Abstract: A clear coat coating composition with a resin solids content comprising a hydroxyl-functional binder component and a crosslinker component, wherein the clear coat coating composition comprises at least one aliphatic polyether polyl additive having \(-\text{OCH}_2\text{F}_2\text{O}_n\) groups with \(n = 1\) or \(2\), wherein the \(-\text{OCH}_2\text{F}_2\) groups provide the clear coat coating composition with a fluorine content of 0.1 to 3 wt.%, calculated on the resin solids content of the clear coat coating composition.
Title of Invention
CLEAR COAT COATING COMPOSITION

Field of the Invention
The present invention relates to a clear coat coating composition which can be used in a process for the preparation of an outer clear coat layer of an automotive multi-layer coating.

Background of the Invention
Modern automotive multi-layer coatings typically comprise a two-layer topcoat consisting of a color- and/or special effect-imparting base coat layer and an outer clear coat layer on top of that base coat layer. The pigmented base coat layer provides the color of the automotive multi-layer coating and the clear coat has a protective as well as decorative function. It is desirable for the clear coat to be self-cleanable, i.e. to allow for easily washing off dirt from its surface just by the action of rain. Such clear coats are called easy-to-clean clear coats.

Easy-to-clean coating compositions have been developed which exhibit good initial self-cleanability due to a surface enrichment of hydrophobic substance in the easy-to-clean coating layer, see for example, WO 2007/1 04654 A 1, US 2004/01 27593 A 1, US 5,597,874 and US 5,705,276.

"Initial self-cleanability" means the maximum level of self-cleanability that an easy-to-clean clear coat layer has at the beginning of its service life. However, the self-cleanability of easy-to-clean clear coats often suffers over time during which the easy-to-clean clear coat layer is exposed to the weather, i.e. its self-cleanability reduces over time as compared to its initial self-cleanability.

The self-cleanability of a coating layer over time can be determined by the following method. First, the initial self-cleanability of a panel provided with the coating layer to be tested is determined by applying Leverkusen standard dirt 09 LD-40 (commercially available from wfk
institute Krefeld, Germany) to all but a 4 centimeter portion of one end of the horizontally positioned panel. Dirt application is performed making use of a sieve. Three 25 µl drops of deionized water are placed on the unsoiled area of the coated panel. The unsoiled end of the panel is slowly and continuously raised from the horizontal position to a 30° angle causing the water drops to move through the soiled area. After 5 minutes the position of the water drops is recorded and it is visually rated how much dirt the water drops on their move downwards have removed from the surface. The coated panel is then carefully cleaned to remove any remaining dirt and it is thereafter subjected to artificial weathering conditions (500 hours according to SAE J2527). Then the self-cleanability test is repeated followed by further cycles of artificial weathering and self-cleanability testing. Finally, self-cleanability data comprising the initial self-cleanability and self-cleanability after 500, 1000 and 2000 hours of artificial weathering are obtained and a trend can be estimated, if or to what extent the self-cleanability of the coating layer reduces over time when exposed to the weather.

SUMMARY OF THE INVENTION

The present invention relates to a clear coat coating composition with a resin solids content comprising a hydroxyl-functional binder component and a crosslinker component, wherein the clear coat coating composition comprises at least one aliphatic polyether polyol additive having \(-\text{OCH}_2\text{C}_n\text{F}_{2n+1}\) groups with \(n = 1 \text{ or } 2\), and wherein the \(-\text{OCH}_2\text{C}_n\text{F}_{2n+1}\) groups provide the clear coat coating composition with a fluorine content of 0.1 to 3 wt. % (weight%), calculated on the resin solids content of the clear coat coating composition.

DETAILED DESCRIPTION OF THE EMBODIMENTS

In the description and the claims the term "aliphatic polyether polyol" is used. The phrase is intended to include moieties having linear, branched and/or cycloaliphatic groups in said polyether polyol.
In the description and the claims the term "aliphatic polyether polyol additive having -OCH$_2$C$_n$F$_{2n+i}$ groups with n = 1 or 2" is used. For brevity, it is also called "fluorine-containing polyether polyol additive" herein.

The clear coat coating composition of the invention is liquid, contains organic solvent(s) and may have a solids content of, for example, 45 to 65 wt.%. The solids content of the clear coat coating composition consists of the solids contributions of the resinous constituents (the resin solids content) of the clear coat coating composition plus the solids contributions of the fluorine-containing polyether polyol additive and of other optionally present non-volatile components like pigments, fillers (extenders) and non-volatile additives other than the at least one fluorine-containing polyether polyol additive.

