(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 December 2018 (20.12.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/229659 A1

(51) International Patent Classification:
C08F 214/26 (2006.01)

(21) International Application Number:
PCT/IB2018/054263

(22) International Filing Date:
12 June 2018 (12.06.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20 2017 003 084.5
13 June 2017 (13.06.2017) DE
15/631,764 23 June 2017 (23.06.2017) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

WO 2018/229659 A1

(54) Title: MODIFIED POLYTETRAFLUOROETHYLENE AND AQUEOUS DISPERSION CONTAINING THE SAME

(57) Abstract: Aqueous fluoropolymer dispersions are described, along with coatings obtained with the dispersions, and methods of making coatings and dispersions.

MODIFIED POLYTETRAFLUOROETHYLENE AND AQUEOUS DISPERSION CONTAINING THE SAME

Field

The disclosure relates to modified polytetrafluoroethylenes and aqueous dispersions containing them. The present disclosure further relates to their application for coating substrates and to the coated substrates.

Background

Fluoropolymers, i.e. polymers having a fluorinated backbone, have been used in a variety of applications because of several desirable properties including heat resistance, chemical resistance, weatherability, etc. Particular examples of commercial fluoropolymers include polytetrafluoroethylene (PTFE); copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), also known as FEP polymers); copolymers of TFE and perfluoroalkoxyvinyl ethers, also known as PFA polymers; copolymer of tetrafluoroethylene and ethylene, also known as ETFE polymers, copolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride (VDF) also known as THV polymers; and homopolymers polyvinylidene fluoride, also known as PVDF. Polytetrafluoroethylenes with a comonomer content of less than 1 % wt. are still considered as PTFE.

Fluoropolymer dispersions, in particular PTFE dispersions, have found wide applications as protective and antifriction ("non-stick") coatings. However, there is a need to provide fluoropolymer coatings of greater transparency.

In EP 1,816,148 PTFE fine powder compositions for shaped article are reported that have an improved transparency determined by their haze value. However, there is a need to provide alternative fluoropolymers. Preferably the polymers have a good or even improved transparency. Desirably, the polymers can be provided as stable dispersions and are suitable for creating coatings.

Summary

In one aspect of the following disclosure there is provided a modified polytetrafluoroethylene (modified PTFE) containing up to 1% by weight of at least one modifier selected from unsaturated perfluorinated allyl ethers of the general formula

$$CF_2=CF\text{-}(CF_2)\text{-}O\text{-}Rf'$$

wherein Rf' represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated oxoalkyl residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof.

In another aspect there is provided an aqueous dispersion comprising the modified polytetrafluoroethylene (modified PTFE) wherein the dispersion further comprises a fluorinated surfactant selected from a linear or branched perfluorinated or partially fluorinated alkanoic acids wherein the alkyl residue of the acid is interrupted once or more than once by an oxygen atom but wherein the dispersion comprises the fluorinated surfactant in an amount of less than 5.000 ppm and wherein the dispersion comprises from about 1 to about 10 % wt (based on the weight of the dispersion) of one or more aliphatic, non-fluorinated, non-ionic surfactants.

In another aspect there is provided a coated substrate obtained from the dispersion and an article comprising the coated substrate.

In a further aspect there is provided a method of coating a substrate said method comprising applying the dispersion to a substrate and removing the aqueous phase.

Detailed Description

Before any embodiments of this disclosure are explained in detail, it is to be understood that the disclosure is not limited in its application to the details of construction and the arrangement of components set forth in the following description. The invention is capable of other embodiments and of being practiced or of being carried out in various ways. As used herein, the term "a", "an", and "the" are used interchangeably and mean one or more; and "and/or" is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B). Also herein, recitation of ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 10 includes 1.4, 1.9, 2.33, 5.75, 9.98, etc.). Also herein, recitation of "at least one" includes all numbers of one and greater (e.g., at least 2, at least 4, at least 6, at least 8, at least 10, at least 25, at least 50, at least100, etc.). Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. Contrary to the use of "consisting", which is meant to be limiting, the use of "including," "containing", "comprising," or "having" and variations thereof is meant to be not limiting and to encompass the items listed thereafter as well as additional items.

Amounts of ingredients of a composition are indicated by % by weight (or "% wt" or "wt %") unless specified otherwise. The weight percentages are based on the total weight of the composition, i.e. the amounts of all ingredients will give 100 % wt, unless specified otherwise. If the amounts of ingredients are identified by % mole the amount of all ingredients gives 100% mole unless specified otherwise.

The fluoropolymer dispersions provided herein allow for fluoropolymer coatings to be prepared that have an improved transparency (e.g. as determined by % of transmittance). The dispersions have good shear stability and film forming properties (e.g. as determined by the critical film thickness test).

Fluoropolymers:

The fluoropolymers provided herein are tetrafluoroethylene (TFE) based polymers. They typically have a melting point of at least 317°C or at least 319°C or at least 321°C. Typically, the polymers have a

melting point between 320 and 330°C. Polymers with a high content of TFE-units tend to have somewhat different melting points when bringing them to the melt, cooling them below the melting point and then re-melting the polymer. Further subsequent cooling and melting cycle do not change the melting point. Therefore, when referring to the melting point, the second melting point is meant, i.e. the melting point after the material has been brought to melt for the first time, cooled to below the melting point and was then molten again according to the ASTM method referred to in the experimental part.

Preferably, the tetrafluoroethylene polymers provided herein are non-meltprocessable. Typically, they have an MFI (372/5) of less than 0.3 g /10 min, preferably less than 0.1 g/10 min more preferably less than 0.01 g/ 10 min. The determination of the MFI has been described, for example, in DIN EN ISO 12086-2: 2006-05. Polymers having an MFI of 0.3 g/ 10 min or greater are regarded as meltprocessable.

Preferably, the fluoropolymers are high molecular weight polymers. Typically, they may have a standard specific gravity (SSG) of from 2.14 and up to 2.20, preferably from 2.15 and up to 2.18 g/cm³, more preferably from 2.16 and up to 2.18 g/cm³. The SSG may be determined, for example, according to DIN EN ISO 12086-2: 2006-05.

The fluoropolymer particles may be spherical or elongated. Elongated particles may have, for example, a ratio of length to diameter of greater than 5 : 1. Preferably the particles approximate spheres or are spherical. Approximate spheres are particles where the length to diameter ratio is less than 5 : 1 and greater than 1 : 1, preferably less than 3 : 1 and greater than 1:1. In case a particle has several lengths or diameters, the greatest length or diameter are referred to herein as "diameter" and "length".

The fluoropolymers according to the present disclosure may have a transmittance of at least 55%, preferably greater than 60%, for example between 60% and 70%, preferably even greater than 70%, more preferably even greater than 75%, for example between 75 and 85%. The transmittance can be determined as described in the experimental section. The greater the transmittance the more transparent is the polymer.

The fluoropolymers are modified PTFE polymers. Modified PTFE polymers are essentially homopolymers of tetrafluoroethylene (TFE) but contain a small amount of one or more perfluorinated comonomers other than TFE. The total amount of the comonomers may be up to 1% by weight. These comonomers include at least one perfluorinated ether and are also referred to herein as "modifiers". The amount of modifiers is up to 1 % by weight based on the total weight of the polymer. In some embodiments, the total amount of modifiers is from 50 to 5,000 ppm, more preferably from 100 to 3,000 ppm (based on the total weight of the polymer). In one embodiment the total amount of comonomers is the same as the total amount of modifiers, i.e. the modified PTFE only contains the one or more modifiers as comonomers.

Modifier(s):

Preferably, the at least one modifier is selected from (a) perfluorinated alkyl ethers and (b) perfluorinated alkoxy ethers.

Examples of perfluorinated alkyl ethers of modifier type (a) include allyl ethers according to the general formula

CF_2=CF-(CF_2)-O-Rf (I),

wherein Rf is a linear or branched C_1 to C_{10} perfluoroalkyl chain (preferably C_1-C_6, more preferably C_3-C_6).. Particular examples include but are not limited to perfluoromethyl allyl ether (MA1), perfluoroethyl allyl ether (MA2) and perfluoropropyl allyl ether (MA3), perfluorobutyl allyl ether (MA4). Particular examples of R_f include CF_3, C_2F_5, and C_3F_7 . and C_4F_9, respectively.

Modifiers of type (b) are perfluoro alkyl allyl ethers whose alkyl chains are interrupted once or more than once by an oxygen atom, (catenary oxygen atom). They are referred to herein as perfluorinated alkoxy allyl ethers. Examples of perfluorinated alkoxy allyl ethers (modifiers of type (b)) include compounds according to the general formula

CF_2=CF-(CF_2)-O-Rf' (II),

wherein Rf' represents a linear or branched, cyclic or acyclic perfluorinated alkyl residue that is interrupted once or more than one by catenary oxygen atom. Typically Rf' contains from 1 to 3 catenary oxygen atoms. Rf' may contain up to 10, preferably up to 6 carbon atoms, and has at least 2 carbon atoms. For example Rf' may have 3, 4, 5, 6, 7, 8 and 9 carbon atoms. Typical examples of Rf' include linear or branched alkyl residues containing 1, 2, 3, 4 or 5 catenary ether oxygen atoms, preferably 1 or 2 catenary oxygen atoms. Further examples of Rf' include residues containing one or more of the following units and combinations thereof:

-(CF_2O)-, -(CF_2CF_2-O)-, (--O-CF_2)-, --(O-CF_2CF_2)-, -$CF(CF_3)$O-, -$CF(CF_3)$-O-, -$CF(CF_2CF_3)$-O-; -O-$CF_2CF(CF_3)$-.

