,200,489, the disclosures of which are herein incorporated by reference. The reduced surface tensions of the modified polyisocyanate mixtures enhance pigment dispersion and substrate wetting.

The coating compositions may also contain other additives such as

- 15 pigments, dyes, fillers, levelling agents and solvents. The coating compositions may be applied to the substrate to be coated in solution or from the melt by conventional methods such as painting, rolling, pouring or spraying.

The coating compositions containing the polyisocyanate mixtures according to the invention provide coatings which have good dry times, adhere surprisingly well to a metallic base, and are particularly light-fast, color-stable in the presence of heat and very resistant to abrasion. They are also characterized by high hardness, elasticity, very good resistance to chemicals, high gloss, good weather resistance, good environmental etch

- 25 resistance and good pigmenting qualities. Above all, the coating compositions have an excellent surface appearance and excellent cleanability.

The invention is further illustrated, but is not intended to be limited by the following examples in which all parts and percentages are by

- 30 weight unless otherwise specified.

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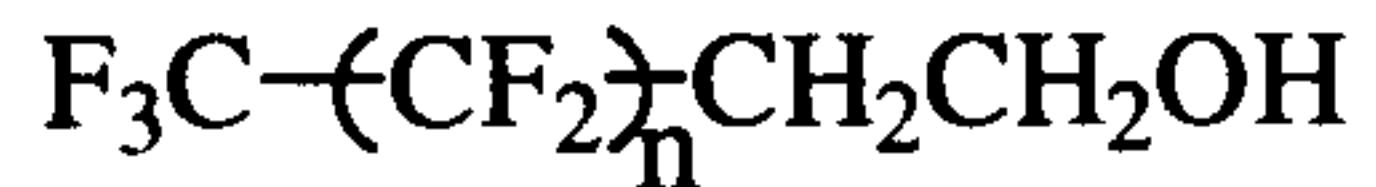
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EXAMPLES

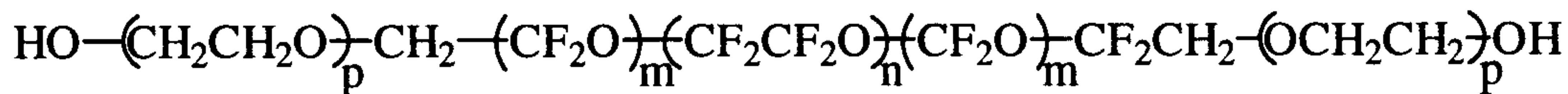
In the examples the allophanate group contents are based on the theoretical content assuming 100% conversion of the urethane groups to allophanate groups.

5 Fluorinated Alcohol BA-L

A fluorinated alcohol having a molecular weight of 443 (available from DuPont as Zonyl BA-L) and corresponding to the general formula

Fluorinated Alcohol D10

10 A fluorinated diol having a molecular weight of about 1000 (available from Solvay Solexis as Fluorolink D10) and corresponding to the general formula

Polyisocyanate 3400

15 An uretdione and isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 21.5%, a content of monomeric diisocyanate of <0.50%, a viscosity at 25°C of 200 mPa.s and a surface tension of 40 dynes/cm (available from Bayer Material Science as Desmodur N 3400).

20 Polyisocyanate 3600

An isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 22.8%, a content of monomeric diisocyanate of <0.25%, a viscosity at 25°C of 1145 mPa.s and a surface tension of 45 dynes/cm (available from 25 Bayer Material Science as Desmodur N 3600).

Polyisocyanate 2410

An isocyanurate and iminoxadiazine dione group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 23.6%, a content of monomeric diisocyanate of

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<0.30%, a viscosity at 25°C of 640 mPa.s and a surface tension of 40 dynes/cm (available from Bayer Material Science as Desmodur XP 2410).

Polyisocyanate 4470

An isocyanurate group-containing polyisocyanate prepared from 5 isophorone diisocyanate, and having an isocyanate content of 11.9%, a content of monomeric diisocyanate of <0.50%, a viscosity at 25°C of 670 mPa.s and a surface tension of 40 dynes/cm as a 70% solution in n-butyl acetate (available from Bayer Material Science as Desmodur Z 4470 BA).

Polyisocyanate 3200

10 A biuret group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 23%, a content of monomeric diisocyanate of <0.70%, a viscosity at 25°C of 1750 mPa.s and a surface tension of 47 dynes/cm (available from Bayer Material Science as Desmodur N 3200).

15 Surface tension of liquid samples

The Wilhelmy plate technique (flamed glass slides) was used to determine surface tension. Samples were analyzed with a Cahn DCA 312 dynamic contact angle analyzer. All samples were stirred prior to analysis.