It has been found that a clear coat layer exhibiting good optical appearance (smooth surface, high gloss) and having a sustainable easy-to-clean effect can be produced from the clear coat coating composition of the invention. In this context "sustainable easy-to-clean effect" means that the initial self-cleanability hardly suffers or does not suffer over the clear coat layer's lifetime or service life during which it experiences long-term exposure to the weather including exposure to sunlight as well as rain water to name only two strain factors.

The resin solids content of the clear coat coating composition comprises a hydroxyl-functional binder component and a crosslinker component, or, to be more precise, it comprises the solids contributions of the hydroxyl-functional binder component and of the crosslinker component. In an embodiment, the resin solids content of the clear coat coating composition consists of the hydroxyl-functional binder component and of the crosslinker component. The resin solids content of the clear coat coating composition may be in the range of, for example, 40 to 64.5 wt.%, based on the total clear coat coating composition.

The hydroxyl-functional binder component comprises one or more hydroxyl-functional binders as are conventionally used in the art of paint.
and coatings. In a typical embodiment, the hydroxyl-functional binder component consists of one or more hydroxyl-functional binders. Examples include conventional hydroxyl-functional binders known to the person skilled in the art, and they are readily available commercially or may be prepared by conventional synthesis procedures. Examples of such hydroxyl-functional binders can include polyester polyols, polyurethane polyols, (meth)acrylic copolymer resin polyols, hydroxyl-functional polymer hybrid resins derived from these classes of resin binders, for example, wherein two or more of said resin types bound by covalent bonds or in the form of interpenetrating resin molecules are present, or a combination of said polymeric polyols. (Meth)acryl or (meth)acrylic is to be understood, both here and in the following, as acryl and/or methacryl or as acrylic and/or methacrylic. The hydroxyl-functional binders are oligomeric or polymeric compounds with a number-average molar mass (Mn) in the range of, for example, 500 to 10000, preferably 1000 to 5000. Their hydroxyl numbers are in the range of, for example, 50 to 300 mg of KOH/g.

The number-average molar mass data stated herein are number-average molar masses determined or to be determined by gel permeation chromatography (GPC; divinylbenzene-cross-linked polystyrene as the immobile phase, tetrahydrofuran as the liquid phase, polystyrene standards).

The crosslinker component comprises one or more cross-linking agents conventionally used in clear coating systems based on hydroxyl-functional binders. Examples of suitable cross-linking agents can include transesterification cross-linking agents; amino resin cross-linking agents, such as, melamine-formaldehyde resins; free or reversibly blocked polyisocyanate cross-linking agents; and/or trisalkoxycarbonylaminotriazine cross-linking agents. In case of free or reversibly blocked polyisocyanate cross-linking agents it is preferred not to employ polyisocyanates with aromatically bonded NCO groups.
As already mentioned, the clear coat coating composition of the invention contains organic solvent(s). The organic solvent content may be, for example, 35 to 55 wt.%; the sum of the wt.% of the solids content and the organic solvent content is, for example, 90 to 100 wt.% (any possible difference in the corresponding range of above 0 to 10 wt.% to make up to the total of 100 wt.% is in general formed by volatile additives). The organic solvents are in particular conventional coating solvents, for example, glycol ethers, such as, butyl glycol, butyl diglycol, ethoxyp propane, dipropylene glycol dimethyl ether, dipropylene glycol monomethyl ether, ethylene glycol dimethylether; glycol ether esters, such as, ethyl glycol acetate, butyl glycol acetate, butyl diglycol acetate, methoxypropyl acetate; glycols, for example, propylene glycol and oligomers thereof; esters, such as, butyl acetate, isobutyl acetate, amyl acetate; ketones, such as, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, cyclohexanone, isophorone; alcohols, such as, methanol, ethanol, (iso)propanol, butanol, hexanol; N-alkyl pyrrolidones, such as, N-ethyl pyrrolidone; aromatic hydrocarbons, such as, xylene, SOLVESSO® 100 (mixture of aromatic hydrocarbons with a boiling range from 155°C to 185°C), SOLVESSO® 150 (mixture of aromatic hydrocarbons with a boiling range from 182°C to 202°C) and aliphatic hydrocarbons. A combination of any of the solvents can also be used.

