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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 January 2009 (29.01.2009)

PCT

(10) International Publication Number
WO 2009/013214 A1

(51) International Patent Classification:
C08F 2/18 (2006.01) *C08F 220/26* (2006.01)

(21) International Application Number:
PCT/EP2008/059367

(22) International Filing Date: 17 July 2008 (17.07.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
07425449.1 20 July 2007 (20.07.2007) EP

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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, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(54) Title: PROCESS FOR POLYMER DISPERSIONS

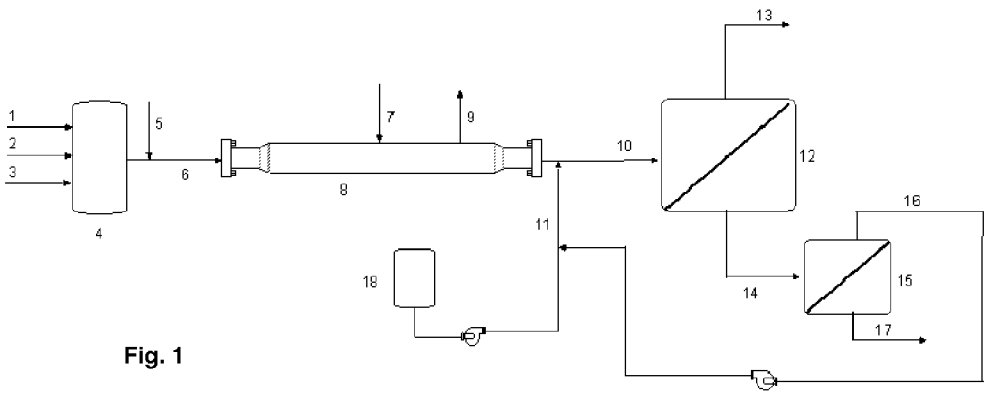

Fig. 1

(57) Abstract: Process for preparing aqueous polymer dispersions, comprising: a) aqueous-phase suspension polymerization of TFE, optionally in the presence of one or more ethylenically unsaturated comonomers, in the presence of a radical initiator, without the initial addition of fluorinated surfactants, without the addition of fluorinated surfactants during the polymerization, and without any in situ formation of fluorinated surfactants.

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PROCESS FOR POLYMER DISPERSIONS

The present invention relates to a process for obtaining aqueous dispersions of TFE-based perfluoropolymers, which are totally free of fluorinated surfactants.

More particularly, the TFE-based fluoropolymers of the dispersions of the present invention may be either thermoprocessable, for instance MFA (tetrafluoroethylene/perfluoromethyl vinyl ether copolymer) and PFA (tetrafluoroethylene/perfluoropropyl vinyl ether copolymer), or non-thermoprocessable, such as polytetrafluoroethylene (PTFE) homopolymer or modified.

According to the present invention, the term "fluoropolymer dispersions free of fluorinated surfactants" means that the dispersion does not contain fluorinated surfactants to levels of 30 ppb (parts per billion) or less, relative to the weight of the fluoropolymer.

It is well known that the term "thermoprocessable polymers", in particular thermoprocessable fluoropolymers, means polymers that are melt-processable by means of conventional extrusion devices (melt-extrusion and injection). Generally, the viscosity of the melt (ASTM D-1238-52T) for thermoprocessable fluoropolymers at the process temperature is not greater than 10^7 poises.

The term "non-thermoprocessable polymers", in particular non-thermoprocessable fluoropolymers, means fluoropolymers that are not melt-processable via conventional techniques. Generally, the viscosity of the melt, determined by means of the same ASTM standard, for non-thermoprocessable fluoropolymers at the process temperature is greater than 10^7 poises, preferably from 10^7 to 10^{13} poises and even more preferably from 10^9 to 10^{12} poises.

As is known, thermoprocessable and non-thermoprocessable TFE-based fluoropolymers are used in many applications, for instance coating, manufactured products, impregnated fabrics, etc.

Thermoprocessable and non-thermoprocessable fluoropolymers are mainly produced via two different polymerization processes: suspension polymerization and emulsion polymerization.

In suspension polymerization, the surfactant may be absent or used in small

amounts. The polymers obtained are in the form of particles of the order of millimetres in size.

In emulsion polymerization, on the other hand, the fluorinated monomers are dispersed in an aqueous phase in the presence of a surfactant capable of stabilizing the polymer latex that forms during the polymerization. The polymerization is performed until a conversion equal to 15-35% by weight of fluoropolymer is obtained, and is performed in the presence of gentle stirring so as to prevent coagulation of the polymer. The surfactants used must be non-telogenic so as to avoid chain transfer and thus obtain high molecular weight fluoropolymers therefore endowed with high mechanical properties. See patent US 2 559 752. From the latex obtained, dispersions with higher concentrations, even up to about 75% by weight, of polymer may be obtained by using concentration processes known in the art. See, for example, US 3 037 953 and US 4 369 266. For other applications, the latex is coagulated to obtain fine powders, of the order of about 500 microns in size in the case of PTFE homopolymer.

