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3,704,272

## CONCENTRATION OF POLYTETRAFLUOROETHYLENE AQUEOUS DISPERSION

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10 Claims

### ABSTRACT OF THE DISCLOSURE

Polytetrafluoroethylene aqueous dispersion having a pH of at least 8.0 is concentrated by dissolving in the dispersion a sufficient amount of an ethoxylated aliphatic alcohol which has a cloud point of no greater than 45° C. to cause the dispersion to form two layers upon heating at temperatures up to 45° C., decanting the upper layer, followed by dissolving in the lower layer sufficient ethoxylated aliphatic alcohol having a cloud point of at least 10° C. greater than that of the first mentioned ethoxylated aliphatic alcohol and in no event less than 50° C.

This invention relates to the concentration of polytetrafluoroethylene aqueous dispersions.

U.S. Pat. 3,037,953 to Marks and Whipple discloses the concentration of basic polytetrafluoroethylene aqueous dispersions which contain an ammonium polyfluorocarboxylate dispersing agent by adding specific amounts of ethoxylates of either alkyl phenols or aliphatic alcohols to the dispersion, followed by heating the dispersion at 50 to 80° C., whereby an upper clear aqueous layer is formed and the polymer particles concentrate in a lower aqueous layer, and decanting the upper layer. U.S. Pat. 3,301,807 to Hoashi discloses heating the dispersion at temperatures no greater than 45° C. to form the two phase system, in which ethoxylates of alkyl phenols are the only dispersing agents disclosed to work; prior to heating a relatively low molecular weight ethoxylate of an alkyl phenol is added to the dispersion, and after decantation of the upper layer, a higher molecular weight ethoxylate of an alkyl phenol is added to the concentrated dispersion (lower layer) for stabilization purposes. While the Hoashi process affords some convenience in operation, it has the disadvantage of his surfactant being difficult to burn out of the polytetrafluoroethylene during sintering and imparts a discoloration to the polymer.

The present invention involves the discovery of a process for concentrating polytetrafluoroethylene aqueous dispersion which employs the advantage of the lower temperature operation disclosed in the Hoashi patent but without the aforementioned disadvantage thereof. The process of the present invention can generally be described as comprising dissolving in the dispersion a sufficient amount of ethoxylated aliphatic alcohol, which has a cloud point of no greater than 45° C. to cause the dispersion to form two layers upon subsequent heating at a temperature of less than 45° C., decanting the resultant aqueous upper layer, and dissolving in the bottom layer which is the concentrated dispersion, a stabilizing amount of an ethoxylated aliphatic alcohol which has a cloud point of at least 10° C. greater than that added prior to heating, and in any event greater than 50° C. The resultant dispersion composition will contain a mixture of these nonionic surfactants and will have a pH of at least 8 which can be adjusted by acid or base addition to get the pH desired.

Cloud point is measured by the following procedure: a 1.00±0.02 percent solution of the surfactant in water is prepared and 15 ml. of this solution is added to a 20 x 150 mm. test tube. This tube is placed in a cold

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water bath and the bath is heated slowly at the rate of 2 to 3° C./min. The contents of the tube are gently stirred with a thermometer graduated in 0.2° C. units and capable of being read to 0.1° C. The temperature at which haze first appears on the sidewall of the tube above the liquid level is the cloud point for the surfactant.

The cloud point is thus a measure of solubility of the surfactant in the water, and the greater cloud point of the second addition of ethoxylated aliphatic alcohol indicates its greater solubility at temperatures less than the cloud point for the first added ethoxylated aliphatic alcohol.

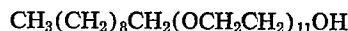
The ethoxylated aliphatic alcohols used in the present invention for both additions to the aqueous dispersion are nonionic surfactants which can be represented by the formula  $ROA_nH$ , wherein  $A_n$  is the group  $\text{-(C}_2\text{H}_4\text{O)}_n$  or a mixture of the groups  $\text{-(C}_2\text{H}_4\text{O)}_a$  and  $\text{-(C}_3\text{H}_6\text{O)}_b$ , wherein  $n$  is in each instance an integer of from 2 to 50, preferably 2 to 18,  $b$  is an integer of 0 to 30, and  $a$  is an integer of at least 2,  $a+b$  being equal to  $n$ ; R is an aliphatic hydrocarbon group which can be saturated or unsaturated, straight chain, branched or cyclic, and will generally contain from 8 to 24 carbon atoms but preferably from 8 to 18 carbon atoms. Examples of R groups include oleyl, stearyl, tridecyl, decyl, and lauryl. The R group provides the hydrophobicity to the surfactant and the A group is the hydrophilic moiety of the surfactant. The proportion of R and A groups in the surfactant and the overall molecular weight of the surfactant determine the cloud point of the surfactant. Therefore, these parameters of the surfactant are selected to give the cloud point desired. Usually, the proportion of  $\text{-(C}_3\text{H}_6\text{O)}_b$  groups in the surfactant will be 50 percent or less relative to the number of  $\text{-(C}_2\text{H}_4\text{O)}_a$  groups present.

The preferred ethoxylated aliphatic alcohols that are added to the dispersion prior to heating are those having a cloud point of from 30 to 45° C. and preferably from 33 to 40° C. Examples of such surfactants include the compounds of the formula



wherein  $n$  is an integer of 6 to 10 and  $m$  is an integer of 3 to 6.

