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(54) Title: AQUEOUS DISPERSIONS OF FLUOROPOLYMERS

(54) Bezeichnung: WÄSSRIGE DISPERSIONEN VON FLUORPOLYMEREN

(57) Abstract

Emulsifiers containing fluorine can be separated out of fluoropolymer solutions by adding a non–ionic emulsifier to the dispersion, by separating the emulsifier which contains fluorine by bringing the same into contact with an anion exchanger, and by separating the dispersion from the anion exchanger. The obtained dispersions can be concentrated and can be used for coating applications.

(57) Zusammenfassung

Fluorhaltige Emulgatoren können aus Fluorpolymerdispersionen abgetrennt werden, indem man die Dispersion mit einem nichtionischen Emulgator versetzt, den fluorhaltigen Emulgator durch Inberührungbringen mit einem Anionenaustauscher abtrennt und die Dispersion vom Anionenaustauscher abtrennt. Die erhaltenen Dispersionen können aufkonzentriert und für Beschichtungsanwendungen verwendet werden.

Description

Aqueous dispersions of fluoropolymers

The invention is concerned with aqueous dispersions of fluoropolymers being essentially free of fluorine-containing emulsifiers, a process for preparing such dispersions and their use. "Essentially free" means a content of less than 100 ppm, preferably less than 50 ppm, especially less than 25 ppm and in particular less than 5 ppm.

Polyfluoroethylene dispersions find wide application in the coating industry due to the unique performance of the coatings in respect of e.g. release properties, good weathering resistance, and flame retardancy. They are mainly used for coating kitchenware, chemical apparatus and glass fabrics. In many such applications, the dispersions are applied at relatively high solids contents, e.g., up to 70% by weight. These concentrated dispersions are mainly stabilized by nonionic emulsifiers such as alkylarylpolyethoxy alcohols and alkylpolyethoxy alcohols, using colloid-chemistry methods.

There are in principle two different polymerization processes for preparing fluoropolymers, namely suspension polymerization leading to polymer granules and, on the other hand the process known as emulsion polymerization, leading to an aqueous colloidal dispersion. This invention concerns emulsion polymerization, the resultant dispersions and their use.

The manufacturing of such dispersions involves in principle the two processing steps polymerization and concentration.

Polymers which are obtainable by aqueous emulsion polymerization are firstly homopolymers not processible from the melt, for example PTFE, secondly "modified" polymers, for example a polymer with more than about 99 mol% of tetrafluoroethylene (TFE) and an amount of comonomer(s) which is so low that the product retains its "not processible from the melt" character and thirdly low-molecular weight "micropowder" dispersions which are processible from the melt, and fourthly copolymers, for example fluorinated thermoplastics or fluoroelastomers. The fluorinated thermoplastics include copolymers which are composed mainly of TFE and the amount needed of one or more comonomers to make the product processible from the melt, for example from 1 to 50 mol%, preferably from 1 to 10 mol%. Customary fluoromonomers, besides TFE, are vinylidene fluoride (VDF), other fluorinated olefins, such as chlorotrifluoroethylene (CTFE), in particular perfluorinated olefins having from 2 to 8 carbon atoms, such as hexafluoropropene (HFP), fluorinated ethers, in particular perfluorinated vinyl alkyl ethers whose alkyl moieties have from 1 to 6 carbon atoms, for example perfluoro (n-propyl vinyl) ether (PPVE). Other comonomers which may be used are nonfluorinated olefins, such as ethylene or propylene. The resultant dispersions of polymers which are processible from the melt or not processible from the melt generally have a solids content of from 15 to 30% by weight. To achieve the abovementioned high solids content for application as a coating, and advantageously also for storage and transport, the solids content has to be increased by raising the concentration. Examples of methods used for this are raising the concentration thermally as in US-A-3 316 201, decanting (US-A-3 037 953) and ultrafiltration (US-A-4 369 266).