Surface energy of film samples

20 Advancing angles of water and methylene iodide, polar and non-polar solvents respectively, were measured using a Rame-Hart goniometer. Total solid surface energies, including the polar and dispersive components, were calculated using the advancing angles according to the Owens Wendt procedure.

25 Example 1 - Preparation of Polyisocyanate Mixture 1

346.5 g (1.89 eq, based on actual titrated value) of Polyisocyanate 3600 and 3.5 g (0.008 eq) of Fluorinated Alcohol BA-L were charged to a 500 ml, 3-neck round bottom flask equipped with mechanical stirring, a cold water condenser, heating mantle, and N₂ inlet. As the reaction was

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stirred and heated to 110°C, a total of 0.06 g of stannous octoate were charged to the mixture. After cooking for 5 hours at 110°C, the NCO content reached the theoretical value of 22.56%; the heat was removed and a cold water/ice bath was applied. The viscosity was 1193 mPa.s @ 5 25°C and the surface energy of the liquid was 29.3 dynes/cm.

Examples 2-10 - Preparation of Polyisocyanate Mixtures 2-9

Other polyisocyanate mixtures were prepared in a similar fashion to Example 1 using different polyisocyanates and different types and amounts of fluorinated alcohols. Isobutanol was used in a comparison 10 example to show that the fluorinated alcohols are needed to provide low surface energy. Comparison Examples 4 and 5 use the same equivalents of alcohol as Examples 1 and 2, respectively. The details of Examples 1-9 are set forth in Table 1.

TABLE 1

Example	1	2	3	4 Comp	5 Comp
Polyisocyanate	3600	3600	3600	3600	3600
Fluorinated Alcohol	BA-L	BA-L	D10	iButanol	iButanol
Wt% -OH	1	10	1	0.17	1.7
Eq% -OH	0.42	4.2	0.37	0.42	4.2
% NCO	22.56	18.58	22.50	21.88	19.60
% F	0.5	4.6	0.5	0.0	0.0
% Allophanate	0.2	2.1	0.1	0.2	2.3
Visc, cps@25	1193	4309	1208	1831	5951
Surface tension, dynes/cm	29.3	22.1	24.5	45.6	44.2

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TABLE 1 - Cont.

Example	6	7	8	9
Polyisocyanate	3400	2410	4470	4470
Fluorinated Alcohol	BA-L	BA-L	BA-L	BA-L
Wt% -OH	1	1	1	10
Eq% -OH	0.45	0.40	0.57	5.7
% NCO	20.78	23.13	11.86	10.31
% F	0.5	0.5	0.4	3.4
% Allophanate	0.2	0.2	0.2	1.5
Visc, cps@25	138	768	834	1391
Surface tension, dynes/cm	24.5	28.4	29.7	23.9

Examples 10-13 - Preparation of moisture cure coatings

Moisture cure coatings were prepared by diluting the

5 polyisocyanate mixtures set forth in Table 2 with ethyl acetate until a viscosity of approximately 200 mPa.s was obtained and then adding 1 weight percent of dibutyl tin dilaurate, based on solids. Coatings were drawn down on unpolished cold roll steel panels using an 8 mil drawdown bar. The coatings were cured overnight on the laboratory bench top under

10 ambient conditions. The details of Examples 10-13 are set forth in

Table 2.

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TABLE 2

Example	10	11	12 (Comp)	13 (Comp)
Polyisocyanate Mixture from Example	1	2	4	5
% F of Polyisocyanate Mixture	0.5	4.6	0.0	0.0
% Allophanate of Polyisocyanate Mixture	0.2	2.1	0.2	2.3
Polyisocyanate Mixture, g	6	6	6	6
Solvent, g	0.7	1.5	0.7	1.5
Catalyst, g	0.06	0.06	0.06	0.06
Surface energy, dynes/cm	11.0	12.1	40.1	40.2

Examples 14-17 - Preparation of Two-Component Coating Compositions

Two-component coating compositions were prepared by mixing the 5 polyisocyanate mixtures set forth in Table 3 with a trifunctional polyester polyol (Desmophen 670A-80, available from Bayer MaterialScience LLC), at an NCO:OH equivalent ratio of 1.05:1.00 and adding 0.05 g of dibutyl tin dilaurate per hundred parts of polyisocyanate/polyol blend. An 8 mil drawdown bar was used to draw coatings on unpolished cold roll steel 10 panels. The coatings were cured overnight on the laboratory bench top under ambient conditions. The details of Examples 15-18 are set forth in Table 3.