The clear coat coating composition of the invention comprises at least one aliphatic polyether polyol additive having \(-OCH_2C_nF_{2n+i}\) groups with \(n = 1\) or 2. The oxygen atom in the formula \(-OCH_2C_nF_{2n+i}\) represents an ether bridge. The fluorine-containing polyether polyol additive has two or more unetherified free hydroxyl groups.

The fluorine-containing polyether polyol additive has a fluorine content provided by its \(-OCH_2C_nF_{2n+1}\) groups in the range of, for example, 24 to 40 wt.%.

The fluorine-containing polyether polyol additive may have a calculated molar mass in the range of, for example, 470 to 5000. The molar mass can be calculated from the fluorine-containing polyether polyol
additive’s formula, which in the case of an oligomer or polymer may take the form of an average formula.

In a preferred embodiment, the fluorine-containing polyether polyol additive is a polyether diol of the formula

$$\text{HO}[\text{CH}_2\text{C(CH}_3)(\text{CH}_2\text{OCH}_2\text{CF}_3)\text{CH}_20]^x\text{CH}_2\text{C(CH}_3)2\text{CH}_2-$$

$$[\text{OCH}_2\text{C(CH}_3)(\text{CH}_20\text{CH}_2\text{CF}_3)\text{CH}_2y\text{OH}]$$

with $$x+y = 6$$ on average, which is commercially available under the trade name POLYFOX™ PF-636 from OMNOVA Solutions, Fairlawn, Ohio.

In another preferred embodiment, the fluorine-containing polyether polyol additive is a polyether diol of the formula

$$\text{HO}[\text{CH}_2\text{C(CH}_3)(\text{CH}_2\text{OCH}_2\text{C}_2\text{F}_5)\text{CH}_20]^x\text{CH}_2\text{C(CH}_3)2\text{CH}_2-$$

$$[\text{OCH}_2\text{C(CH}_3)(\text{CH}_20\text{CH}_2\text{C}_2\text{F}_5)\text{CH}_2y\text{OH}]$$

with $$x+y = 6$$ on average, which is commercially available under the trade name POLYFOX™ PF-656 also from OMNOVA Solutions.

The $$-\text{OCH}_2\text{C}_n\text{F}_{2n+1}$$ groups of the at least one fluorine-containing polyether polyol additive provide the clear coat coating composition with a fluorine content of 0.1 to 3 wt.%, preferably 0.2 to 1.5 wt.%, calculated on the resin solids content of the clear coat coating composition.

The proportion of the at least one fluorine-containing polyether polyol additive in the clear coat coating composition may be in the range of, for example, 0.5 to 8 wt.%, preferably 0.5 to 4 wt.%, calculated on the resin solids of the clear coat coating composition.

While not wishing to be bound by any theory, it is surmised that the at least one fluorine-containing polyether polyol additive is chemically incorporated in the polymer network of the clear coat layer formed during curing of the clear coat.

The clear coat coating composition may also contain volatile or non-volatile additives other than the at least one fluorine-containing polyether polyol additive. Examples of such additives other than the at least one fluorine-containing polyether polyol additive can include catalysts, levelling agents, wetting agents, anticratering agents, dyes, rheology control agents, antioxidants and/or light stabilizers. The additives...
are used in conventional amounts of, for example, up to 10 wt.% in total, calculated on the resin solids of the clear coat coating composition.

The clear coat coating composition is a transparent coating composition which can be applied and cured to form a transparent clear coat layer. However, this does not necessarily exclude the presence of a small amount of pigments in the clear coat coating composition. For example, if a colored clear coat coating composition is desired, pigments may be comprised.

The clear coat coating composition may also comprise transparent fillers like, for example, silica.

The clear coat coating composition can be spray-applied to form a clear coat layer on an automotive substrate. Therefore, the invention relates also to a process for producing an outer clear coat layer of an automotive multi-layer coating, or, respectively, to a process for the production of an automotive base coat/clear top coat two-layer coating. The process comprises the steps:

(1) providing an automotive substrate provided with an uncured pigmented base coat layer,

(2) applying the clear coat coating composition of the invention on the uncured base coat layer to form a clear coat layer thereon, and

(3) jointly curing the base coat and the clear coat layer.