Further examples of Rf' include but are not limited to:

-$(CF_2)_{r1}$-O-C_3F_7,

-$(CF_2)_{r2}$-O-C_2F_5,

-$(CF_2)_{r3}$-O-CF_3,

-$(CF_2$-O$)_{s1}$-C_3F_7,

-$(CF_2$-O$)_{s2}$-C_2F_5,

-$(CF_2$-O$)_{s3}$-CF_3,

-$(CF_2CF_2$-O$)_{t1}$-C_3F_7,

-$(CF_2CF_2$-O$)_{t2}$-C_2F_5,

-$(CF_2CF_2$-O$)_{t3}$-CF_3,

wherein r1 and s1 represent 1, 2, 3, 4, or 5, r2 and s2 represent 1, 2, 3, 4, 5 or 6, r3 and s3 represent 1, 2, 3, 4, 5, 6 or 7; t1 represents 1 or 2; t2 and t3 represent 1, 2 or 3.

Specific examples of suitable perfluorinated alkoxy allyl ethers include but are not limited to

$F_2C=CF-CF_2-O-(CF_2)_3-(OCF_2)_2-F$,

$F_2C=CF-CF_2-O-CF_2-(OCF_2)_3-CF_3$,

$F_2C=CF-CF_2-O-CF_2-(OCF_2)_4-CF_3$,

$F_2C=CF-CF_2-O-(CF_2O)_2-CF_3$,

$F_2C=CF-CF_2-O-(CF_2O)_3-CF_3$,

$F_2C=CF-CF_2-O-(CF_2O)_4-CF_3$,

$F_2C=CF-CF_2-O-(CF_2)-O-(CF_2)-F$,

$F_2C=CF-CF_2-O-CF_2-O-(CF_2)_2-F$,

$F_2C=CF-CF_2-O-CF_2-O-(CF_2)_3-F$,

$F_2C=CF-CF_2-O-CF_2-O-(CF_2)_4-F$,

$F_2C=CF-CF_2-O-(CF_2)_2-OCF_3$ (MA21);

$F_2C=CF-CF_2-O-(CF_2)_3-OCF_3$ (MA31);

$F_2C=CF-CF_2-O-(CF_2)_4-OCF_3$ (MA41);

In one embodiment the at least one modifier is selected $F_2C=CF-CF_2-O-CF_2CF_2CF_3$ (MA3); $F_2C=CF-CF_2-O-CF_3$ (MA1); $F_2C=CF-CF_2-O-CF_2CF_3$ (MA2); $F_2C=CF-CF_2-O-(CF_2)_3-O-CF_3$ (MA31) and combinations thereof. In another embodiment the modifiers include allyl ethers having at least one branched propyleneoxy group (e.g. a –(O-CF_2-$CF(CF_3)$)- group). Particular exammples inlcude but are not limited to $CF_2=CF-CF_2-(O-CF_2-CF(CF_3))-O-CF_2CF_2CF_3$ (PPAE-2), $CF_2=CF-CF_2-(O-CF_2-CF(CF_3))_2-O-CF_2CF_2CF_3$ (PPAE-3).

In one embodiment the modifiers include, in addition to one or more allyl ethers as described one or modifiers selected from perfluorinated alkyl vinyl ethers and/perfluorinated vinyl alkoxy ethers. Examples of perfluorinated alkyl vinyl ethers include compounds according to the general formula

$$CF_2=CF-O-Rff \qquad (III),$$

wherein Rff is a linear or branched C_1 to C_{10} perfluoroalkyl chain (preferably C_1-C_6, more preferably C_3-C_6). Particular examples include those where Rff is identical with Rf of formula (I).

Examples of perfluorinated vinyl alkoxy ethers include those according to the general formula (IV)

$$CF_2=CF-O-Rfff \qquad (IV),$$

wherein Rfff is identical with Rf' of formula (II).

Particular examples of perfluorinated vinylethers include but are not limited to vinyl ethers having at least one branched propyleneoxy group (e.g. a –(O-CF_2-$CF(CF_3)$)- group). Particular exammples

inlcude but are not limited to CF_2=CF-(O-CF_2-CF(CF_3))-O-$CF_2CF_2CF_3$ (PPVE-2), CF_2=CF-(O-CF_2-CF(CF_3))$_2$-O-$CF_2CF_2CF_3$ (PPVE-3).

In one embodiment the modifiers are selected from combinations of F_2C=CF-CF_2-O-$CF_2CF_2CF_3$ (MA3); F_2C=CF-CF_2-O-CF_3 (MA1); F_2C=CF-CF_2-O-CF_2CF_3 (MA2); F_2C=CF-CF_2-O-(CF_2)$_3$-O-CF_3 (MA31) CF_2=CF-(O-CF_2-CF(CF_3))-O-$CF_2CF_2CF_3$ (PPVE-2); CF_2=CF-(O-CF_2-CF(CF_3))$_2$-O-$CF_2CF_2CF_3$ (PPVE-3), and CF_2=CF-O-C_3F_7 (PPVE-1).

Another combination includes the combination of one or more allyl ether as described above with perfluoromethylvinyl ether (PMVE).

Perfluorinated comonomers as described above are either commercially available, for example from Anles Ltd. St. Peterburg, Russia, or can be prepared according to methods known in the art, for example as described in EP 1 240 125 (Worm et al.), EP 0 130 052 (Uschold et al.), EP 1 148 041 B1 (Navarini et al), or in Modern Fluoropolymers, J. Scheirs, Wiley 1997, p 376 – 378.

In an embodiment of the present disclosure a combination of at least two of the above modifiers is used. The combination may be between modifiers of the same type (a), of the same type (b) or combinations of the (a) and (b) types.

In one embodiment the polymers may be core-shell polymers containing a core and at least one shell. The core and the shell may contain different modifiers. For example the at least one shell may contain at least one perfluoro propoxy vinyl or allyl ether. In another embodiment the polymer is a core-shell polymer wherein both the core and at least one shell contains a perfluoro propoxy vinyl or allyl ether.

It is also possible that the core contains a combination of modifiers while the shell contains only one modifier and vice versa.

In one embodiment the modified polytetrafluoroethylene polymer is a core-shell polymer and wherein either the core or at least one shell or the core and at least one shell comprise at least one modifier selected from F_2C=CF-O-CF_2-O-(CF_2)-F (MV 11), F_2C=CF-O-CF_2-O-(CF_2)$_2$-F (MV 12), F_2C=CF-O-CF_2-O-(CF_2)$_3$-F (MV 13), F_2C=CF-O-CF_2-O-(CF_2)$_4$-F (MV 14), F_2C=CF-O-(CF_2)$_2$-OCF_3 (MV 21), F_2C=CF-O-(CF_2)$_3$-OCF_3 (MV 31), F_2C=CF-O-(CF_2)$_4$-OCF_3, (MV 41); F_2C=CF-CF_2-O-$CF_2CF_2CF_3$ (MA3); F_2C=CF-CF_2-O-CF_3 (MA1); F_2C=CF-CF_2-O-CF_2CF_3 (MA2); F_2C=CF-CF_2-O-(CF_2)$_3$-O-CF_3 (MA31) CF_2=CF-O-CF_2-CF(CF_3)-O-$CF_2CF_2CF_3$ (PPVE-2); CF_2=CF-(O-CF_2-CF(CF_3))$_2$-O-$CF_2CF_2CF_3$ (PPVE-3) and combinations thereof.

In one embodiment the modified polytetrafluoroethylene polymer is a core-shell polymer and wherein at least one shell and the core comprises at least one modifier selected from CF_2=CF-O-C_3F_7 (PPVE-1).

The dispersion of claim 1 wherein the polytetrafluoroethylene polymer is a core-shell polymer and wherein the shell and the core comprises at least one modifier selected from CF_2=CF-O-CF_2-CF(CF_3)-O-$CF_2CF_2CF_3$ (PPVE-2); CF_2=CF-(O-CF_2-CF(CF_3))$_2$-O-$CF_2CF_2CF_3$ (PPVE-3) and combinations thereof.

Core-shell tetrafluoroethylene polymers are known and can be prepared, for example, as described in EP 1,533,325 B1 and references cited therein. The polymers may also be, for example but not limited

thereto, random polymers, for example the polymers may be prepared by co-feeding the comonomers continuously or discontinuously at the same ratio, and the polymers may not be core-shell polymers.

An advantage of the modified PTFE provided herein is that it has greater transparency. Another advantage of the modified PTFE provided herein, other than, for example, improved transparency, is that it may contain lower amounts of extractable perfluorinated alkanoic acids, in particular perfluorinated alkanoic carboxylic acids and their salts having from 8 to 14 carbon atoms. An example includes perfluorooctanoic acid, a C8-acid. Such acids appear to be generated as by-products during the polymerization reaction using vinyl ethers and may be found as extractables in the polymer, even if no perfluorinated alkanoic acid has been used in the polymerization reaction. Th amounts are generally very low, but reducing the amounts of extractable emulsifiers is advantageous as it provides purer polymers and may also facilitate or accelerate work up and purification procedures. Therefore, in one embodiment there is provided a modified PTFE as described herein that has a total amount of extractable perfluorinated alkanoic carboxylic acids and their salts of less than 200 ppb based on the amount of polymer, preferably less than 100 ppb and more preferably less than 50 ppb, even more preferably less than 20 ppb, wherein the perfluorinated carboxylic acids and their salt have from 8 to 14 carbon atoms and the total amount is the sum of the amounts of these acids and their salts.