The surfactants used with improved stabilizing efficacy are fluorinated surfactants, for example perfluorooctanoic acid or salts thereof. The latter surfactant is the one most commonly used industrially and allows the production of dispersions of high molecular weight fluoropolymers. In general, the TFE-based fluoropolymer dispersions that may be obtained by emulsion polymerization in the presence of fluorinated anionic surfactants, for instance PFOA, have the following characteristics:

- mean particle diameter of from 10 nm to 400 nm,
- fluoropolymer concentration of from 15% to 35% by weight,
- amount of fluorinated anionic surfactants of from 800 ppm to 10,000 ppm and preferably from 1,200 ppm to 6,000 ppm, relative to the weight of the polymer.

It is known that PFOA is classified as potentially hazardous to the environment and to man since it appears to have a low rate of bioelimination from the human body. As a result, it is necessary to reduce the emissions of PFOA and homologues thereof into the environment. PFOA can contaminate the environment by means of washing liquors and also during the phases of drying and/or sintering

of the fluoropolymers, since it may become dispersed into the atmosphere. In January 2006, the Environmental Protection Agency (EPA) invited fluoropolymer and telomer producers to participate in the 2010/1015 Stewardship Program concerning PFOA and homologues thereof. The producers were requested to undertake to reduce by 95% by 2010 the PFOA in emissions and in products and to work with a view towards its total elimination by 2015.

Processes for obtaining aqueous dispersions of fluoropolymers with a reduced content of fluorinated surfactants are known in the art. See, for example, CA 2 354 138 and WO 2006/086796.

Aqueous emulsion polymerization of fluorinated monomers to produce fluoropolymers in which fluorinated surfactants of PFOA type are neither used nor added during the polymerization, are also known. However, fluorinated surfactants are formed during the polymerization. See, for example, patent application US 2007/0 072 985, which describes a process for preparing fluoropolymers that comprises the aqueous emulsion polymerization of one or more fluorinated monomers, optionally in the presence of one or more fluorinated comonomers, the polymerization being initiated in the absence of fluorinated surfactants and no fluorinated surfactant is added during the polymerization. The fluoropolymer is recovered from the dispersion, thus obtaining the fluoropolymer and effluent water, which is placed in contact with anion-exchange resin. Instead of performing the last two steps, the aqueous fluoropolymer dispersions obtained may be placed in contact with anion-exchange resin and subsequently separated from the resin. In the said patent application, it is stated that, during the treatment with the anion-exchange resin, both of the effluent water and of the aqueous dispersion for the elimination of the fluorinated anionic surfactants that are formed during the polymerization, no coagulation of the system takes place. Therefore, during contact with the anion-exchange resin, it is not necessary to add any nonionic surfactant, as is indicated in the prior art, for example in CA 2 354 138. In the description, in paragraph [0039], it is stated that in the dispersions obtained via the process described in the said patent application, low molecular weight fluorinated surfactants with anionic end groups are present. Thus, even though fluorinated

surfactants are not added at the start or during the polymerization, they are formed during the polymerization. Due to the fact that the dispersion obtained contains fluorinated surfactants, it is essential to treat the dispersions obtained with anion-exchange resin in order to reduce their content thereof to low levels. This is likewise the case for the effluent water. It should be noted that the examples report the presence of a very high number of fluorinated surfactants. It should be noted that many of these surfactants need to be studied for their toxicity and their potential bioaccumulation in live organisms. Thus, the process described in the said patent application has the drawback of leading to the uncontrolled formation of fluorinated surfactants. In addition, even after treatment with anion-exchange resin, the amount that remains is still relatively high. For other patent applications concerning polymerization processes for obtaining fluoropolymers in which fluorinated surfactant is not used at the start or added during the polymerization, see, for example, RU 2 158 274. However, in these patents, it is stated that fluorinated surfactant is formed during the polymerization. See WO 02/088 206, WO 02/088 207, WO 97/17381 and WO 02/088 203.

There was thus seen to be a need for a process for preparing aqueous dispersions of TFE-based perfluoropolymers, which are thermoprocessable and non-thermoprocessable, such that the polymers obtained may afford the following combination of properties:

- absence of fluorinated surfactants and preferably of fluorinated anionic surfactants,
- high molecular weight of the polymers of the dispersions.

The term "absence of fluorinated surfactants" means that their residual amount is less than 30 ppb (parts per billion).

A process for preparing fluoropolymers that solves the indicated technical problem has been found by the Applicant.

One subject of the present invention is a process for preparing dispersions of TFE-based perfluoropolymers with a high melt viscosity, which are thermoprocessable and non-thermoprocessable, comprising:

a) aqueous-phase suspension polymerization of TFE, optionally in the presence of one or more ethylenically unsaturated fluorinated comonomers, in the presence of a radical initiator, without the initial addition of fluorinated surfactants, without the addition of fluorinated surfactants during the polymerization, and without any *in situ* formation of fluorinated surfactants.

Preferably, in a), the polymerization is performed by working at a temperature generally of between about 20°C and about 120°C, preferably between 30°C and 100°C and more preferably between 40°C and 90°C. Non-fluorinated water-soluble initiators are used. Mention may be made of the salts of inorganic peracids, for example the following: persulfates, for instance ammonium persulfate (APS), and permanganates. A redox couple, for instance APS and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Mohr's salt) may also be used as initiator. In addition, mixtures of salts of inorganic peracids and C_2-C_4, preferably C_4, dicarboxylic acids may also be used: for example, mention may be made of the mixture of ammonium persulfate with succinic acid. Peroxides may also be used, for instance disuccinic acid peroxide (DSAP).