The known emulsion polymerization mostly takes place within a pressure range from 5 to 30 bar and within a temperature range from 5 to 100°C as described in

EP-B-30 663, for example. The polymerization process for preparing PTFE dispersions substantially corresponds to the known process for preparing fine resin powders, known as paste product (US-A-3 142 665). The polymerization process for preparing copolymers, such as dispersions of fluorinated thermoplastics, corresponds to the process for preparing these materials in the form of melt pellets.

In all of these emulsion polymerizations an emulsifier is required which does not disrupt the polymerization by chain transfer. These emulsifiers are termed nontelogenic emulsifiers (US-A-2 559 752). Use is mainly made of perfluorooctanoic acid (PFOA for example n-PFOA, CAS No. 335-67-1) in the form of ammonium and/or alkali metal salts. However, the abbreviation PFOA when used in the text below is not intended to exclude other fluorinated emulsifiers. The content of this emulsifier is generally within the range from 0.02 to 1% by weight, based on the polymer.

Occasionally, other fluorinated emulsifiers are used. For example, EP-A-822 175 describes the use of salts of CH_2-containing fluorocarboxylic acids for the emulsion polymerization of TFE. WO-A-97/08214 describes the use of 2-perfluorohexylethanesulfonic acid or salts thereof for TFE polymerization.

US-A-2 559 752 describes other fluorinated emulsifiers, but these have not been widely used since their volatility is low. These chemicals can cause discoloration of the final products at high processing temperatures.

One of the greatest advantages of PFOA is its high volatility. PFOA is a very effective emulsifier and is practically indispensible due to its inertness in the polymerization reaction. However, PFOA is not

biodegradable and has recently been classified as hazardous to the environment.

However, it is known that PFOA can be removed from exhaust gases (EP 731 081), and moreover advantageous processes for removing PFOA from wastewater have been described (US-A-4 282 162 and the as yet unpublished German Patent Applications 198 24 614.5 and 198 24 615.3 filed on June 2, 1998).

In the techniques listed above for raising concentration, the majority of the PFOA remains in the polymer dispersion, even in the case of ultrafiltration or removal by decanting using a 100-fold excess of the nonionic emulsifier.

For example, in the ultrafiltration of US-A-4 369 266 about 30% of the initial PFOA content remains in the marketable dispersions. In specific cases the residual PFOA content can be reduced to below 10%, but the process is generally not cost-effective: achieving a reduction of this type requires addition of water and of a nonionic emulsifier to the dispersion whose concentration is to be raised. This gives unacceptably long process times.

During subsequent use of these dispersions, PFOA can pass into the environment, for example with the wastewater inevitably arising from cleaning the equipment, and into the atmosphere as aerosol. The latter emission is still more pronounced when coatings are produced, since PFOA and its ammonium salt are highly volatile. In addition, PFOA and its salts decompose by decarboxylation at the sintering temperatures normally employed, from 350 to 450°C, to give fluorinated hydrocarbons, which have a major global-warming effect ("greenhouse effect").

The present invention provides high solids dispersions essentially free of PFOA. In this invention, "essentially free" means a content of less than 100 ppm, preferably less than 50 ppm, especially preferably less than 25 ppm and in particular less than 5 ppm. These values are based on the entire dispersion, and not just the solids content. This is achieved by the removal of fluorinated amulsifiers, e.g. PFOA, from fluoropolymer dispersions, such as PTFE, fluoro-thermoplast or fluoroelastomer dispersions, via anion exchange, namely by adding a nonionic emulsifier to the fluoropolymer dispersion and contacting this stabilized dispersion with a basic anion exchanger. This process works without any jamming or clogging of the ion exchange bed by coagulated latex particles. The concentration of resulting dispersion may optionally be increased.

Fluoropolymer dispersions useful in this invention include dispersions of homopolymers and of copolymers of one or more fluorinated monomers, such as TFE, VDF or CTFE or of other fluorinated olefins of 2 to 8 carbon atoms, perfluorinated olefins of 2 to 8 carbon atoms, e.g., HFP, of fluorinated ethers, especially perfluorinated vinyl alkyl ethers with alkyls of 1 to 6 carbon atoms, such as perfluoro (n-propyl vinyl) ether and perfluoro (methyl vinyl) ether. Useful comonomers also include non-fluorinated olefins, such as ethylene and propylene. The invention is intended to include such dispersions whether the resulting fluoropolymer is melt-processible or not.