While the coating properties of perfluorinated vinyl ethers, for example film forming thickness, transparency and gloss are good, replacing them completely or partially with allyl modifiers as described herein may reduce the overall content of extractable perfluorinated alkanoic acids as described above.

Another advantage of the modified PTFE provided herein is that is has fewer polar end groups and it more hydrophobic (for example as determined by contact angle measurements). This may improve the antistick properties of the polymer or polymer coating. On the other hand, it may reduce the adhesion to certain substrates and lower the critical film forming thickness. Therefore, the one or more modifiers provided herein may be combined with other modifiers or comonomers to fine tune the coating properties.

Another advantage of the modified PTFE provided herein is that it contains few polar end groups (-COOH and -COF groups). These endgroups may degrade upon thermal treatment which may negatively impact on the optical properties of the polymer or polymer coating, in particular its transparency. Therefore, the modified PTFE provided herein may be of greater thermal stability at least in regard to its optical properties.

Functional and other comonomers:

The modified PTFE provided herein may optionally also include further comonomers other than the modifiers described above. Suitable comonomers include the known comonomers in the production of PTFE as known in the art. Examples include but are not limited to C_3 - C_8 perfluorolefins, like, but not limited to, hexafluoropropylene (HFP) and perfluoro-n-butene (PFB).

In addition to the above modifiers minor amounts of functional comonomers may be used in the polymerization to produce more polar groups on the polymer surface, in case this is desired, for example

to increase the low amounts of polar end groups of the modified polymer prepared without such functional comonomers. Such functional comonomers include perfluorinated olefins with at least one polar functional groups. Examples include compounds according to the general formula

$CF_2=CF(CF_2)_x\text{-}A_p\text{-}R_f\text{-}Y$

wherein R_f is C1 to C10 linear or branched perfluoroalkylene residue with at least one oxygen atom, Y is COO-, COOR, CN, COF, SO_3-, SO_2F, $SO_2NR^1R^2$, R^1 and R^2 may be the same or different and represent a hydrocarbon group such as a C1 to C10 alkyl group, x is 1, 2 or 3. A is $(O)_y\text{-}(CF_2)_n$, $OCF_3(CF_3)CF_2$ or a combination thereof, y is 0 or 1 and n is 0, 1, 2 or an integer from 3 to 8 and p is 1 or an integer from 2 to 8. Specific examples include but are not limited to $CF_2=CF\text{-}O\text{-}CF_2CF_2Y$, $CF_2=CF\text{-}O\text{-}[CF_2CF_2]_2Y$, $CF_2=CF\text{-}O\text{-}[CF_2CF_2]_3Y$, $CF_2=CF\text{-}O\text{-}CF(CF_3)CF_2OCF_2CF_2Y$ with Y being selected from SO_3-; COO-, and COOR, for example $COOCH_3$.

The functionalized comonomers are preferably added towards the end of the polymerization, for example during the last 25%, preferably the last 10% or even the last 5% of the polymerization reaction. The amount of functionalized comonomer is less than 0.5 % by weight, preferably less than 0.1 % by weight, more preferably 0.05% by weight based on the total weight of the polymer and the amount of the functional comonomers is adjusted to the amount of the modifiers used to ensure the total amounts of comonomers (functional comonomers and modifiers) does not exceed 1 % wt, preferably does not exceed 0.5 % wt, most preferably does not exceed 0.3 % wt. based on the total weight of the fluoropolymer.

Preparation of the fluoropolymers:

The tetrafluoroethylene copolymers are usually prepared by emulsion or suspension polymerisation. In a suspension polymerisation the reaction mixture coagulates and settles as soon as stirring of the reaction mixture is discontinued. Suspension polymerisations are carried out in the absence of emulsifiers. Usually vigorously stirring is required.

The polymers according to the present disclosure are preferably prepared by aqueous emulsion polymerisation. Such polymerisations are carried out in a way that stable dispersions are obtained and are well known in the art. The dispersions remain stable after stirring of the reaction mixture has stopped for at least 2 hours, or at least 12 hours or at least 24 hours. To generate stable dispersions one or more fluorinated emulsifiers are employed in the aqueous emulsion polymerisation, however, preferably no perfluorinated alkanoic acid is added to the reaction mixture. The dispersions are essentially free of perfluorinated alkanoic acids, which means they contain no or less than 50ppm preferably less than 5 ppm of such acids (based on the total weight of the dispersion). The fluorinated emulsifiers employed in the preparation of the polymers described include emulsifiers of the general formula:

$$[R_f\text{-}O\text{-}L\text{-}Y^-]_iX_i^+ \qquad (V)$$

wherein L represents a linear or branched or cyclic partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a linear or branched or cyclic, partially or fully fluorinated aliphatic group or a linear or branched partially or fully fluorinated group interrupted with one or more oxygen atoms, X_i^+ represents a cation having the valence i and i is 1, 2 and 3 and Y represents COO or SO_3, preferably the emulsifiers are carboxylates and Y is COO. In case the emulsifier contains one or more partially fluorinated aliphatic group it is referred to as a partially fluorinated emulsifier. Preferably, the molecular weight of the emulsifier is less than 1,000 g/mole (anionic part of the emulsifier – excluding the weight of the cation(s) X), more preferably less than 500 g/mole. In one embodiment an emulsifier is used with L being a branched perfluorinated group. In another embodiment an emulsifier is used with L being a linear partially fluorinated group. In yet another embodiment an emulsifier is used with L being a linear perfluorinated group.

Specific examples are described in, for example, US Pat. Publ. 2007/0015937 (Hintzer et al.). Exemplary emulsifiers include: $CF_3CF_2OCF_2CF_2OCF_2COOH$, $CHF_2(CF_2)_5COOH$, $CF_3(CF_2)_6COOH$, $CF_3O(CF_2)_3OCF(CF_3)COOH$, $CF_3CF_2CH_2OCF_2CH_2OCF_2COOH$, $CF_3O(CF_2)_3OCHFCF_2COOH$, $CF_3O(CF_2)_3OCF_2COOH$, $CF_3(CF_2)_3(CH_2CF_2)_2CF_2CF_2CF_2COOH$, $CF_3(CF_2)_2CH_2(CF_2)_2COOH$, $CF_3(CF_2)_2COOH$, $CF_3(CF_2)_2(OCF(CF_3)CF_2)OCF(CF_3)COOH$, $CF_3(CF_2)_2(OCF_2CF_2)_4OCF(CF_3)COOH$, $CF_3CF_2O(CF_2CF_2O)_3CF_2COOH$, and their salts.

In one embodiment, the emulsifier may be added as a microemulsion with a fluorinated liquid, such as described in U.S. Publ. No. 2008/0015304 (Hintzer et al.), WO Publ. No. 2008/073251 (Hintzer et al.), and EP Pat. No. 1245596 (Kaulbach et al.). In another embodiment, the fluorinated emulsifier is not added as a microemulsion. For example it may be added to the aqueous phase before or while the reaction is started and proceeds.

The fluorinated emulsifier is typically used in an amount of 0.01% by weight to 1% by weight based on solids (polymer content) to be achieved. The resulting polymer dispersion is usually treated to remove the fluorinated emulsifiers as will be described in greater detail below.

The aqueous emulsion polymerization may be initiated with a free radical initiator or a redox-type initiator. Any of the known initiators for initiating an aqueous emulsion polymerization of TFE can be used. Suitable initiators include organic as well as inorganic initiators, although the latter are generally preferred. Exemplary organic initiators include: organic peroxide such as bissuccinic acid peroxide, bisglutaric acid peroxide, or tert-butyl hydroperoxide. Exemplary inorganic initiators include: ammonium- alkali- or earth alkali salts of persulfates, permanganic or manganic acids, with potassium permanganate preferred. A persulfate initiator, e.g. ammonium persulfate (APS), may be used on its own or may be used in combination with a reducing agent. Suitable reducing agents include bisulfites such as for example ammonium bisulfite or sodium metabisulfite, thiosulfates such as for example ammonium, potassium or sodium thiosulfate, hydrazines, azodicarboxylates and azodicarboxyldiamide (ADA). Further reducing agents that may be used include sodium formaldehyde sulfoxylate or fluoroalkyl sulfinates. The reducing agent typically reduces the half-life time of the persulfate initiator. Additionally, a metal salt catalyst such as for example copper, iron, or silver salts may be added.

The amount of the polymerization initiator may suitably be selected to generate the desired yield and particle sizes, but it is usually preferably from 2 to 600 ppm, based on the mass of water used in the polymerisation. The MFI can also, or additionally, be adjusted by using a chain transfer agent. Typical chain transfer agents include ethane, propane, butane, alcohols such as ethanol or methanol or ethers like but not limited to dimethyl ether, tert butyl ether, methyl tert butyl ether. Preferably, the polymerization is carried out with using a chain-transfer agent.

The aqueous emulsion polymerization system may further comprise auxiliaries, such as buffers, and complex-formers. It is preferred to keep the amount of auxiliaries as low as possible to ensure a higher colloidal stability of the polymer latex. The aqueous emulsion polymerization further comprises the comonomers (modifiers) as described above and –if present- the functional comonomers.

Preferably the reaction conditions and ingredients are chosen such that the resulting fluoropolymer dispersion has a particle size from 100 to 400 nm, preferably 150 to 300 nm, most preferably 150 to 250 nm.