As stated, in step a), fluorinated surfactants are not used at the start of the polymerization, nor are they added during the polymerization, and nor is there any *in situ* formation of fluorinated surfactants. In step a), the pressure used is generally between 5 and 30 bar (0.5-3 MPa).

Preferably, in step a), no chain-transfer agent is used.

According to one preferred embodiment of the invention, the polymerization in step a) is stopped when the concentration of the polymer in the dispersion is such that it does not lead to coagulation of the polymer and/or the coagulate is present in an amount of less than 1% and preferably less than 0.1% relative to the weight of the polymer.

Stopping of the polymerization according to the methods described above constitutes the subsequent step b) of the process according to the preferred embodiment of the present invention.

Preferably, in step b), the concentration of the fluoropolymer, expressed as a weight percentage relative to the total weight of the dispersion, is between 0.2%

and about 15%, preferably between 1% and less than 10% and even more preferably 2-9.5%.

As stated, step b) is preferably stopped before coagulation of the system takes place. A person skilled in the art is readily capable of determining with little testing the extent of conversion of the system under these conditions. What was surprising and unexpected with the process of the invention is that, by stopping the polymerization before coagulation, or when the coagulate is present is small amounts, generally less than 1%, the sizes of the particles obtained are in the range 10-400 nm. Furthermore, the dispersion is stable despite the fact that no fluorinated surfactant is present therein. The dispersion is characterized as being shear-stable for the time sufficient to perform thereon stabilization by means of adding non-fluorinated surfactants. The shear stability of the dispersion before adding the surfactant should be greater than 10 seconds and preferably greater than 20 seconds, via the test reported later.

The dispersions thus obtained contain fluoropolymer particles with a mean diameter of between 10 nm and 400 nm and preferably between 150 and 300 nm. Gas-phase or liquid-phase (HPLC) chromatographic analysis did not reveal any presence of fluorinated surfactant. Thus, the polymerization of the dispersion of the invention was performed in the absence of fluorinated surfactants, and furthermore no fluorinated surfactants were formed during the polymerization. Thus, the polymerization of the present invention (step a)) is a suspension polymerization rather than an emulsion polymerization.

Preferably, step c): addition of a non-fluorinated surfactant, is then performed on the dispersion thus obtained.

Preferably, in step c), the amount of non-fluorinated surfactant (weight % relative to the polymer) is between 0.5% and 20%, more preferably between 1.0% and 15% and even more preferably between 2% and 10%.

In this step, the non-fluorinated surfactants are nonionic, anionic and cationic surfactants; nonionic surfactants are preferably used.

Nonionic surfactants are known in the art. Mention may be made, for example, of the book "Nonionic Surfactants" Ed. M.J. Schick, Marcel Dekker 1967,

pp. 76-85 and 103-141. Among the nonionic surfactants that are particularly preferred are polyethoxylated alcohols optionally containing one or more propylene oxide units. The following surfactants are even more preferred:

Tergitol®TMN100x (Dow) having the formula:
sec-$C_{12}H_{25}$-$(OCH_2CH_2)_{10.1}OH$;

Antarox®863 (Rhodia) having the formula:
iso-$C_{13}H_{27}$-$(OCH_2CH_2CH_2)$-$(OCH_2CH_2)_{10}$-OH;

Rhodasurf®870 (Rhodia) having the formula:
iso-$C_{13}H_{27}$-$(OCH_2CH_2)_{10}$-OH;

Genapol®X080 (Clariant) having the formula:
iso-$C_{13}H_{27}$-$(OCH_2CH_2)_8$-OH;

Genapol®X090 (Clariant) having the formula:
iso-$C_{13}H_{27}$-$(OCH_2CH_2)_9$-OH.

The non-fluorinated anionic surfactants are linear or branched, bearing one or more, preferably one, anionic group. They generally have an equivalent weight, defined as the molecular weight/number of anionic groups present in the surfactant, of greater than 350 and preferably greater than 600. Generally, the equivalent weight of the anionic surfactants that may be used in the process of the present invention is less than 5,000, preferably less than 3,000 and even more preferably less than 1,500. The molecular weight of the anionic surfactants is greater than 350, preferably greater than 400 and even more preferably greater than 600. See patent application EP 1 676 868 in the name of the Applicant.

The following anionic surfactants are preferred:

- $C_{10}H_{21}OOC$-CH_2-$CH(SO_3^-)$-$COOC_{10}H_{21}$
  diisodecyl sulfosuccinate, sodium salt, known under the brand name Emulsogen® SB10 (Clariant);
- $C_{13}H_{27}OOC$-CH_2-$CH(SO_3Na)$-$COOC_{13}H_{27}$
  diisotridecyl sulfosuccinate, sodium salt, known under the brand name Polirol® TR/LNA (Cesalpinia Chemicals).

Mixtures of the non-fluorinated surfactants indicated above may be used in

step c).

After step c), a further optional step represented by step d): concentration of the dispersion, may be performed.

In step d), the concentration of the dispersion, expressed as weight of fluoropolymer/kg of solution, is not greater than 70% and is preferably between 55% and 65%. The concentration method also known as clouding, as described in US 3 037 953, US 3 301 807 and EP 1 526 142 in the name of the Applicant, may be used, for example. Another concentration process, which is also the preferred process, is that of ultrafiltration, described in US 4 369 266.