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TABLE 3

Example	14	15	16 (Comp)	17 (Comp)
Polyisocyanate Mixture from Example	1	2	4	5
% F of Polyisocyanate Mixture	0.5	4.6	0.0	0.0
% Allophanate of Polyisocyanate Mixture	0.2	2.1	0.2	2.3
Polyisocyanate Mixture, g	5	5	5	5
Polyol, g	12.79	10.53	12.40	11.11
Catalyst, g	0.01	0.01	0.01	0.01
Surface energy, dynes/cm	11.5	9.6	30.9	28.1

Examples 18-24 - Use of Polyisocyanate Mixtures as Concentrates

1 g of the polyisocyanate mixtures from Examples 1, 2, 4, 5 and 9
 5 were mixed by hand with 9 g of the unmodified polyisocyanates set forth
 in Table 4. This resulting polyisocyanate mixtures possessed a low
 surface tension value, which indicates that the polyisocyanate mixtures
 according to the invention could be used as concentrates for diluting
 unmodified polyisocyanates. The details of Examples 18-24 are forth in
 10 Table 4.

TABLE 4

Example	18	19	20	21	22 Comp	23	24 Comp
Polyisocyanate Mixture from Example	2	2	2	9	5	1	4
Weight, g	1	1	1	1	1	1	1
Unmodified Polyisocyanate	3600	3200	3400	4470	3600	3600	3600
Weight, g	9	9	9	9	9	9	9
% F of Blend	0.5	0.5	0.5	0.3	0.0	0.5	0.0
% Allophanate of Blend	0.2	0.2	0.2	0.2	0.2	0.02	0.02
surface tension, dynes/cm	26	24	24	28	45	28	45

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This data shows that the Polyisocyanate Mixtures from Examples 1, 2 and 9 can be diluted with unmodified polyisocyanates, which did not contain fluorine, and still provide low surface tension. Dilution of the polyisocyanates from Comparison Examples 4 and 5 with the same 5 unmodified polyisocyanates did not change the high surface tension.

Examples 25-30 - Preparation of moisture cure coatings

Moisture cure coatings were prepared by diluting the Polyisocyanate Mixtures set forth in Table 5 with ethyl acetate until a viscosity of approximately 200 mPa.s was obtained and then adding 10 weight percent of dibutyl tin dilaurate, based on solids. Coatings were drawn down on unpolished cold roll steel panels using an 8 mil drawdown bar. The coatings were cured overnight on the laboratory bench top under ambient conditions. The details of Examples 25-30 are set forth in

Table 5.

15

TABLE 5

Example	25	26 comp	27	28 comp	29	30 comp
Polyisocyanate Mixture from Example	2	5	1	4	18	22
% F of Polyisocyanate Mixture	4.6	0.0	0.5	0.0	0.5	0.5
% Allophanate of Polyisocyanate Mixture	2.1	2.3	0.2	0.2	0.2	0.2
Polyisocyanate Mixture, g	6	6	6	6	6	6
Solvent, g	1.5	1.5	0.7	0.7	0.7	0.7
Catalyst, g	0.06	0.06	0.06	0.06	0.06	0.06
Surface energy, dynes/cm	12	40	11	40	14	42

This data shows that moisture cure coatings made from polyisocyanate mixtures, which were prepared from concentrates, had the same low surface energy as coatings made from polyisocyanate mixtures,

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which were directly made with the same amounts of fluorine. Coatings prepared from the comparison polyisocyanates had high surface energies.

Examples 31-36 - Preparation of Two-Component Coating Compositions

Two-component coating compositions were prepared by mixing the 5 polyisocyanate mixtures set forth in Table 3 with a trifunctional polyester polyol (Desmophen 670A-80, available from Bayer MaterialScience LLC), at an NCO:OH equivalent ratio of 1.05:1.00 and adding 0.05 g of dibutyl tin dilaurate per hundred parts of polyisocyanate/polyol blend. An 8 mil drawdown bar was used to draw coatings on unpolished cold roll steel 10 panels. The coatings were cured overnight on the laboratory bench top under ambient conditions. The details of Examples 31-36 are set forth in Table 6.

TABLE 6

Example	31	32 comp	33	34 comp	35	36 comp
Polyisocyanate Mixture from Example	2	5	1	4	18	22
% F of Polyisocyanate Mixture	4.6	0.0	0.5	0.0	0.5	0.5
% Allophanate of Polyisocyanate Mixture	2.1	2.3	0.2	0.2	0.2	0.2
Polyisocyanate Mixture, g	5	5	5	5	5	5
Catalyst, g	0.01	0.01	0.01	0.01	0.01	0.01
Surface energy, dynes/cm	10	28	12	31	12	33

15 This data shows that coatings made from two-component coating compositions containing polyisocyanate mixtures, which were prepared from concentrates, had the same low surface energy as coatings made from two-component coating compositions containing polyisocyanate mixtures, which were directly made with the same amounts of fluorine.