In one embodiment of the present disclosure a seeded polymerization is used to produce the fluoropolymer according to the present disclosure. A seeded polymerization involves as a first step the formation of seed polymer particles. The seed polymerization is known in the art of making fluoropolymers and is described, for example, in U.S. Pat. No. 4,391,940 (Kuhls et al.) or WO03/059992 A1, or EP 1,533,325 B1. The seed particles can be prepared as described above regarding the preparation of fluoropolymers and as recited in the above seed polymerization references. Preferably, the seed polymerization is carried out by aqueous emulsion polymerization to reach fluoropolymer particles of average particle size 30 to 149 nm, preferably 50 to 130 nm. The fluoropolymer seed particles may form the core of a core-shell polymer (for example if the polymer composition or polymerization speed or polymerization conditions in the subsequent polymerization are different). The seed particles used to make the core may have an SSG from for example 2.13 – 2.20, preferably from 2.14 – 2.19 g/cm³. In one embodiment the core of the fluoropolymer particles have a lower molecular weight than the shell(s) of the particles. The core of the particles may have a lower SSG than the outer shell. In another embodiments the core of the particle has a molecular weight that is greater than that of the outer shell or of all shells.

The fluorinated emulsifiers may be used as described above. Co-monomers may be used in the seed polymerization as described above. Their amount is adapted to the amount used in the preparation of the shell to limit the maximum amounts of co-monomers to the values indicated above and below. The polymerization may then be stopped. Typically the resulting seed dispersion may be diluted, for example by factor 2 to 20, with water before the shell is polymerized onto the seed particles, which then form the core of the core-shell particles generated in the second step. The polymerization of the shell may also be carried out as aqueous emulsion polymerization. Initiator and – if necessary fluorinated emulsifiers- are added and TFE and comonomers as described above may be fed to the composition during the polymerization. The comonomer may be added continuously till the end of the polymerization or for a substantial amount of the polymerization, for example for at least 50% of the polymerization time, preferably for 75% or more preferably for 90% of the polymerization time. In one embodiment the

modifiers are added at the end of the polymerization, for example after 50%, 75% or even 90% of the polymerization. The weight ratio of core to shell (weight determined by TFE consumption) may be from 1 : 99 to 1 : 9.

In one embodiment of the present disclosure there is provided a method of preparing the fluoropolymers as described herein comprising (i) preparing a seed composition by aqueous emulsion polymerization of TFE and one or more of the modifiers as described herein, (ii) preparing a shell onto the seed particles by aqueous emulsion polymerization of TFE and at least one or more of the modifiers as described herein wherein the total amount of modifiers does not exceed 1% by weight based on the total weight of the fluoropolymer and wherein at least the preparation of the seed composition is carried out in the presence of the fluorinated surfactants described herein and wherein the amount of fluorinated emulsifier does not exceed 5.000 ppm based on the total weight of the dispersion of step (ii) and, optionally isolating the fluoropolymer. The functional comonomers as described herein may be added in step (ii).

The aqueous emulsion polymerization, whether done with or without seed particles, will preferably be conducted at a temperature of at least 10°C, 25°C, 50°C, 75°C, or even 100°C; at most 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, or even 150°C. The polymerization will preferably be conducted at a pressure of at least 0.5, 1.0, 1.5, 1.75, 2.0, or even 2.5 MPa (megaPascals); at most 2.25, 2.5, 3.0, 3.5, 3.75, 4.0, or even 4.5 MPa.

Usually the aqueous emulsion polymerization is carried out by mildly stirring the aqueous polymerization mixture. The stirring conditions are controlled so that the polymer particles formed in the aqueous dispersion will not coagulate. The aqueous emulsion of the present disclosure may be carried out in a vertical kettle (or autoclave) or in a horizontal kettle. Paddle or impeller agitators may be used. The reaction is typically completed by interrupting the monomer feed.

Fluoropolymer Dispersions:

The aqueous emulsion polymerization usually is carried out until the concentration of the polymer particles in the resulting aqueous dispersion is at least 15, 20, 25, or even 30 % by weight; at most 20, 30, 35, 40, or even 50 % by weight (also referred to a solid content).

In the resulting dispersion, the average particle size of the polymer particles is typically from about 100 to 400 nm, preferably 150 to 300 nm, most preferably 150 to 250 nm.

The dispersions are subjected to a purification step during which the amount of fluorinated emulsifiers is reduced. Before or afterwards, the dispersions may be upconcentrated to increase the solid content. The fluoropolymer content in the dispersions may be increased by upconcentration, for example using ultrafiltration as described, for example in US 4,369,266 or by thermal decantation (as described for example in US 3,037,953) or by electrodecantation. The polymer content (typically expressed as "solid content") of upconcentrated dispersions is typically about 50 to about 70% by weight.

The removal of fluorinated emulsifiers is carried out most conveniently by anion exchange. Methods of removing the emulsifiers from the dispersions by anion-exchange and addition of stabilizing

non-ionic emulsifiers are disclosed for example in European Patent EP 1 155 055 B1. Typically, dispersions subjected to a treatment of reducing the amount of fluorinated emulsifiers contain a reduced amount thereof, such as for example amounts of from about 1 to about 500 ppm (or 2 to 200 ppm) based on the total weight of the dispersion. Preferably, the dispersions are treated to have a content of fluorinated emulsifiers of less than 100 ppm, preferably less than 50 ppm. The residual amount of the fluorinated emulsifiers used may be from 5 to 20 ppm or from 0.5 to 5 ppm, typically those according to formula (V) above.

Coating compositions:

To generate shear stable coating compositions the resulting fluoropolymer dispersions may have their content of non-fluorinated emulsifiers adjusted to reach a total amount of stabilizing non-fluorinated emulsifiers of from 1 to 20 % wt based on polymer content, (preferably 1 to 12 % wt) or from 1 to 10 % wt. (preferably 1 to 6 %wt) based on the total weight of the dispersion of the non-fluorinated emulsifiers described below. In case such emulsifiers have been used as stabilising emulsifier during the anion exchange and/or upconcentration step further emulsifiers of the same or of a different type may be added if necessary to reach the final desired amounts of such emulsifiers, for example to reach the desired viscosity transition temperature (VTT) or other properties. The conductivity of the dispersion may be adjusted to the level described herein for example by adding salts and/or non-fluorinated ionic emulsifiers, preferably anionic emulsifiers. Examples of such emulsifiers will be described in greater detail below.

The dispersions may have a conductivity of at least 500 µS, typically between 500 µS and 5,000 µS or between 500 and 1,500 µS. The desired level of conductivity of the dispersion may also be adjusted by adding a salt thereto such as for example inorganic salts including chlorides, sulfates, sulfonates, phosphates and the like. Particular examples include sodium chloride and ammonium chloride. The level of conductivity may also be adjusted by adding an anionic non-fluorinated surfactant to the dispersion as disclosed in WO 03/020836. Adding cationic emulsifiers to the dispersions is also possible, as described for example in WO 2006/069101.

Typical anionic non-fluorinated surfactants that may be added to the dispersions (not only to adjust the conductivity but also to influence the wetting properties of the dispersions), include surfactants that have an acid group, in particular a sulfonic or carboxylic acid group. Examples of non-fluorinated anionic surfactants include surfactants that have one or more anionic groups. Anionic non-fluorinated surfactants may include in addition to one or more anionic groups, other hydrophilic groups such as polyoxyalkylene groups having 2 to 4 carbons in the oxyalkylene group (for example, polyoxy ethylene groups). Typical non-fluorinated surfactants include anionic hydrocarbon surfactants. The term "anionic hydrocarbon surfactants" as used herein comprises surfactants that include one or more hydrocarbon moieties in the molecule and one or more anionic groups, in particular acid groups such as sulfonic, sulfuric, phosphoric and carboxylic acid groups and salts thereof. Examples of hydrocarbon moieties of the anionic hydrocarbon surfactants include saturated and unsaturated aliphatic groups having for example 6 to 40

carbon atoms, preferably 8 to 20 carbon atoms. Such aliphatic groups may be linear or branched and may contain cyclic groups. The hydrocarbon moiety may also be aromatic or contain aromatic groups. Additionally, the hydrocarbon moiety may contain one or more hetero-atoms such as for example oxygen, nitrogen and sulfur.

Particular examples of non-fluorinated, anionic hydrocarbon surfactants include alkyl sulfonates such as lauryl sulfonate, alkyl sulfates such as lauryl sulfate, alkylarylsulfonates and alkylarylsulfates, and alkylsulfosuccinates, fatty (carboxylic) acids and salts thereof such as lauric acids and salts thereof and phosphoric acid alkyl or alkylaryl esters and salts thereof. Commercially available anionic hydrocarbon surfactants that can be used include those available under the trade designation Polystep Al 6 (sodium dodecylbenzyl sulphonate) from Stepan Company, Germany; Hostapur SAS 30 (secondary alkyl sulphonate sodium salt), Emulsogen LS (sodium lauryl sulfate) and Emulsogen EPA 1954 (mixture of C2 to C4 sodium alkyl sulfates) each available from Clariant GmbH, Germany; Edenor C-12 (Lauric acid) available from Cognis, Germany; and TRITON X-200 (sodium alkylsulfonate) available from Dow Chemical, Midland, MI. Further suitable anionic surfactants include the sulfosuccinates disclosed in EP 1538177 and EP 1526142. Mixtures of different anionic surfactants may also be used. Typical amounts of these emulsifiers may include from 0.02 to 10% wt. based on the weight of the composition, preferably from 0.01 up to 5 %wt. based on weight of fluoropolymer, more preferably from 0.05 up to 1% wt. based on weight of fluoropolymer.