Optionally, the non-fluorinated surfactant that is used may be recovered and reused.

In one preferred embodiment, the process of the present invention is performed continuously using a plant in which is used a continuous reactor of the plug flow type (plug flow reactor, PFR): see Fig. 1 in which the numbers correspond to the following parts of the plant:

(1) water feed,
(2) tetrafluoroethylene monomer feed,
(3) comonomer feed,
(4) mixing reactor with stirrer,
(5) initiator or initiator mixture feed,
(6) PFR feed,
(7) optional comonomer feed into the reactor (8),
(8) continuous plug flow reactor (PFR),
(9) reactor vent pipe,
(10) feed from the ultrafiltration (UF) apparatus,
(11) feed of the aqueous solution of non-fluorinated surfactant,
(12) ultrafiltration UF apparatus,
(13) concentration polymer aqueous dispersion outlet,
(14) UF aqueous permeate outlet,
(15) reverse osmosis apparatus,
(16) recovery of the concentrated aqueous solution of the non-fluorinated

surfactant with recycling into (11),

(17) permeate outlet from the reverse osmosis apparatus.

The process represented in Fig. 1 is performed in the following manner. The water fed in at (1), the TFE fed in at (2) and the optional comonomers fed in at (3) are transferred into a stirred mixing reactor (4). The aqueous phase exiting from (4) is mixed with the initiator or the mixture of initiators fed in at (5) and constitutes the mixture of reagents fed at (6) into the PFR (8). During the polymerization, by means of (7), it is optionally possible to introduce other comonomers into the PFR (8). Venting of the PFR takes place via the pipe (9), which is fitted with a valve, not shown in Fig. 1. An aqueous solution of a non-fluorinated surfactant is added at (11) to the polymer dispersion exiting from (8). The aqueous dispersion containing the non-fluorinated surfactant is fed at (10) into the ultrafiltration apparatus (12), which has two outlets, respectively (13), from which is collected the concentrated polymer dispersion, and (14), from which is collected the permeate containing the non-fluorinated surfactant, which is conveyed to the reverse osmosis apparatus (15) for recovery of the non-fluorinated surfactant, a concentrated solution of recovered non-fluorinated surfactant being recovered at (16); the concentrated solution is mixed with a solution of fresh non-fluorinated surfactant originating from the tank (18) before being fed via (11) with the polymer dispersion leaving the reactor (8).

The throughput of the monomer or monomer mixture in the PFR (8) ranges from about 0.5 to about 600 kg/hour and preferably from about 5 to about 300 kg/hour. The residence times in the PFR (8) range from about 1 minute to about 30 minutes, preferably between about 3 and about 20 minutes and even more preferably between about 5 and about 10 minutes. It is possible to arrange several ultrafiltration units in series.

The thermoprocessable and non-thermoprocessable TFE-based perfluoropolymers that may be obtained via the process of the present invention are, for example, tetrafluoroethylene (TFE) homopolymers and copolymers of TFE with monomers bearing at least one unsaturation of ethylenic type. The amount of comonomer is preferably less than 15% by weight, more preferably less than 10%

and even more preferably less than 1% to obtain non-thermoprocessable copolymers ("modified PTFE").

Among the fluorinated comonomers that may be mentioned are:

- C_3-C_8 perfluoroolefins, for instance hexafluoropropene (HFP);
- C_2-C_8 hydrogenated fluoroolefins, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, perfluoroalkylethylene CH_2=CH-R_{f0}, in which R_{f0} is a C_1-C_6 perfluoroalkyl;
- C_2-C_6 chloro- and/or bromo- and/or iodo-fluoroolefins, such as chlorotrifluoroethylene (CTFE);
- (per)fluoroalkyl vinyl ethers (PAVE) CF_2=CFOR_{f0}, in which R_{f0} is a C_1-C_6 (per)fluoroalkyl, for example CF_3, C_2F_5 or C_3F_7;
- (per)fluorooxyalkyl vinyl ethers CF_2=CFOX_0, in which X_0 is a C_1-C_{12} alkyl or a C_1-C_{12} oxyalkyl, or a C_1-C_{12} (per)fluorooxyalkyl containing one or more ether groups, for example perfluoro-2-propoxypropyl;
- fluorodioxoles, preferably perfluorodioxoles.

As examples of TFE-based thermoprocessable fluoropolymers, mention may be made of PFA and MFA.

Preferred fluoropolymers include PTFE homopolymer and modified PTFE.

As stated, the TFE-based fluoropolymer dispersions that may be obtained via the process of the invention are entirely free of fluorinated surfactants, in particular PFOA, since no fluorinated surfactant is used for the polymerization for their preparation in the process of the invention. It should also be noted that during the polymerization of the invention, no fluorinated or non-fluorinated surfactants are used. The reason for this is that it is well known that the latter surfactants would lead to a decrease in the molecular weight and thus to a reduction in the mechanical properties of the polymer. It is well known that hydrogenated surfactants act as chain transfer agents in the polymerization of TFE. Thus, with the analytical methods currently available, in the dispersion that may be obtained via the dispersion process, no presence of fluorinated surfactant can be detected in the effluent water at levels of 30 ppb (parts per billion) or less, relative to the polymer. In any case, the fluorinated surfactants cannot be detected by more

sensitive methods either.