The automotive substrate provided with the uncured pigmented base coat layer may be an automotive substrate to be OEM (original equipment manufacture) clear coated or an automotive substrate to be repair clear coated. The term "automotive substrate to be OEM clear coated" refers to the case where the clear coat is to be applied as an original coating. The term "automotive substrate to be repair clear coated" refers to the case where the clear coat is to be applied as a refinish clear coat.

Automotive substrates include in particular automotive bodies and automotive body metal or plastic parts. Examples of automotive bodies
can include truck and vehicle bodies, for example, passenger car bodies and van bodies. Examples of automotive body metal or plastic parts include doors, bonnets, boot lids, hatchbacks, wings, spoilers, bumpers, collision protection strips, side trim, sills, mirror housings, door handles and hubcaps.

The uncured pigmented base coat layer on the automotive substrate represents the color and/or special effect-imparting coating layer of the automotive multi-layer coating produced by the process of the invention. The uncured pigmented base coat layer may have been applied from an automotive OEM base coat or from an automotive repair base coat.

The clear coat coating composition may be applied by spraying in a dry film thickness in the range of, for example, 20 to 60 µm. The clear coat application is performed by the so-called wet-on-wet method on the uncured pigmented base coat layer. Preferably after a brief flash-off phase the clear coat layer is jointly cured together with the so far uncured pigmented base coat layer. The curing conditions depend on the binder/crosslinker system of the clear coat coating composition and the circumstances under which the coating and curing process is carried out. The curing temperature may range from 20 to 160°C, for example. If the clear coat coating composition is used for refinish coating purposes, more gentle curing conditions may be required than in automotive OEM clear coating. Curing conditions as prevail in automotive OEM coating mean, for example, 20 to 30 minutes at an object temperature of, for example, 80 to 160°C, whereas curing conditions in refinishing may mean an object temperature of, for example, 20 to 80°C, in particular, 20 to 40 minutes at an object temperature of, for example, 40 to 80°C.

The cured automotive multi-layer coating produced by the process of the invention has an outer easy-to-clean clear top coat layer. Its self-cleanability is sustainable; even when exposed to the weather it hardly reduces or it does even not reduce over the clear coat layer's service life.
Examples

Example 1 (Preparation of a base paint formulation)

67.6 pbw (parts by weight) of an OH-functional copolymer resin (monomer composition by weight: 62% styrene, 21% 2-hydroxyethyl methacrylate, 11% methyl methacrylate, 6% 2-ethylhexyl methacrylate), 7.2 pbw of an OH-functional polyester resin (polyester composition by weight: 54% 2,3-epoxypropyl neodecanoate, 36% methylhexahydrophthalic anhydride, 10% pentaerythritol), 6.7 pbw methyl isobutyl ketone, 6.7 pbw butyl acetate, 0.6 pbw of an UV absorber and 0.01 pbw of dibutyltindilaurate were mixed together as a base paint.

Example 2 (Preparation of a polyisocyanate crosslinker formulation)

73 pbw trimeric 1,6-hexane diisocyanate (DESMODUR® N 3600 from Bayer AG, Leverkusen, Germany) were mixed with 5.6 pbw of butyl acetate and 33.7 pbw of propylene glycol monobutyl ether acetate.

Example 3 (Preparation of a clear coat coating composition, according to the invention)

95 pbw of the base paint of example 1 were thoroughly mixed with 2 pbw of POLYFOX™ PF-656 and then further mixed with 37.4 pbw of the polyisocyanate crosslinker formulation of example 2.

Example 4 (Preparation of a clear coat coating composition, comparative example)

95 pbw of the base paint of example 1 were mixed with 37.4 pbw of the polyisocyanate crosslinker formulation of example 2.

Example 5 (Self-cleanability testing)

To understand the self-cleanability properties of the clear coat systems of examples 3 and 4, the latter were applied to test panels in a
dry film thickness of 30 µm. The panels were baked 30 min at 60°C and the first testing was done after 3 days of application.