Non-fluorinated non-ionic surfactants:

The coating compositions according to the present disclosure contain non-fluorinated non-ionic surfactants. Typically, they contain these surfactants in an amount of from about 1 to 6 % weight based on the total weight of the composition, or from 2 to 12 % wt. based on the weight of fluoropolymer in the dispersion. The surfactants are non-aromatic. Suitable surfactants include those of the general formula (VI):

$$R_1O\text{-}[CH_2CH_2O]_n\text{-}[R_2O]_m\text{-}R_3 \qquad (VI)$$

wherein R_1 represents a linear or branched aliphatic hydrocarbon group having at least 8 carbon atoms, preferably 8 to 18 carbon atoms. In formula (V) above R_2 represents an alkylene having 3 carbon atoms, R_3 represents hydrogen or a C1-C3 alkyl group, n has a value of 0 to 40, m has a value of 0 to 40 and the sum of n+m is at least 1 and preferably n is at least 1. In a preferred embodiment, residue R1 corresponds to (R')(R'')HC- wherein R' and R'' are the same or different, linear, branched or cyclic alkyl residues, R_3 is H, and m is 0. Such embodiment includes branched secondary alcohol ethoxylates. Commercially available non-ionic surfactant or mixtures of non-ionic surfactants include those available from Clariant GmbH under the trade designation GENAPOL such as GENAPOL X-080 and GENAPOL PF 40. Branched secondary alcohol ethoxylates are commercially available under the trade designation

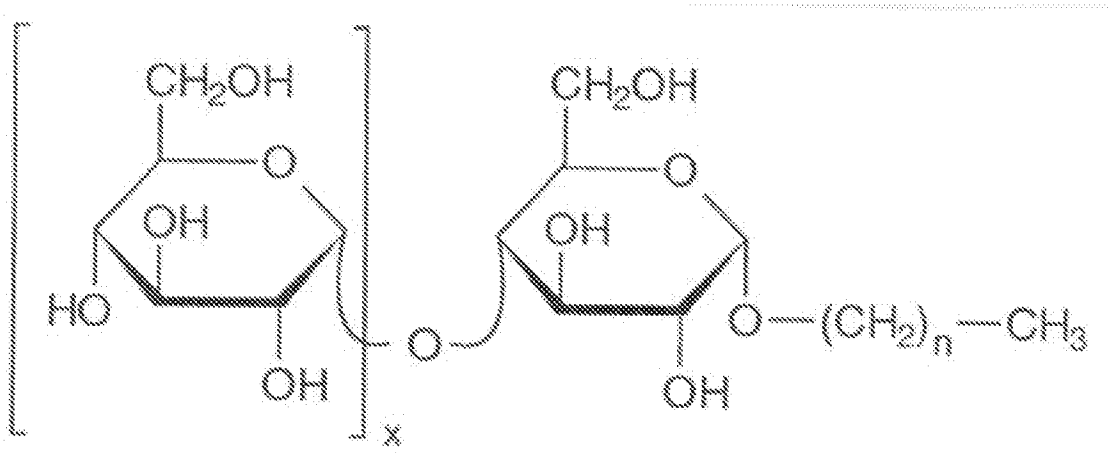
TERGTIOL TMN from Dow Chemical Company, e.g. Tergitol TMN 6, Tergitol TMN 100X and Tergitol TMN 10 from Dow Chemical Company.

Another suitable class of non-ionic non-fluorinated emulsifiers include ethoxylated amines and amine oxides.

Further non-fluorinated, non-ionic surfactants that can be used include alkoxylated acetylenic diols, for example ethoxylated acetylenic diols. The ethoxylated acetylenic diols for use in this embodiment preferably have a HLB between 11 and 16. Commercially available ethoxylated acetylenic diols that may be used include those available under the trade designation SURFYNOL from Air Products, Allentown, PA (for example, SURFYNOL 465). Still further useful non-ionic surfactants include polysiloxane based surfactants such as those available under the trade designation Silwet L77 (Crompton Corp., Middlebury, CT).

Other examples of non-ionic surfactants include sugar-based surfactants, such as alkylpolyglycosides and the like. Sugar-based surfactant contain one or more cyclic aliphatic polyols and comprise one or more linear or branched alky chain residue that may optionally be interrupted by oxygen atoms (ether atoms). The linear or branched residues typically include alkyl, alkoxy or polyoxy alkyl residues and may contain at least 6 carbon atoms or at least 8 carbon atoms and typically between 6 to 26 or 8 to 16 carbon atoms

A preferred type of sugar-based emulsifiers includes alkyl glucosides. Alkyl glucosides contain at least one glucose moiety. Examples of alkyl poly glucosides include compounds represented by formula (VII):



wherein x represents 0, 1, 2, 3, 4 or 5 and n represents an integer of from 6 to 22. In case x is 0, the ether oxygen contains a hydrogen and forms a hydroxyl group.

It is understood that the above formula represents specific examples of alkyl poly glucosides showing glucose in its pyranose form. Other suitable examples include, for example but are not limited to, molecules where one or more of the hydroxy hydrogens in the above formula are substituted by alkyl, alkyoxy or polyoxy alkyl residues. Also the repeating glucose residue in the square brackets on the left

hand-site of formula (VII) may be replaced by other sugar moieties, which may or may not contain further alkyl-, alkoxy or polyoxyalkyl residues. Alkyl poly glucosides are available, for example, by acid-catalysed reaction of glucose, starch or n-butyl glucosides with fatty alcohols which typically yields a mixture of various alkyl glucosides (Alkylpolygylcoside, Römpp, Lexikon Chemie, Version 2.0, Stuttgart/New York, Georg Thieme Verlag, 1999). Examples of fatty alcohols include hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol (lauryl alcohol), tetradecanol, hexadecanol (cetyl alcohol), heptadecanol, octadecanol (stearyl alcohol), eicosanoic acid and combinations thereof. Alkyl glucosides are also commercially available under the trade designation Glucopon from Cognis GmbH, Düsseldorf, Germany.

Another class of non-ionic surfactants includes polysorbates. Polysorbates include ethoxylated, propoxylated or alkoxylated sorbitans and may further contain linear cyclic or branched alkyl residues, such as but not limited to fatty alcohol or fatty acid residues. Useful polysorbates include those available under the trade designation Polysorbate 20, Polysorbate 40, Polysorbate 60 and Polysorbate 80. Polysorbate 20, is a laurate ester of sorbitol and its anhydrides having approximately twenty moles of ethylene oxide for each mole of sorbitol and sorbitol anhydrides. Polysorbate 40 is a palmitate ester of sorbitol and its anhydrides having approximately twenty moles of ethylene oxide for each mole of sorbitol and sorbitol anhydrides. Polysorbate 60 is a mixture of stearate and palmitate esters of sorbitol and its anhydrides having approximately twenty moles of ethylene oxide for each mole of sorbitol and sorbitol anhydrides.

While the fluoropolymers provided herein already have good or improved shear stability and film forming properties such properties of the aqueous dispersions containing them may be further improved by the non-ionic emulsifiers employed. The dispersion properties may be optimized for shear stability and/or film forming properties by choosing the type of non-ionic emulsifier and if desired combination of non-ionic and ionic emulsifiers.

Typical amounts of non-ionic emulsifiers include 1 to 20 % by weight (preferably 1 to 12% wt) based on the weight of fluoropolymer in the dispersion or from 1 to 10 % wt (preferably 1 to 6% wt) based on the total weight of the dispersion.

The dispersion may have a critical film thickness (CFT) in the test as described in the example section of greater than 2 µm, preferably at least 5µm or more preferably greater than 10 µm. The dispersions may have a shear stability according to the shear stability test as described in the example section of at least one minute.

The dispersions may further contain ingredients that may be beneficial when coating or impregnating the dispersion on a substrate, such as adhesion promoters, friction reducing agents, coalescent agents, pigments and the like, hereinafter also referred to as "additives". Optional components include, for example, buffering agents and oxidizing agents as may be required or desired for the various applications.

In many applications, the PTFE dispersions resulting after polymerization and upconcentration are combined with further additives or components to produce a coating composition. Such coating

compositions may be applied to a substrate, for example by spray coating, roller coating, dip coating and curtain coating.

Possible coating compositions include base coats, intermediate coats and top coats. For example, in metal coating, in particular for coating cookware, a base coat composition may be obtained by further blending heat resistant polymers such as polyamide imide, polyimide or polyarylene sulphide with the PTFE dispersion. Still further ingredients such as pigments and mica particles may be added as well to obtain a base coate composition for coating metal. Such additional components are typically dispersed in organic solvents such as toluene, xylene or N-methylpyrrolidone. The fluoropolymer dispersions typically represent about 10 to 80% by weight of the coating composition. Coating compositions for metal coatings and components used therein have been described in e.g. WO 02/78862, WO 94/14904, EP 22257 and US 3,489,595. Preferably, the dispersions provided herein are top coat compositions. Top coat compositions are typically applied to a coated substrate, typically a coated metal substrate. Typically, the coated substrate is coated by a composition containing one or more fluoropolymers.