The latex particles usually have a submicroscopic diameter of less than 400 nm and preferably from 40 to 400 nm. Smaller particle sizes may be obtained by what is known as "micro-emulsion polymerization." The latex particles are anionically stabilized by colloid chemistry methods. The anionic stabilization is provided by anionic end groups, mostly COOH groups, and

by the anionic emulsifier, such as PFOA. Such anionically stabilized dispersions coagulate rapidly in an anion exchange bed and thus jam the ion exchange bed. The reason for that is the breakdown of the electrical double layer at the ion exchange sites. The treatment of an anionically stabilized dispersion with an anion exchanger is therefore considered to be technically not feasible, in particular for higher concentrations.

The impairing or clogging of the ion exchange bed is observed even at concentrations 1000 times lower than those of the raw polymer dispersions, that is to say of the dispersion after polymerization.

A helpful observation in choosing a useful ion exchanger is that the pKa value of the acid corresponding to the counterion of the anion exchanger has to be higher than the pKa value of the anionic end groups of the polymer. Preferably, the anion exchanger has a counterion corresponding to an acid with a pKa value of at least 3.

In contrast, coagulation is observed after prolonged periods if the anion exchanger is in the SO_4^{-2} or Cl^- form, even with dispersions of copolymers of TFE and HFP, called "FEP", and of TFE and PPVE, called "PFA". These copolymers both have strongly acidic end groups. The formation of such end groups is explained in "Modern Fluoropolymers", John Scheirs (Editor), John Wiley & Sons, Chichester (1997), pages 227 to 288, 244. The jamming or clogging of ion exchange beds when processing TFE-ethylene or VDF copolymer dispersions occurs almost instantly under such conditions.

Therefore, at the outset, the anion exchange is performed in an essentially basic environment. Preferably, the ion exchange resin is transformed to the OH^- form, but anions like fluoride or oxalate

corresponding to weak acids can also be used. These anions are generally present in the dispersion and originate from the polymerization recipe.

The specific basicity of the anion exchanger used is not critical. Strongly basic resins are preferred due to the observed higher efficiency in removing PFOA. The effective removal of PFOA from the dispersions depends on the ion exchange conditions. Weakly basic ion exchange resins show earlier PFOA breakthrough. The same is true for higher flow rates.

The flow rate is not critical, standard flow rates can be used. The flow can be upward or downward.

The ion exchange process can also be carried out as a batch process by mildly stirring the dispersion with the ion exchange resin in a vessel. After this treatment the dispersion is isolated by filtration. Use of this invention will minimize coagulation during a batch process.

Non ionic emulsifiers are described in detail in "Nonionic Surfactants", M. J. Schick (editor), Marcel Dekker, Inc., New York 1967.

The choice of the nonionic emulsifier is also not critical. Alkylarylpolyethoxy alcohols, alkylpolyethoxy alcohols, or any other nonionic emulsifier can be used. This is a big advantage since the removal of PFOA from commercial dispersions leaves the formulation of the applied dispersions essentially unchanged.

No differences could be observed using nonionic surfactants such as those of alkylarylpolyethoxy alcohol type, e.g., Triton™ X100, or of alkylpolyethoxy alcohol type, e.g., GENAPOL™ X 080, with respect to effectiveness of the PFOA removal, flow rates, or jamming of the ion exchange bed.