This result is surprising and unexpected since, by using the process of the invention, there is no *in situ* formation of fluorinated surfactants that stabilize the fluorinated polymer dispersions. In point of fact, surfactants are relatively short molecules, containing a maximum of about 20 carbon atoms, preferably up to 14, which bear a terminal functional group, for example -COOH or $-COO^-$, and have the capacity to reduce the surface tension of water. In the process of the invention, it was found, surprisingly and unexpectedly, that by using the polymerization conditions indicated above, a polymer with very high molecular weights is obtained, as evidenced by the melt viscosity, which, for non-thermoprocessable TFE polymers or copolymers thereof, is greater than 10^7 poises, and for thermo-processable TFE polymers or copolymers thereof, is greater than 10^2 poises (ASTM D-1238-52T). This fact is surprising and unexpected since, in the processes of the prior art using radiation-mediated polymerization of TFE, fluorinated surfactants with a number of carbon atoms of less than 20, which stabilize the dispersion, are always present. For these prior art processes, the dispersions must be subjected to purification processes to reduce the fluorinated surfactants.

Thus, the fluoropolymer dispersions that may be obtained in steps a)-c) of the process of the present invention are characterized by the following combination of properties:

- absence of fluorinated surfactants, in particular of PFOA, which means that the said surfactants cannot be detected by analysis with a sensitivity of 30 ppb using the method described below,
- shear stability, determined according to the test described below, of greater than 10 seconds and preferably greater than 20 seconds,
- mean particle diameter of between 10 nm and 400 nm and preferably between 150 and 300 nm,
- amount of fluoropolymer, expressed as a weight percentage relative to the total weight of the dispersion, of between 0.2% and about 15% and preferably between 1% and less than 10%,

- presence of one or more non-fluorinated surfactants, which are preferably nonionic, in an amount, expressed as a weight percentage relative to the polymer, of between about 0.5% and 20%, preferably between 1% and 15% and more preferably between 2% and less than 10%.

When the optional step d) is also performed, dispersions having the same characteristics as those described above are obtained, except that the amount of fluoropolymer, as stated, may also reach high concentrations, of not greater than 70%, preferably between 55% and 65%.

When the dispersions of the invention contain as fluoropolymers TFE homopolymers or TFE copolymers modified with one or more comonomers up to 1% by weight, these fluoropolymers have a specific weight SSG (ASTM D 4895) of between 2.00 and 2.29 g/cm^3 and preferably from 2.12 to 2.25 g/cm^3.

The analysis to determine in the dispersions of the present invention the absence of PFOA at ppb levels is performed using HPLC apparatus equipped with an Alltima C18 3 mm × 50 mm × 4.6 mm column, with a mass detector.

2 grams of acetone are added to 1 gram of latex, the mixture is stirred and the supernatant organic phase is separated out. The resultant phase is filtered, 3 g of water are added, and 100 μl of the final solution are injected into the liquid chromatograph. The sensitive limit of the method is 30 ppb.

The test for determining the shear stability of the polymerization latex is as follows. A volume of latex equal to 150 ml is introduced into a container equipped with two breakwaters and is subjected to mechanical stirring at a speed of 843 rpm. The stability of the dispersion is evaluated by determining the time interval, in seconds, between the start of stirring and the moment at which it is observed that the dispersion begins to gel, i.e. assumes the consistency of a gel.

The thermoprocessable fluoropolymers of the invention generally have a melt viscosity (ASTM D-1238-52T) at the process temperature of greater than 10^2 poises and less than 10^7 poises.

The non-thermoprocessable fluoropolymers generally have a melt viscosity (ASTM D-1238-52T) of greater than 10^7 poises, preferably from 10^7 to 10^{13} poises and even more preferably from 10^9 to 10^{12} poises.

The dispersions of TFE-based fluoropolymers of the invention, preferably after the concentration step d), may be used in the typically applications of fluoropolymers, for example for producing coatings.

The methods for obtaining coatings are known in the art. Mention may be made of the following: spin coating, casting, deep coating.

With the dispersions of the present invention, it is possible to obtain coatings on the surfaces of manufactured products. The surfaces of the said manufactured products may be constituted of organic or inorganic polymers, glass, ceramic, metals, etc.

In addition, it is possible to impregnate fabrics, for example glass or fibre fabrics, for example carbon fabrics, to prepare cast films, characterized by good application properties, in particular absence of colour, fractures (cracks) and microgels. In practice, these coatings, impregnated glass fabrics and cast films have properties substantially identical to those obtained with fluoropolymer dispersions containing PFOA.

The examples that follow illustrate the present invention in a non-limiting manner.

EXAMPLES

Analytical methods

Determination of the residual amount of coagulate

500 g of dispersion are filtered through a nylon gauze of known weight with a mesh size equal to 50 μm. After filtration, 500 ml of water are passed through the gauze to remove the excess dispersion. The gauze with the residue, if any, is dried in an oven at 105°C for one hour and then weighed. The amount of coagulate is determined by difference relative to the initial weight of the gauze. By dividing the difference by the amount of polymer contained in 500 g of dispersion and multiplying by 100, the percentage of coagulate in the polymer is obtained.

The sensitivity limit of the method is 0.005% by weight relative to the polymer.