The resulting polymer dispersion can also be used to prepare dispersions with bimodal, and multimodal particle size distributions for example by mixing different dispersions. These distributions may have a wide distribution, such as, for example, particle sizes ranging from 20 nm to 1000 nm as disclosed in e.g. US 5,576,381, EP 0 990 009 B1 and EP 969 055 A1. Multi-modal fluoropolymer particle dispersions may present advantageous properties in coatings, such as better adhesion to the substrate and denser film formation. For example, the fluoropolymer dispersions may comprise a mixture of first fluoropolymer particles having an average particle size of at least 180 nm in combination with second fluoropolymer particles that have an average particle size of less than 180 nm, preferably an average particle size of not more than 0.9 or not more than 0.7 times the average particle size of the first fluoropolymer particles (as disclosed, for example, in US 5,576,381). Bimodal or multi-modal fluoropolymer dispersions can be conveniently obtained by blending the aqueous fluoropolymer dispersion of different fluoropolymer particle sizes together in the desired amounts. The fluoropolymer population may not only be bimodal or multimodal with respect to the particle sizes but may also be bimodal or multimodal with respect to the fluoropolymers or the molecular weight of the fluoropolymers used. For example, the first polymer having an average particle size of at least 180 nm may be a fluoropolymer as provided herein and the second fluoropolymer having an average particles size that is not more than 0.9 or not more than 0.7 times the average particle size of the first polymer may be a non-melt processable PTFE or a melt-processable fluoropolymer, for example a PFA. Similarly, the second fluoropolymer may be a fluoroelastomer. Suitable dispersion of melt-processible fluoropolymers that can be mixed with the non-melt processable fluoropolymer dispersions include dispersions of the following fluoropolymers: copolymers of TFE and a perfluorinated vinyl ether (PFA) and copolymers of TFE and HFP (FEP). PFA polymers typically contain from 2 to 12% by weight of comonomers, typically comonomers being selected from the "modifiers" described above. FEP polymer typically contain from 70-90 %wt of TFE, 30-10%wt of HFP and 0-1 % wt of other perfluorinated comonomers the total composition giving 100% wt. Such dispersions may be monomodal, bi-modal or multimodal as disclosed

in e.g. EP 990 009 A1. The dispersion provided herein may also contain one or more of the fluoropolymers provided herein and one or more PTFE micropowder. PTFE micropowders are PTFEs having an SSG of greater than 2.20 g/cm^3.

Examples are provided to further illustrate the present disclosure. Embodiments and examples are illustrative only and are not meant to limit the disclosure to the following particular embodiments and examples.

List of particular embodiments

The following list of embodiments is provided to further illustrate the present disclosure. There is no intention to limit the specific embodiments listed. Other embodiments within the scope of the claims may also be used.

First particular embodiment: A modified polytetrafluoroethylene (modified PTFE) containing up to 1% by weight of at least one modifier selected from unsaturated perfluorinated allyl ethers of the general formula

$$CF_2=CF-(CF_2)-O-Rf'$$

wherein Rf' represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated oxoalkyl residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof.

Second particular embodiment: The modified polytetrafluoroethylene (modified PTFE) of the first embodiment wherein the perfluorinated allyl ethers are selected from those wherein Rf' represents a perfluorinated alkyl residue and combinations thereof.

Third particular embodiment: The modified PTFE of the first embodiment wherein the allyl ethers are selected from $F_2C=CF-CF_2-O-CF_3$ (MA1); $F_2C=CF-CF_2-O-CF_2CF_3$ (MA2); $F_2C=CF-CF_2-O-CF_2CF_2CF_3$ (MA3), $F2C=CF-CF_2-O-C_4F_9$ (MA4) and combinations thereof.

Fourth particular embodiment: The modified PTFE of any one of the preceding embodiments wherein the modified PTFE further comprises at least one modifier selected from alkyl vinyl ethers of the general formula

$$CF_2=CF-O-Rf$$

wherein Rf represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated oxoalkyl

residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof.

Fifth particular embodiment: The modified PTFE of the fourth embodiment wherein the modified PTFE further comprises at least one modifier selected from perfluorinated alkyl vinyl ethers selected from F_2C=CF-O-CF_2-O-(CF_2)-F (MV 11), F_2C=CF-O-CF_2-O-(CF_2)$_2$-F (MV 12), F_2C=CF-O-CF_2-O-(CF_2)$_3$-F (MV 13), F_2C=CF-O-CF_2-O-(CF_2)$_4$-F (MV 14), F_2C=CF-O-(CF_2)$_2$-OCF_3 (MV 21), F_2C=CF-O-(CF_2)$_3$-OCF_3 (MV 31), F_2C=CF-O-(CF_2)$_4$-OCF_3, (MV 41); CF_2=CF-O-C_3F_7 (PPVE-1), CF_2=CF-O-CF_2-$CF(CF_3)$-O-$CF_2CF_2CF_3$ (PPVE-2); CF_2=CF-(O-CF_2-$CF(CF_3)$)$_2$-O-$CF_2CF_2CF_3$ (PPVE-3) and combinations thereof.

Sixth particular embodiment: The modified PTFE of any one of the first to fifth embodiments having a transmission of greater than 60% when measured according to ASTM-D 1003, preferably greater than 70%, more preferably greater than 75%.

Seventh particular embodiment: The modified PTFE of any one of the first to the sixth particular embodiments wherein the perfluorinated allyl ether content is from 50 ppm to 5,000 ppm, preferably less than 5.000 ppm, more preferably from 100 ppm to 3,000 ppm (based on the total weight of the polymer).

Eight particlular embodiment: The modified PTFE of any one of the first to the seventh particular embodiments having a standard specific gravity from 2.14 to 2.20 g / cm^3.

Ninth particular embodiment: The modified PTFE of any one of the first to the eighth particular embodiment wherein the modified PTFE has an MFI (372/5) of less than 0.1 g/ 10 min, preferably less than 0.01 g/10 min.

Tenth particular embodiment: The modified PTFE of any one of the first to the ninth particular embodiments wherein the modified PTFE has a melting point of at least 321°C.

Eleventh particular embodiment: The modified PTFE of any one of the first to the tenth particular embodiment having a total amount of extractable perfluorinated alkanoic carboxylic acids and their salts of less than 200 ppb based on the amount of polymer, preferably less than 100 ppb and more preferably less than 50 ppb, wherein the perfluorinated carboxylic acids and their salt have from 8 to 14 carbon atoms.

Twelfth particular embodiment: the modified PTFE of any one of the first to the eleventh particular embodiment wherein the modified PTFE has less than 50, preferably less than 10 -COOH and -COF end groups per 10^6 carbon atoms.

Thirteenth particular embodiment: An aqueous dispersion comprising a modified polytetrafluoroethylene (modified PTFE) according to any one of the first to the tenth particular embodiments and further comprising a fluorinated surfactant selected from a linear or branched or cyclic perfluorinated or partially fluorinated alkanoic acids wherein the alkyl residue of the acid is interrupted once or more than once by an oxygen atom but wherein the dispersion comprises the fluorinated surfactant in an amount of less than 5.000 ppm and wherein the dispersion comprises from about 1 to about 10 % wt (based on the weight of the dispersion) of one or more aliphatic, non-fluorinated, non-ionic surfactants

Fourteenth particular embodiment: The aqueous dispersion of the thirteenth particular embodiment wherein the average particle size (DIN ISO 13321 1996) of the modified PTFE is from 150 nm to 300 nm.

Fifteenth particular embodiment: The aqueous dispersion of the thirteenth or fourteenth particular embodiment wherein the fluorinated emulsifier corresponds to the general formula

$$[R_f\text{-}O\text{-}L\text{-}Y^-]_iX_i^+$$

wherein L represents a linear or branched, partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a linear or branched, partially or fully fluorinated aliphatic group or a linear or branched partially or fully fluorinated group interrupted once or more than once with oxygen atoms, X_i^+ represents a cation having the valence i and i is 1, 2 and 3 and Y represents COO or SO_3 and wherein the molecular weight of anionic part of the emulsifier is less than 1,000 g/mole.

Sixteenth particular embodiment: The dispersion of any one of the thirteenth to fifteenth particular embodiment comprising from about 1 to about 12 % wt. (based on the weight of the dispersion) of one or more aliphatic, non-fluorinated, non-ionic surfactant.

Seventeenth particular embodiment: The dispersion of any one of the the thirteenth to sixteenth particular embodiments containing from 0 to 50 ppm of perfluoroalkanoic acids.

Eighteenth particular embodiment: The dispersion of any one of the thirteenth to seventeenth particular embodiment further comprising from about 1 to about 12 % wt. (based on the weight of the dispersion) of one or more aliphatic, non-fluorinated, non-ionic surfactants selected from (i) alkylpolyglycosides, (ii) sorbitan esters and (iii) ethoxylates of the general formula

$$R_1O\text{-}[CH_2CH_2O]_n\text{-}[R_2O]_m\text{-}R_3$$

wherein R_1 represents a linear or branched aliphatic hydrocarbon group having at least 8 carbon atoms, preferably 8 to 18 carbon atoms, R_2 represents an alkylene having 3 carbon atoms, R_3 represents hydrogen or a C1-C3 alkyl group, n has a value of 1 to 40 and m has a value of 0 to 40 and wherein the groups denoted by n and m can be arranged at random or in blocks.

Nineteenth particular embodiment: The dispersion of any one of the thirteenth to eighteenth embodiment being a coating composition and further comprising at least one additional polymer other than the modified PTFE.

Twentieth particular embodiment: The dispersion of any one of the thirteenth to nineteenth particular embodiment being a coating composition and further comprising at least one additional polymer other than the modified PTFE wherein the at least one additional polymer is selected from perfluorinated polymers having an MFI of at least 0.3 g/ 10 min, from polyamide imides, polyimides and combinations or blends thereof.

Twenty-first particular embodiment: A coated substrate obtained from the dispersion of any one of the thirteenth to twentieth particular embodiment.

Twenty-second particular embodiment: An article comprising a coated substrate obtained with the dispersion of any one of the thirteenth to twentieth particular embodiment.