The self-cleanability of the panels was tested by applying Leverkusen standard dirt 09 LD-40 to all but a 4 centimeter portion of one end of the horizontally positioned panels. Dirt application was performed making use of a sieve. Three 25 µl drops of deionized water were placed on the unsoiled area of the coated panels. The unsoiled end of the panels was slowly and continuously raised from the horizontal position to a 30° angle causing the water drops to move through the soiled area. After 5 minutes the position of the water drops was recorded and it was visually rated how much dirt the water drops on their move downwards had removed from the surface. The coated panels were then carefully cleaned to remove any remaining dirt and they were thereafter subjected to artificial weathering conditions (500 hours according to SAE J2527). Then the self-cleanability test was repeated followed by further cycles of artificial weathering and self-cleanability testing. Finally, self-cleanability data comprising the initial self-cleanability and self-cleanability after 500, 1000 and 2000 hours of artificial weathering were obtained and a trend was estimated, if or to what extent the self-cleanability of the clear coat layer reduces over time when exposed to the weather. The rating was done in numbers (1 = excellent dirt removal, 3 = medium dirt removal, 6 = no dirt removal) and letters (A = water droplet went to the bottom of the panel, B = droplet stopped at the second half of the panel, C = droplet stopped at the first half of the panel):

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<th>Clear coat example</th>
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**Claims**

What is claimed is:

1. A clear coat coating composition with a resin solids content comprising a hydroxyl-functional binder component and a crosslinker component, wherein the clear coat coating composition comprises at least one aliphatic polyether polyl additive having -OCH2CnF2n+i groups with n = 1 or 2, and wherein the -OCH2CnF2n+i groups provide the clear coat coating composition with a fluorine content of 0.1 to 3 wt.%, calculated on the resin solids content of the clear coat coating composition.

2. The clear coat coating composition of claim 1, wherein the crosslinker component comprises one or more cross-linking agents selected from transesterification cross-linking agents; amino resin cross-linking agents, free polyisocyanate cross-linking agents, reversibly blocked polyisocyanate cross-linking agents, and trisalkoxycarbonylaminotriazine cross-linking agents.

3. The clear coat coating composition of claim 1 or 2 containing organic solvent(s).

4. The clear coat coating composition of claim 1, 2 or 3, wherein the at least one fluorine-containing polyether polyl additive has a fluorine content provided by its -OCH2CnF2n+i groups in the range of 24 to 40 wt.%.

5. The clear coat coating composition of any one of the preceding claims, wherein the at least one fluorine-containing polyether polyl additive is a polyether diol of the formula

\[ \text{HO}[\text{CH2C(CH3)(CH}2\text{OCH2CF3)}\text{CH2]}_x \text{CCH2(C(CH3)}2\text{C H2-} \text{]}_y \text{OH with } x+y = 6 \text{ on average.} \]
6. The clear coat coating composition of any one of claims 1 to 4, wherein the at least one fluorine-containing polyether polyol additive is a polyether diol of the formula

\[ \text{HO[CH}_2\text{C(CH}_3\text{)(CH}_2\text{OCH}_2\text{C}_2\text{F}_5\text{)CH}_2\text{0}} \times \text{CH}_2\text{C(CH}_3\text{)2CH}_2\text{-}
\]

\[ [\text{OCH}_2\text{C(CH}_3\text{)(CH}_2\text{OCH}_2\text{C}_2\text{F}_5\text{)CH}_2\text{]}y\text{OH} \text{ with } x+y = 6 \text{ on average.}
\]

7. The clear coat coating composition of any one of the preceding claims, wherein the proportion of the at least one fluorine-containing polyether polyol additive in the clear coat coating composition is in the range of 0.5 to 8 wt.%, calculated on the resin solids of the clear coat coating composition.

8. A process for the production of an automotive base coat/clear top coat two-layer coating comprising the steps:

(1) providing an automotive substrate provided with an uncured pigmented base coat layer,

(2) applying the clear coat coating composition of any one of the preceding claims on the uncured base coat layer to form a clear coat layer thereon, and

(3) jointly curing the base coat and the clear coat layer.
INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/064870

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D 171/00

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 0622 391 A2 (AUSIMONT SPA [IT]) 2 November 1994 (1994-11-02) claims 1-10; examples 4-9</td>
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<td>EP 0812 890 A2 (AUSIMONT SPA [IT]) 17 December 1997 (1997-12-17) claims 1-31 examples 1-4; comparative examples 5-10</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search
4 March 2013

Date of mailing of the international search report
18/03/2013

Name and mailing address of the ISA/
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Fax: (+31-70) 340-3016

Authorized officer
Kositzka, Matthias
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<td>T. TEMTCHEKO ET AL: “New developments in perfluoropolyether resin technology: high solid and durable polyurethanes for heavy duty and clear OEM coatings”, PROGRESS IN ORGANIC COATINGS, vol. 43, 2001, pages 75-84, XP002692631, 2. Experimental 3. Results and Discussion figures 1,6; tables 1,2,5</td>
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