The removal of PFOA is preferably carried out with crude dispersions from polymerization. Such dispersions generally have a solids content of 15 to 30% by weight. Sufficient nonionic emulsifier is added to provide dispersion stability during subsequent processing, such as concentration. A sufficient quantity of nonionic emulsifier generally means from 0.5 to 15% by weight and preferably from 1 to 5% by weight. These percentages are based upon the solids content of the dispersion. After removal of the PFOA, the dispersions may be concentrated using conventional procedures, such as ultrafiltration or thermal concentration. It is advantageous that the concentration of the nonionic emulsifier in the final product is not much higher than in comparable commercial products. The absence of PFOA in these processes does not impair the concentration process, that is, no more coagulum is formed than in the presence of PFOA during thermal concentration and ultrafiltration.

The removal of PFOA via anion exchange can also be carried out with previously concentrated dispersions with a solids content of up to 70% by weight. However, due to the higher viscosity and density of such dispersions this process is technically more cumbersome. In this case the ion exchange is preferably operated by the upflow method, to avoid difficulties due to the flotation of the ion exchange bed. The high viscosity does not usually permit high flow rates. For such high solids dispersions the batch process appears to be more advantageous.

The removal of PFOA is carried out by adding typically 1-5% by weight of nonionic emulsifier to the dispersion under mild agitation conditions and passing the dispersion over the anion exchanger. The anion exchanger may be preconditioned with a solution of nonionic emulsifier as used with the dispersion to be

exchanged. The anion exchange resin is preferably brought into the OH^- form. This is accomplished by bringing the anion exchange resin into contact with an NaOH solution.

Dispersions are generally used for the ion exchange process without adjusting the pH value but the pH value may also be increased to enhance the colloidal stability of the dispersion by adding a base, such as aqueous ammonia or sodium hydroxide solution. A pH value in the range of 7 to 9 is sufficient. The increased pH value does not greatly affect the efficiency of the removal of PFOA. This is believed to be due to the fact that PFOA is not only exchanged but also strongly absorbed on the ion exchange resin.

Subsequently the ion exchanged dispersions are subjected to concentration, preferably using thermal concentration or ultrafiltration. No impairment of these processes could be observed. There are moreover no changes in end user processing or end use properties for such dispersions according to the invention.

The anion exchange process in the presence of a nonionic emulsifier, without jamming of the ion exchange bed, can be successfully used for the removal of any other anionic emulsifier used in any polymerization process.

This process may also be used for any crude fluoropolymer dispersions, such as dispersions of PFA, FEP, THV (THV is a terpolymer of TFE, HFP and VDF), ET (ET is a copolymer of TFE and ethylene), TFE/P (a copolymer of TFE and propylene), copolymers of VDF and HFP, as well as homopolymers or copolymers comprising other fluorinated olefins or vinyl ethers. These polymers are described in detail in "Modern Fluoropolymers", cited above.

The work-up procedure as disclosed in US-A 5 463 021 describes inter alia a treatment of crude THV dispersions via an ion exchange process as one work-up step. However, this is a cationic exchange process to remove manganese ions originating from the permanganate used as polymerization initiator. During the cationic exchange process the stabilizing electrical double layer is not affected because the latex particles are anionically stabilized.

The invention will now be explained in more detail by the following examples.

Experimental details:

All percentages are by weight unless otherwise stated.

Determination of PFOA

The PFOA content of the anion exchanged dispersion may be quantitatively analyzed using the method described in "Encyclopedia of Industrial Chemistry Analysis", Vol. 1, pages 339 to 340, Interscience Publishers, New York, NY, 1971 and in EP-A 194 690. Another method used is the conversion of the PFOA to the methyl ester and analysis the ester content by gas chromatography using an internal standard. The detection limit for PFOA for the latter method is 5 ppm. The latter method was used in the following examples

Anion exchange

Standard equipment was used. The dimensions of the column were 5 x 50 cm. AMBERLITE™ IRA 402 with a capacity of 1.2 meq/ml was used as strong basic anion exchange resin (AMBERLITE is a trademark of Rohm & Haas). The bed volume was usually 400 ml. The ion exchanger was brought into the OH^- form with NaOH solution. The exchanger was preconditioned with a 5%

solution of the nonionic emulsifier. The ion exchange was carried out at room temperature. The experiments were performed at different flow rates as given in Table 1. The nonionic emulsifier was added to the dispersions as a 10% concentrated solution. The content was varied as given in Table 1. The values are based on the polymer content. The technical feasibility of this process is considered to have been achieved if at least 5% of the theoretical capacity of the ion exchange resin used is consumed by the PFOA-containing dispersion without jamming of the bed and without breakthrough of PFOA.