Twenty-third particular embodiment: A method of coating a substrate said method comprising applying the dispersion of any one of the thirteenth to twentieth particular embodiment to a substrate and removing the aqueous phase.

Examples and Methods

The following abbreviations are used in this section: mL=milliliters, g=grams, mmHg=millimeters of mercury, min=minutes, h=hours, NMR=nuclear magnetic resonance, ppm=parts per million, r.t. = room temperature, mol = moles, mmol = millimoles, °C = degrees Celsius, MHz = Megahertz.

Determination of Solid Content:

The solid content was determined gravimetrically according to DIN EN ISO 12086-2 : 2006-05. Correction for non-volatile inorganic salts was not considered.

Particle size:

Particle size of the PTFE particles was determined by photon correlation spectroscopy according to DIN ISO 13321 1996 using a Malvern 1000 HAS Zetasizer. The average particle size reported is the harmonic intensity-averaged diameter (Z- average).

Shear stability test

150 g dispersion, thermostated at 20 °C, were put into a 250 mL standard glass beaker of an inner diameter of 65 mm. The agitation head (S 25 N – 25 G) of an Ultra Turrax T25, supplied by Janke & Kunkel, was immersed in the center of the beaker such that the end of the head was 7 mm above the beaker bottom. The Ultra Turrax was switched on a revolution speed of 8000 rpm. Agitation rendered the surface of the dispersion "turbulent" or "wavy". 10 seconds after the Turrax has started 2.0 g xylene were added within less than 10 s to the agitated dispersion. Time measurement started with the addition of xylene was complete and was stopped when the surface of the agitated dispersion no longer showed visible turbulence. The surface "freezes" or smoothes due to coagulation. Coagulation was accompanied by a distinct change of sound of the Ultra Turrax. In case that the "surface freezing" could not be clearly observed due to foam formation time measurement was stopped within the onset of the change of sound. Reported shear stability values in the examples are the average of 5 measurements. Observed reproducibility was 10 %. The shear stability is expressed as the time from the complete addition of xylene till coagulation was observed.

Standard specific gravity (SSG)

The standard specific gravity (SSG) was measured by the water displacement method according to DIN EN ISO 12086-2: 2006-05.

Transmission:

The transmission was measured according to ASTM D 1003 using a direct reading haze meter, (the transparency meter "haze-gard plus", from BYK-Gardner GmbH, Geretsried, Germany, serial number 111156). Samples were prepared as follows: The dispersion was precipitated by adding 1 litre of dispersion into a 2L beaker and mixing it with 20 ml of concentrated hydrochloric acid at a stirring speed of 800 rpm and agglomerated by adding 10 ml of gasoline (Shellsol 80-110). The precipitate was washed with distilled water and dried in a rotary evaporator at 90°C at reduced pressure. The dried agglomerates were then dried in a vacuum oven at 210°C for 16 h. 10 g of the precipitate were sieved through a 2 mm sieve and then compressed in a 4-stations press (350 bar, 5 min holding time) into a sheet having a diameter of 80 mm. This sheet was sintered as follows: heating from room temperature to 290 °C at the maximum heating rate. Then the sample was heated from 290 °C to 380 °C at a heating rate of 120 °C per hour and holding the temperature of 380 °C for 30 min before cooling the sample down to a temperature of 294 °C at a cooling rate of 60 °C per hour after which the oven was switched off and the samples were allowed to reach room temperature. The haze meter indicates transmission values (in per cent) of the samples.

Critical film thickness (CTF):

A 200ml ml beaker was filled with the dispersion. Foam, if present, was removed by a pipette. A degreased aluminum test plate (200 x 40 x 1 mm; degreasing by rinsing with acetone), was immersed into the dispersion for 10 seconds and then hung at a plate holder at an angle of 20° and dried at ambient conditions for 5 minutes. The test sample was then put in an oven kept at 380°C for 10 minutes. The aluminum plate was then taken out of the oven and allowed to cool down at ambient conditions to reach room temperature. The plate was then examined by an optical microscope (100 x magnification) for the formation of cracks. The thickness of the layer formed on the aluminum plate was determined (using a MiniTest 3100 from ElektroPhysik Dr. Steingroever GmbH& Co. KG, Cologne, Germany). The procedure was repeated until cracks were visible. The thickness of the layer before cracks have appeared is determined as critical film thickness. The results reported were the average from two measurements.

Melting point:

The determination of the melting point by DSC has been described, for example, in DIN EN ISO 12086-2 : 2006-05.

Melt flow index (MFI):

The determination of the MFI can be carried out as described, for example, in DIN EN ISO 12086-2 : 2006-05. For an MFI (372/5) the measurement temperature is 372°C and the load is 5 kg.

Conductivity:

Conductivity was measured with the 712 Conductometer, supplied by Metrohm AG. In case that the conductivity of the upconcentrated dispersions was less than 1000 µS/cm, aqueous ammonium sulfate solution (1 %) was added to adjust the conductivity to about 1000 µS/cm.

Amounts of fluorinated emulsifiers:

Extractables:

For an effective extraction of fluorinated emulsifiers from solid polymer samples, the particle size of the polymer sample should be less than 250 µm. Samples with larger particles should be ground before the extraction. Samples from aqueous dispersions or latexes are freeze-dried to remove water.

The fine-grained material is spiked with a methanolic surrogate recovery standard (SRS) $^{13}C_4$-PFOA (perfluorooctanoic acid having 4 of its carbon atoms replaced by ^{13}C isotopes) solution at a concentration of 25 ppb based on polymer mass and allowed to dry. The dried, spiked polymer material is treated with methanol (1 g polymer + 3 ml methanol, 16 h @ 250 rpm and 50°C) to extract fluorinated acids. The extract is centrifuged (~10 min @ 4400 rpm) and an aliquot of the supernatant was transferred into a 2ml autosampler vial. The extract is analyzed for fluorinated acids with reversed phase HPLC coupled with a triple quadrupole mass spectrometer (e.g. Agilent 6460 or AB Sciex API 5000 QQQ-MS) in negative

Multiple Reaction Mode (MRM) using analyte typical transitions, e.g. m/z 413 -> 369 for PFOA (perfluorinated octanoic acid). The HPLC (Agilent 1200) is equipped with an Agilent C18 column (Zorbax Eclipse XDB-C18 4.6x50mm 1.8 µm) and run in gradient mode with high purity water and methanol @ 50°C, both liquids were LC-MS grade and modified with 10 mmol ammonium acetate (gradient 15% MeOH -> 100% MeOH). The analytes are quantified using equivalent or similar isotope labelled internal standards (e.g. $^{13}C_8$-PFOA as internal standard for PFOA) in a calibration range of 0.5 – 200 ng/ml analyte in methanolic extract, resulting in a lower level of quantification (LLOQ) related to polymer of 1.5 ppb and an upper limit of quantification (ULOQ) of 600 ppb. Analytes with concentrations higher than ULOQ are diluted with methanol into the calibration range and the analysis is repeated. Emulsifier content for other acids salts can be obtained in an analogue way.

Emulsifier content of aqueous dispersions, e.g. after work up and purifications, typically used for emulsifiers other than perfluorinated alkanoic acids can be analyzed as known in the art, for example by head space gas chromatography by converting the salts to methanol esters (addition of methanol). Reference solution from the pure acids are used as standards. This method allows for the determination of a levels down to about 1 – 5 ppm.

Polar end groups determination:

The total amount of -COOH and -COF groups in the polymer can be determined by FTIR spectrometry as described in EP-A-226 668. A film is used having a thickness of 0.1 mm that is prepared at 350 °C. As reference a film prepared in the same way made of a material with known amounts (for example known to have no end groups) is used. A Nicolet Magna 560 FTIR-spectrommeter may be used. The total amount includes the isolated and associated groups.

Examples

Comparative example 1

A fluoropolymer dispersion was prepared by aqueous emulsion polymerization using seed polymerization and a partially fluorinated emulsifier to produce a PTFE having an HFP-modified PTFE seed and a homopolymer PTFE shell. Total amount of HFP was less than 1.0 % by weight. The dispersion was subjected to anion-exchange using GENAPOL X 089 as stabilising emulsifier to reduce the content of fluorinated emulsifier to about 1ppm. The dispersion was upconcentrated by ultrafiltration to a solid content of 58%. Particle size was 215 nm (Z-average), SSG was between 2.14 and 2.18, MFI (372/5) of less than 0.3 g / 10 min and the melting point was greater than 217°C. Content of GENAPOL X 089 was 5.0% based on solid.

Comparative Example 2

A fluoropolymer dispersion was prepared by seed polymerization to produce a PPVE-1 modified PTFE seed and a PPVE-1 modified shell. Total amount of modifiers was less than 1.0 % wt. The

dispersion was subjected to the same anion-exchange treatment as comparative example 1 using GENAPOL X 080 as stabilising emulsifier to reduce the content of fluorinated emulsifier to about 1 ppm. The dispersion was upconcentrated as described in comparative example 1. Solid content was 58%, particle size was 259 nm, MFI (372/5) of less than 0.3 g/ 10 min and SSG was between 2.14 and 2.18 and the melting point was greater than 217°C. The GENAPOL content was 5.0% wt. based on polymer content.

Both dispersions were subjected to shear stability and critical film thickness tests. The visual appearance of the polymer in the dispersion was carried out on the coagulated polymer as described above and measured as transmittance. The results are shown in table 1.

	Comparative Example 1	Comparative Example 2
Transmittance [%]	66	45
Shear stability of dispersion [min]	1.6	0.22
CFT [µm]	12	10

Table 1: Comparison between dispersion and modified polymer and polymer dispersions according to example 1 with the polymer and polymer dispersion of comparative example 1.