20 Coatings prepared from the comparison polyisocyanates had high surface energies.

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Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the

5 invention except as it may be limited by the claims.

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Claims:

1. A polyisocyanate mixture
 - i) having an NCO content of 5 to 35% by weight and a monomeric diisocyanate content of less than 3% by weight, and prepared from
 - 5 a polyisocyanate adduct,
 - ii) containing allophanate groups in an amount such that there are more equivalents of allophanate groups than urethane groups and
 - iii) containing fluorine (calculated as F, AW 19) in an amount of 0.001 to 50% by weight,
 - 10 wherein the preceding percentages are based on the solids content of the polyisocyanate mixture and wherein fluorine is incorporated by reacting an isocyanate group with a compound containing two or more carbon atoms, one or more hydroxyl groups and one or more fluorine atoms.
 2. The polyisocyanate mixture of Claim 1 wherein fluorine is
 - 15 incorporated by reacting an isocyanate group with a compound containing two or more carbon atoms, one hydroxyl group and one or more fluorine atoms.
 3. The polyisocyanate mixture of Claim 1 wherein said polyisocyanate adduct comprises an isocyanurate group-containing
 - 20 polyisocyanate prepared from 1,6-hexamethylene diisocyanate or isophorone diisocyanate.
 4. The polyisocyanate mixture of Claim 2 wherein said polyisocyanate adduct comprises an isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate or
 - 25 isophorone diisocyanate.
 5. The polyisocyanate mixture of Claim 1 wherein the polyisocyanate mixture contains 0.1 to 10% by weight, based on solids, of fluorine.

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6. The polyisocyanate mixture of Claim 2 wherein the polyisocyanate mixture contains 0.1 to 10% by weight, based on solids, of fluorine.

7. The polyisocyanate mixture of Claim 3 wherein the 5 polyisocyanate mixture contains 0.1 to 10% by weight, based on solids, of fluorine.

8. The polyisocyanate mixture of Claim 4 wherein the polyisocyanate mixture contains 0.1 to 10% by weight, based on solids, of fluorine.

10 9. The polyisocyanate mixture of Claim 1 wherein the polyisocyanate mixture contains 10 to 40% by weight, based on solids, of fluorine.

10. The polyisocyanate mixture of Claim 2 wherein the polyisocyanate mixture contains 10 to 40% by weight, based on solids, of 15 fluorine.

11. The polyisocyanate mixture of Claim 3 wherein the polyisocyanate mixture contains 10 to 40% by weight, based on solids, of fluorine.

12. The polyisocyanate mixture of Claim 4 wherein the 20 polyisocyanate mixture contains 10 to 40% by weight, based on solids, of fluorine.

13 A process for the production of a polyisocyanate mixture
25 i) having an NCO content of 5 to 35% by weight and a monomeric diisocyanate content of less than 3% by weight, and prepared from a polyisocyanate adduct,
ii) containing allophanate groups in an amount such that there are more equivalents of allophanate groups than urethane groups and
iii) containing fluorine (calculated as F, AW 19) in an amount of 0.001 to 50% by weight,

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wherein the preceding percentages are based on the solids content of the polyisocyanate mixture,

which comprises

- a) reacting a portion of the isocyanate groups of a polyisocyanate adduct with 0.01 to 500 millimoles, per mole of polyisocyanate adduct, of a compound containing two or more carbon atoms, one or more hydroxyl groups and one or more fluorine atoms to form urethane groups,
- b) adding an allophanatization catalyst prior to, during or after step a),
- 10 c) converting a sufficient amount of the urethane groups formed in step a) to allophanate groups to satisfy the requirements of ii) and
- d) terminating the allophanatization reaction at the desired NCO content by adding a catalyst poison and/or by thermally deactivating the catalyst and recovering the polyisocyanate mixture without
- 15 removing monomeric diisocyanates.

14. The process of Claim 13 wherein fluorine is incorporated by reacting an isocyanate group with a compound containing one hydroxyl group directly attached to a carbon atom and one or more fluorine atoms.

15. The process of Claim 13 wherein said polyisocyanate adduct 20 comprises an isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate or isophorone diisocyanate.

16. The process of Claim 14 wherein said polyisocyanate adduct comprises an isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate or isophorone diisocyanate.

25 17. A one- or two-component coating composition containing the polyisocyanate mixture of Claim 1, optionally blocked by blocking agents for isocyanate groups, and optionally a compound containing isocyanate-reactive groups.