Determination of the mean particle diameter

The mean particle diameter is determined on the basis of the method according to ISO standard 13321. The diameter is measured using an instrument based on laser light scattering, in particular on photon correlation spectroscopy, equipped with a model 2030 At Brookhaven correlator and an argon laser light source with a wavelength of 514.5 nm from the company Spectra-Physics. The samples of latex to be subjected to measurement are diluted with water filtered at 0.2 μm through a Millipore filter. The scattering measurement is performed at room temperature at an angle of 90°. The latex particle diameter is obtained via the cumulative method.

Determination of the fluoropolymer content of the latex

The polymer content of the latex removed from the reactor and of the supernatant obtained by ultracentrifugation is determined after drying at 150°C for 1 hour. About 20 grams of latex are weighed in a glass beaker and placed in a drying oven for 1 hour at 150°C. The dry content of the latex is obtained by means of the formula:

% dry matter = (weight after drying) × 100/(initial latex weight).

Determination of the PFOA content

The PFOA content was determined with HPLC apparatus comprising the following parts:

- a Thermo Finnigan model AS3000 autosampler with an injection volume of 100 μl;
- an Alltima C18 3 mm × 50 mm × 4.6 mm column;
- a Spectra Physics model P 4000 pump, flow rate of 0.4 ml/minute;
- a Thermo Finnigan MS/MS SYSTEM LCQ DECA mass detector with an ESI LC interface.

The sample for analysis is prepared by adding 1 gram of latex to 2 grams of acetone, with stirring. The supernatant organic phase (acetone) is separated out and filtered to obtain about 1 g of filtrate. 3 grams of water are added, the mixture is stirred briefly to homogenize and 0.1 ml of the final solution is injected into the liquid chromatograph.

The analysis time is about 12 minutes. The sensitivity limit of the method is 30 ppb.

Shear stability of the polymerization latex

A volume of 150 ml of latex is introduced into an open container equipped with two breakwaters and subject to mechanical stirring with a twin-impeller stirrer at a speed of 843 rpm. The stability of the dispersion is expressed by means of the time interval, in seconds, between the start of stirring and the moment at which gelling of the dispersion begins.

Determination of the absolute specific weight (SSG)

The absolute specific weight is determined according to ASTM standard D 4895-04.

Determination of the molecular weight

The molecular weight is calculated from the SSG value by applying the following formula, described by R.C. Doban et al. in the document "Formula from molecular weight of Polytetrafluoroethylene", American Chemical Society Meeting, Atlantic City, N.J., September 1956:

$$MWn = 0.597[\log \frac{0.157}{2.306 - SSG}]^{-1} \times 10^6.$$

This formula is also given in column 3 of US 6 956 078.

FTIR determination

The evaluation of the COO^- and COF end groups was performed as described in the article by M. Pianca et al. "End groups in fluoropolymers", J. Fluorine Chem. 95 (1999), 71-84. The IR spectrum was recorded using a Nicolex 20 SX or a Nicolet 850 FT-IR instrument. The collected parameters have a resolution of 2 cm^{-1} and a scansion of 500. The spectra obtained were developed by means of the Lab Calc software (Galactic Industries). The test samples were analysed in the form of pellets, obtained by cold-pressing. The COO^- group is detected at a frequency of 1670 cm^{-1}, the COF group at a frequency of 1884 cm^{-1}, the extinction coefficient being 215/mol cm. The sensitivity limit of the method is 0.05 mmol/kg of polymer for each end group.

Determination of the content of fluorinated surfactants by GC

An aliquot of the dispersion is coagulated so as to obtain about 0.5 g of dry powder. The coagulated polymer is immersed in ethanol and then brought to basic pH with NH_4OH solution. It is again dried under a stream of nitrogen. 2 ml of acidic methanol are added to the dried powder. The esterification is conducted at 70°C for 16 hours in a hermetically sealed test tube. At this point, 0.5 ml of Delifrene® A113 and 4 ml of water are added to the mixture.

The mixture is stirred and left to stand. The 2 phases are separated, and 1 μl of the lower fluorinated phase containing the ester of the surfactant is taken. The solution is injected into a gas chromatograph with a capillary column (capillary gas chromatographic system equipped with a split/splitless introduction set at 200°C - capillary column of CP - SIL 8CB 25 cm × 0.32 mm × 1.3 μm type - carrier, helium = 50 KPa - split flow 26 ml/min - makeup carrier: nitrogen 40 KPa - volume introduced 1 μl - temperature profile 40°C × 4 minutes, 40°C/minute up to 60°C, 8°C/minute up to 84°C, 40°C/minute up to 220°C × 10 minutes - FID detector set at 250°C (air/hydrogen ratio = 100/90 KPa) - electrometer: range 0, AT 0).

The peak area is related to the amount of surfactant present by means of the calibration curve.

The sensitivity limit of the determination method in the case of PFOA is 10 ppm.

EXAMPLE 1

Batch polymerization of TFE and subsequent concentration of the polymer obtained

32 litres of thoroughly degassed demineralized water are introduced into a 50 litre autoclave equipped with a mechanical stirrer and placed beforehand under vacuum. 320 grams of paraffin with a softening point of between 52°C and 54°C were also placed beforehand in the reactor. 270 ml of a solution containing 100 mg of $(NH_4)_2S_2O_8$ (APS) and 2 g of disuccinic acid peroxide (DSAP) are introduced into the autoclave. The autoclave is stirred mechanically at 256 rpm and is pressurized with TFE up to a pressure of 20 bar at a temperature of 70°C.