Comparative examples 3 to 5:

Two dispersions were prepared with different comonomer content analogue to comparative example 2 and with properties similar to those of the dispersion of comparative example 2. The dispersion was upconcentrated to 60% solid content. Films were coated from the dispersions and the resulting films were measured for their gloss. The polymer according to comparative example 3 had a content of 0.05 wt % of PPVE-1 while the polymer of comparative example 4 had a PPVE-1 content of 0.03 wt%. Both dispersions had a transmittance of greater than 60%. In comparative example 5, a polymer was prepared similar to comparative example 1 using no PPVE as comonomer but HFP instead. The film prepared from comparative example 2 was also analyzed for its gloss.

	PPVE content	Gloss value
Comparative Example 3	0.05	24
Comparative Example 4	0.03	16
Comparative example 5	0.0	28

These examples show that comonomers with low ether modifier content have a reduced gloss compared to a non-ether comonomer.

Example 1:

A PTFE dispersion modified with MA-3 (0.2 wt % of MA-3 (CF_2=CF-CF_2-O-C_3F_7)) was prepared by aqueous emulsion polymerization at 40°C using $KMnO_4$-initiator in the presence of a partially fluorinated emulsifier at TFE-pressure of 15bar. The resulting latex had a solid content of 22.0% and the average polymer particle size was 110 nm. The latex was subjected to anion-exchange using GENEAPOL X 080 as stabilizing emulsifier to reduce the content of the fluorinated emulsifier to about 1 ppm as described in comparative example 1. The modified PTFE had an SSG of 2.173 g/cm^3, an MFI (372/5) of less than 0.3 g / 10 min, and the melting point was greater than 321°C. The transmission was 80.0%. The dispersion was tested for its stability (Turrax test) and had a shear stability of greater than 1.6 min. Critical film thickness was less than 10 µm.

The allyl ether modified PTFE obtained in example 1 was also submitted to an adhesion test on an aluminum substrate (pressing polymer on aluminum substrates and measuring force to separate polymer from the aluminum substrate). The polymer of example 1 had much lower adhesion than PPVE-modified PTFEs tested. This is an indication that the allyl ether modified PTFEs was very hydrophobic and had very few polar end groups. PPVE-modified PTFEs have been found to have less than 200 but more than 50 polar end groups. This indicates that the amount of polar end groups (-COOH, -COF) of the modified PTFEs provided herein may be less than 50, for example less than 25 or even less than 10 per 10^6 carbon atoms.

CLAIMS

1. A modified polytetrafluoroethylene (modified PTFE) containing up to 1% by weight of at least one modifier selected from unsaturated perfluorinated allyl ethers of the general formula

CF_2=CF-(CF_2)-O-Rf'

wherein Rf' represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated oxoalkyl residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof.

2. The modified polytetrafluoroethylene (modified PTFE) of claim 1 wherein the perfluorinated allyl ethers are selected from those wherein Rf' represents a perfluorinated alkyl residue and combinations thereof.

3. The mdofied PTFE of claim 1 wherein the allyl ethers are selected from F_2C=CF-CF_2-O-CF_3 (MA1); F_2C=CF-CF_2-O-CF_2CF_3 (MA2); F_2C=CF-CF_2-O-$CF_2CF_2CF_3$ (MA3), F2C=CF-CF_2-O-C_4F_9 (MA4) and combinations thereof.

4. The modified PTFE of any one claims 1 to 3 wherein the modified PTFE further comprises at one modifier selected from alkyl vinyl ethers of the general formula

CF_2=CF-O-Rf

wherein Rf represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated oxoalkyl residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof.

5. The modified PTFE of any one of claims 1 to 3 wherein wherein the modified PTFE further comprises at one modifier selected from perfluorinated alkyl vinyl ethers selected from F_2C=CF-O-CF_2-O-(CF_2)-F (MV 11), F_2C=CF-O-CF_2-O-(CF_2)$_2$-F (MV 12), F_2C=CF-O-CF_2-O-(CF_2)$_3$-F (MV 13), F_2C=CF-O-CF_2-O-(CF_2)$_4$-F (MV 14), F_2C=CF-O-(CF_2)$_2$-OCF_3 (MV 21), F_2C=CF-O-(CF_2)$_3$-OCF_3 (MV 31), F_2C=CF-O-(CF_2)$_4$-OCF_3, (MV 41); CF_2=CF-O-C_3F_7 (PPVE-1), CF_2=CF-O-CF_2-CF(CF_3)-O-$CF_2CF_2CF_3$ (PPVE-2); CF_2=CF-(O-CF_2-CF(CF_3))$_2$-O-$CF_2CF_2CF_3$ (PPVE-3) and combinations thereof.

6. The modified PTFE of any one of claims 1-5 having a transmission of greater than 60% when measured according to ASTM-D 1003, preferably greater than 70%, more preferably greater than 75%.

7. The modified PTFE of any one of claims 1-6 wherein the perfluorinated allyl ether content is from 50 to 5,000, preferably from 100 to 3,000 ppm (based on the total weight of the polymer).

8. An aqueous dispersion comprising a modified polytetrafluoroethylene (modified PTFE) containing up to 1% by weight of at least one modifier selected from unsaturated perfluorinated allyl ethers of the general formula

$$CF_2=CF-(CF_2)-O-Rf'$$

wherein Rf' represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated oxoalkyl residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof; wherein the dispersion further comprise a fluorinated surfactant selected from a linear or branched perfluorinated or partially fluorinated alkanoic acids wherein the alkyl residue of the acid is interrupted once or more than once by an oxygen atom but wherein the dispersion comprises the fluorinated surfactant in an amount of less than 5.000 ppm and wherein the dispersion comprises from about 1 to about 10 % wt (based on the weight of the dispersion) of one or more aliphatic, non-fluorinated, non-ionic surfactants.

9. The aqueous dispersion of claim 8 wherein the perfluorinated allyl ethers are selected from those wherein Rf' represents a perfluorinated alkyl residue and combinations thereof.

10. The aqueous dispersion of claim 8 wherein the allyl ethers are selected from $F_2C=CF-CF_2-O-CF_3$ (MA1); $F_2C=CF-CF_2-O-CF_2CF_3$ (MA2); $F_2C=CF-CF_2-O-CF_2CF_2CF_3$ (MA3), $F2C=CF-CF_2-O-C_4F_9$ (MA4) and combinations thereof.

11. The aqueous disperison of claim 8 wherein the modified PTFE further comprises at one modifier selected from alkyl vinyl ethers of the general formula

$$CF_2=CF-O-Rf$$

wherein Rf represents a linear or branched, cyclic or acyclic perfluorinated residue having from 1 up to 10 carbon atoms, wherein the residue is a perfluorinated alkyl residue, or a perfluorinated

oxoalkyl residue, i.e. an alkyl residue containing one or more catenary oxygen atoms, preferably from 1 – 3 catenary oxygen atoms, and combinations thereof.

12. The aqueous dispersion of any one of claims 8 to 11 wherein the modified PTFE further comprises at one modifier selected from perfluorinated alkyl vinyl ethers selected from F_2C=CF-O-CF_2-O-(CF_2)-F (MV 11), F_2C=CF-O-CF_2-O-$(CF_2)_2$-F (MV 12), F_2C=CF-O-CF_2-O-$(CF_2)_3$-F (MV 13), F_2C=CF-O-CF_2-O-$(CF_2)_4$-F (MV 14), F_2C=CF-O-$(CF_2)_2$-OCF_3 (MV 21), F_2C=CF-O-$(CF_2)_3$-OCF_3 (MV 31), F_2C=CF-O-$(CF_2)_4$-OCF_3, (MV 41); CF_2=CF-O-C_3F_7 (PPVE-1), CF_2=CF-O-CF_2-CF(CF_3)-O-$CF_2CF_2CF_3$ (PPVE-2); CF_2=CF-(O-CF_2-CF(CF_3))$_2$-O-$CF_2CF_2CF_3$ (PPVE-3) and combinations thereof.

13. The aqueous dispersion of any one of claims 8 to 12 wherein the modified PTFE has a transmission of greater than 60% when measured according to ASTM-D 1003, preferably greater than 70%, more preferably greater than 75%.

14. The aqueous dispersion of any one of claims 8 to 13 wherein the perfluorinated allyl ether content is from 50 to 5,000, preferably 100 to 3,000 ppm (based on the total weight of the polymer).

15. A coated substrate obtained from the dispersion of any one of claims 8 to 14.

16. An article comprising a coated substrate obtained with the dispersion of any one of claims 8 to 14.

17. Method of coating a substrate said method comprising applying the dispersion of any one of claims 1 to 14 to a substrate and removing the aqueous phase.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054263

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F214/26
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/130904 A1 (3M INNOVATIVE PROPERTIES CO [US]) 18 August 2016 (2016-08-18) example 3 page 5, paragraph 2 - paragraph 3 page 10, paragraph 2 - page 11, paragraph 2 claim 1	1-5,7
X	EP 3 103 836 A1 (3M INNOVATIVE PROPERTIES CO [US]) 14 December 2016 (2016-12-14) claims 1,3,6,8,11,13,15 page 4, paragraph 21	1,2,4, 6-17
X,P	EP 3 284 762 A1 (3M INNOVATIVE PROPERTIES CO [US]) 21 February 2018 (2018-02-21) claims 1-3,6,10 paragraph [0052] - paragraph [0054]	1-3,8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 August 2018	12/09/2018

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2018/054263

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