The following nonionic surfactants were used:

NIS 1: octyl phenoxy polyethoxy ethanol (commercial product TRITON™ X 100, TRITON is a trademark of Union Carbide Corp.).

NIS 2: ethoxylate of a long-chain alkohol (commercial product GENAPOL™ X 080, GENAPOL is a trademark of Hoechst AG).

Examples 1 to 7

All experiments were carried out with AMBERLITE IRA 402 in the OH^- form. Changes to the preconditioning of the anion exchange resin with an aqueous solution of the nonionic surfactant were as indicated in Table 1.

The fluoropolymer dispersion was obtained by homopolymerization of TFE according to EP-B 30 663. The solids content of the crude dispersion used is about 20%, and the average particle size is about 200 to 240 nm. The pH value is 7. The amount and type of the nonionic emulsifier added to the crude dispersion were changed as indicated in Table 1.

The PFOA content of the dispersion is about 0.13% by weight (amounting to 3.14 mmol/kg dispersion). This

corresponds to 2.7 ml of ion exchange resin per kg of crude dispersion. Example 3 shows that 54 ml of the total volume of 400 ml ion exchange resin are consumed. Thus, the ion exchange capacity provided was a more than 5-fold excess for all examples.

The experimental details in Table 1 show different flow rates. During a given experiment no changes in the flow rate were observed. This is an indication of the absence of jamming of the ion exchange bed. The run time of the experiments was up to 67 h without interruption. All the examples result in dispersions with PFOA contents of less than 5 ppm, the analytical detection limit of the method used.

TABLE 1

Example No.	1	2	3	4	5	6	7
Ion exchange resin, ml	400 ml	400 ml	400 ml	4 parallel columns 400 ml each	4 parallel columns 400 ml each	400 ml	400 ml
Ion exchange resin preconditioned with an aqueous solution of	1% by weight NIS 1	5% by weight NIS 1	3% by weight NIS 1	5% by weight NIS 1	5% by weight NIS 2	5% by weight NIS 2	1% by weight NIS 2
Crude dispersion:							
Solids content	22.7%	22.6%	22.7%	22.7%	22.5%	23%	22.8%
PFOA content	0.132%	0.130%	0.132%	0.136%	0.138%	0.138%	0.136%
Crude dispersion							
Stabilized with*)	1% NIS 1	3% NIS 1	4% NIS 1	5% NIS 1	5% NIS 2	4% NIS 2	1% NIS 2
Amount passed through	5 kg	19 kg	20 kg	40 kg	50 kg	18 kg	8 kg
Flow rate	0.5 l/h	0.6 l/h	0.3 l/h	0.6 l/h	0.6 l/h	0.6 l/h	0.5 l/h
Run time	10 h	35 h	67 h	17 h	21 h	30 h	16 h
Jamming yes/no	no	no	no	no	no	no	no
Ion exchanged dispersion							
PFOA content	<5 ppm	<5 ppm	<5 ppm	<5 ppm	<5 ppm	<5 ppm	<5 ppm
	*) based on solids content of the dispersion						

Example 8

800 ml of AMBERLITE IRA 402 (OH^- form, preconditioned with a 5% solution of NIS 1) were slowly added to a stirred vessel containing 20 liters of dispersion similar to that used in examples 1 to 7, but concentrated by ultrafiltration (solids content: 52.5%, PFOA content: 0.065%, NIS 1 content: 5% based on polymer content). After mild stirring for 8 h at room temperature the anion exchanger was filtered off and the PFOA content of the dispersion was analyzed resulting in less than 5 ppm PFOA.