When the pressure in the reactor falls by 0.5 bar, the introduction of TFE is

begun by means of a compressor so as to maintain a constant pressure of 20 bar inside the reactor. Simultaneously, the internal temperature of the reactor is raised to 80°C. The introduction of TFE is stopped when 1% by weight of PTFE is reached in the latex produced, which is obtained after 10 minutes, during which time 500 grams of TFE are reacted; the reactor is then depressurized, emptied and cooled.

The primary particle diameter of the polymer measured by laser light scattering (LLS) is equal to 260 nm. The shear stability is greater than 10 seconds. This stability is sufficient to perform the subsequent concentration step.

The latex removed from the reactor has a coagulant content of less than 0.01% by weight relative to the polymer. The latex is concentrated via the clouding concentration method as described below. The latex is then filtered through a 200 μm filter. The latex is placed under stirring and heating is commenced. 5% by weight of nonionic surfactant (Triton®) and 0.05% of ammonium sulfate are added to the dispersion (2,200 g of latex). At 65°C, separation of the dispersion into two phases takes place. The mixture is maintained at this temperature for 3 hours 30 minutes with continued stirring, and is left to cool for 12 hours without stirring. The concentrated polymer phase, which corresponds to the lower phase, is removed and filtered through a filter with a mesh size of 100 μm. The titre of the concentrated latex is 11.6% PTFE, and the pH is 3.17. This operation is repeated to obtain a dispersion containing 65% by weight of fluoropolymer.

The absolute specific weight is 2.159 g/cm^3. The calculated molecular weight MWn is 2.09×10^7.

An aliquot of the dispersion obtained in the polymerization is dried at 140°C for 24 hours. The polymer thus obtained is analysed by FTIR to determine the COOH and/or COF end groups. The analysis does not show any peaks corresponding to these groups.

EXAMPLE 2

Batch polymerization of TFE

580 litres of thoroughly degassed demineralized water are introduced into a 1,100 litre autoclave equipped with a mechanical stirrer and placed beforehand

under vacuum. 2,900 ml containing 3.5 g of $(NH_4)_2S_2O_8$ (APS) and 2,000 ml containing 1.2 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Mohr's salt) are then added to the autoclave. The autoclave is pressurized with TFE up to a pressure of 16 bar and is stirred mechanically at 441 rpm during the reaction, which is initially performed at a temperature of 20°C.

When the pressure in the reactor falls by 0.5 bar, the introduction of TFE is begun at a temperature of 22°C so as to maintain a constant pressure of 16 bar inside the reactor. The introduction of TFE is stopped after 6 minutes, when an amount of PTFE equal to 0.3% by weight is formed in the latex. During this interval, 7 kg of TFE are reacted; the reactor is then depressurized, emptied and cooled. The primary particle diameter of the polymer measured is 292 nm, and the absolute specific weight is 2.156 g/cm^3. The calculated molecular weight MWn is 3.01×10^7. The PFOA content is below the analytical limit, i.e. less than 30 ppb. The shear stability is greater than 20 seconds.

The dispersion is concentrated to 65% by weight of fluoropolymer via ultrafiltration using six Koch membranes in series, each with a surface area of 0.1 m^2. The average yield under the conditions used in the example was good and was 200 litres/(h m^2).

An aliquot of the dispersion obtained in the polymerization is dried at 140°C for 24 hours. The polymer thus obtained is analysed by FTIR to determine the COOH and/or COF end groups. The analysis does not reveal any peaks corresponding to these groups.

CLAIMS

1. Process for preparing aqueous dispersions of TFE-based perfluoropolymers with a high melt viscosity, which are thermoprocessable and non-thermoprocessable, comprising:
   a) aqueous-phase suspension polymerization of TFE, optionally in the presence of one or more ethylenically unsaturated comonomers, in the presence of a radical initiator, without the initial addition of fluorinated surfactants, without the addition of fluorinated surfactants during the polymerization, and without any in situ formation of fluorinated surfactants.
2. Process according to Claim 1, in which, in step a), the polymerization is performed by working at a temperature of between 20°C and 120°C.
3. Process according to Claims 1 and 2, in which, in step a), water-soluble initiators are used.
4. Process according to Claims 1 to 3, in which, after step a), the following step b) is performed:
   b) stopping the polymerization when the concentration of polymer in the dispersion is such that it does not lead to coagulation of the polymer and/or the coagulate is present in an amount of less than 1% and preferably less than 0.1% relative to the weight of the polymer.
5. Process according to Claims 1 to 4, in which, in step b), the concentration of the fluoropolymer, expressed as a weight percentage relative to the total weight of the dispersion, is between 0.2% and 15%.
6. Process according to Claims 1 to 5, comprising the subsequent step c):
   c) adding a non-fluorinated surfactant to the dispersion obtained.
7. Process according to Claim 6, in which the amount of non-fluorinated surfactant, expressed as a weight percentage relative to the polymer, is between 0.5% and 20%.
8. Process according to Claims 1 to 7, in which the non-fluorinated surfactants of step c) are nonionic or anionic surfactants.

9. Process according to Claim 8, in which the non-fluorinated surfactants are nonionic.

10. Process according to Claims 1 to 9, in which, after step c), step d) is optionally performed:

d) concentration of the dispersion.

11. Process according to Claims 1 to 10, in which, in step d), ultrafiltration is used.

12. Process according to Claims 1 to 11, which is performed continuously.

13. Process according to Claim 12, performed according to Fig. 1:

- feeding at (1) water, at (2) TFE and at (3) optional comonomers into a mixer (4),
- mixing the aqueous phase leaving (4) with the initiator or the mixture of initiators fed in at (5), which forms the mixture of reagents fed at (6) into the continuous plug flow reactor (8);
- optionally feeding other comonomers into the reactor (8) via (7) during the polymerization;
- degassing the reactor (8) via (9);
- feeding via (11) an aqueous solution of a non-fluorinated surfactant to the polymer dispersion leaving the reactor (8),
- feeding at (10) the aqueous dispersion containing the non-fluorinated surfactant into the ultrafiltration apparatus (12),
- collecting at the outlet (13) of the apparatus (12) the concentrated polymer dispersion and at the outlet (14) the permeate,
- feeding the permeate into the reverse osmosis apparatus (15) and recovering at (16) the concentrated aqueous solution of non-fluorinated surfactant recovered,
- mixing the concentrated aqueous solution of non-fluorinated surfactant recovered with an aqueous solution of non-fluorinated surfactant fed from the tank (18).

14. TFE thermoprocessable and non-thermoprocessable perfluoropolymer dispersions that may be obtained according to Claims 1 to 13.

15. Use of the dispersions according to Claim 14 for coating, for impregnating fabrics and fibres or for casting films.

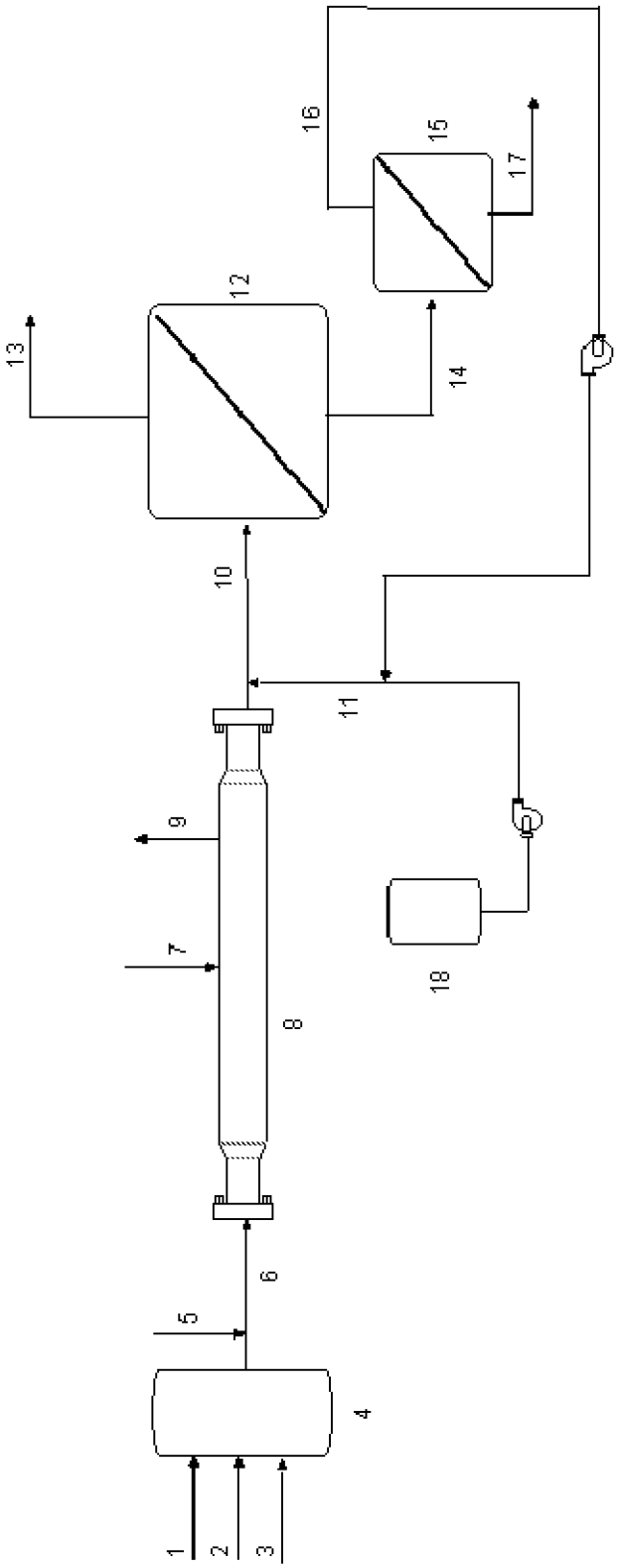

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/059367

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/18 C08F220/26

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

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/072985 A1 (HINTZER KLAUS [DE] ET AL) 29 March 2007 (2007-03-29) examples paragraph [0048] table 1	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 December 2008	18/12/2008

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/059367

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007072985 A1	29-03-2007	CN 101273069 A	24-09-2008
		EP 1928922 A1	11-06-2008
		GB 2430437 A	28-03-2007
		KR 20080046684 A	27-05-2008
		WO 2007038561 A1	05-04-2007