Example 9

The same procedure as for examples 1 to 7 was used for purification of a PFA crude dispersion. 400 ml of AMBERLITE IRA 402 (OH^- form, preconditioned with a 1% solution of NIS 2) were used. The PFA dispersion (1500 ml, solids content 20%) was stabilized with 5% by weight of NIS 2 based on the solids content of the dispersion. This dispersion comprised 0.066% by weight of PFOA and had a pH value of 4. The dispersion was passed over the anion exchange bed with a flow rate of 100 ml/h. This corresponds to a run time of 15 h. No jamming of the bed was observed and the resulting dispersion had a PFOA content of <5 ppm.

Example 10

Example 9 was repeated using a crude FEP dispersion (solids content 20% by weight, PFOA content 0.08% by weight) stabilized with 5% by weight of NIS 2. The ion exchange process resulted in an FEP dispersion comprising <5 ppm of PFOA. No jamming of the bed was observed.

Example 11

Example 9 was repeated but with a THV dispersion having a solids content of 20% and an average particle size of 80 nm. Before subjecting the dispersion to the anion exchange it was treated with a cation exchange resin as described in US-A 5 463 021. The anion exchange process resulted in a THV dispersion comprising <5 ppm of PFOA and no jamming of the bed was observed.

Comprises/comprising and grammatical variations thereof when used in this specification are to be taken to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An aqueous fluoropolymer dispersion, comprising less than 50 ppm of fluorine-containing emulsifier prepared in the presence of a fluorine-containing emulsifier by aqueous emulsion polymerisation.

2. The dispersion as claimed in claim 1, wherein said dispersion comprises less than 25 ppm of fluorine-containing emulsifier.

3. The dispersion as claimed in claim 2, wherein said dispersion comprises less than 5 ppm of fluorine-containing emulsifier.

4. The dispersion as claimed in any one of claims 1 to 3, wherein the fluoropolymer is a tetrafluoroethylene polymer.

5. The dispersion as claimed in claim 4, wherein the polymer comprises at least one monomer selected from the group consisting of fluorinated olefins of 2 to 8 carbon atoms and fluorinated vinylalkyl ethers with an alkyl radical having 1 to 6 carbon atoms.

6. The dispersion as claimed in claim 5, wherein the fluorinated olefin and the fluorinated ether are perfluorinated.

7. The dispersion as claimed in claim 5, wherein the fluorinated olefin is hexafluoropropene and/or vinylidene fluoride.

8. The dispersion as claimed in claim 6, wherein the ether is perfluoro(n-propyl vinyl) ether or perfluoro(methyl vinyl) ether.

9. The dispersion as claimed in claim 4, wherein the polymer contains 90 to 100 mol-% of tetrafluoroethylene.

10. The dispersion as claimed in any one of claims 1 to 3, wherein the fluoropolymer contains one or more fluorinated monomers, with the proviso that none of the monomers is tetrafluoroethylene.

11. A process for removing fluorine-containing emulsifier from an aqueous fluoropolymer dispersion which comprises adding to the dispersion an effective amount of a non-ionic emulsifier to stabilize the dispersion, bringing the stabilized dispersion into contact with an effective amount of an anion exchanger to extensively remove fluorine-containing emulsifier and separating the dispersion from the anion exchanger and optionally subjecting the resultant dispersion to concentration.

12. The process as claimed in claim 11, wherein the solids content of the dispersion is 10 to 70% by weight.

13. The process as claimed in claim 12, wherein the solids content is 15 to 30% by weight.

14. The process as claimed in any one of claims 11 to 13, wherein 0.5 to 15% by weight of non-ionic emulsifier are added, based on the weight of the solids content of the dispersion.

15. The process as claimed in claim 14, wherein the non-ionic emulsifier concentration is preferably 1 to 5%, based on the solids content.

16. The process as claimed in any one of claims 11 to 15, wherein the anion exchanger has a counterion corresponding to an acid with a pKa value of at least 3.

17. The process as claimed in any one of claims 11 to 16, wherein the anion exchanger is used in the OH form.

18. An aqueous fluoropolymer dispersion as substantially hereinbefore described with reference to the examples.

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