The preferred ethoxylated aliphatic alcohols that are added after heating and decantation of the upper aqueous layer are the compounds having a cloud point of at least 55° C., and preferably from 65 to 98° C. The compound can have a cloud point in excess of 100° C. but generally such cloud points are not measured. Examples of such compounds include the compounds represented by the formulae



and



The ethoxylated aliphatic alcohol added to the concentrated layer can be a mixture of such compounds having different cloud points which average out to the cloud point desired.

Polytetrafluoroethylene aqueous dispersions which can be concentrated are any of the dispersions of colloidal sized particles of polytetrafluoroethylene in water. One process for making the dispersion involves pressuring tetrafluoroethylene into an aqueous solution of polymerization initiator and dispersing agent under mild agitation, whereby the dispersion is formed generally having concentrations of 15 to 45 percent by weight of polymer solids based on the weight of dispersion. Any polymerization initiator and dispersing agent can be used to form the aqueous dispersion of polytetrafluoroethylene. Typically, however, the initiator will be a water-soluble peroxy com-

pound such as the inorganic persulfates, e.g. ammonium persulfate, or organic peroxides, e.g. disuccinic acid peroxide, and the dispersing agent used during polymerization will be an anionic dispersing agent which imparts a negative charge to the polymer particles in the dispersion. The most common anionic dispersing agents are the fluorinated carboxylic acid or carboxylates, e.g. an ammonium polyfluorocarboxylate containing from 7 to 10 carbon atoms. The amount of dispersing usually used is from 0.2 to 0.4 percent based on the weight of polymer solids. The particle size of the polytetrafluoroethylene particles in the dispersion will generally be an average particle diameter of 0.1 to 0.45 micron. The larger particle sizes within this range can be made by the process disclosed in U.S. Pat. No. 3,391,099 to Punderson. The particles can be spherical or irregular in shape such as elongated. Particle size is determined by the light scattering method disclosed in the Punderson patent, except that the refractive index increment is taken as 0.020 because of the presence of surfactant.

The amount of ethoxylated aliphatic alcohol added initially to the dispersion can be selected as desired to obtain the amount of phase formation desired during subsequent heating at a temperature above room temperature (20–25° C.) but less than 45° C. Generally, the amount of surfactant initially added will be from 6 to 40 percent based on the weight of polymer in the dispersion. The surfactant is added by itself or as a solution in up to about 50 percent by weight of water and under mild agitation to avoid coagulation of the dispersion.

Following or accompanying the initial addition of ethoxylated aliphatic alcohol to the dispersion, the dispersion is made basic by addition of a water-soluble basic compound to the dispersion. Typically, the basic compound is sodium hydroxide or an ammonium compound, base or salt, such as ammonium hydroxide or ammonium carbonate. Generally, sufficient basic compound is added to produce a pH of at least 8.0.

Following addition of the surfactant, the dispersion is heated at a temperature no greater than 45° C. for a sufficient period of time that usually observable liquid phases appear, with the upper layer being clear and the lower layer being cloudy by virtue of the polymer particles dispersed therein. The preferred heating temperature is in the range of 30 to 45° C. The heating is carried out for sufficient time until the depth of the upper layer appears to have stabilized at which time this layer is separated from the lower layer by conventional technique such as decantation.

The resultant lower layer is the concentrated polytetrafluoroethylene aqueous dispersion usually containing from 45 to 75 percent by weight of polymer solids based on the total weight of the lower layer. This lower layer over a period of time in storage at room temperature (20–25° C.) tends to continue concentrating by forming a new clear upper layer and an even more concentrated lower layer, accompanied by agglomeration and coagulation of polymer solids in the lower layer, especially in the case of the larger particle sizes of the polymer.

To avoid this storage instability, the higher cloud point ethoxylated aliphatic alcohol is added to the lower layer in a sufficient amount to stabilize the dispersion, thereby preventing further concentration during storage. The amount of this surfactant that is required for stabilizing will generally be from 1 to 12 percent by weight based on the weight of the polymer solids in the concentrated dispersion. The preferred total concentration of ethoxylated aliphatic alcohol in the dispersion is from 4 to 15 percent based on the weight of polymer solids; most of the initially added ethoxylated aliphatic alcohol ends up in the decanted layer, but usually at least 1.0 percent based on the weight of polymer solids remains in the concentrated dispersion layer to add to the stabilizing effect

of the later added higher cloud ethoxylated aliphatic alcohol.

The resultant concentrated polytetrafluoroethylene aqueous dispersion is useful in the same manner as polytetrafluoroethylene aqueous dispersions heretofore.

In the following examples of the process of the present invention certain procedures were used for determining percent solids and percent dispersing agent in the dispersion, for the stability, the concentrate of the dispersion and for forming a film of the polytetrafluoroethylene of the dispersion. These procedures were as follows:

Percent solids and percent dispersing agent: A  $5 \pm 0.5$  g. sample, weighed to the nearest 0.0001 g. was heated in a  $100 \pm 1^\circ$  C. oven for 90 minutes. After cooling, the sample was reweighed to the nearest  $\pm 0.0001$  g. The sample was then heated for  $10 \pm 1$  minutes at  $380^\circ$  C. in a circulating air oven. After removal from the oven and cooling, the sample was weighed to the nearest 0.0001 g. The percent solids was found by dividing the final weight by the initial weight. The percent surfactant was found by dividing the weight loss during the final drying ( $380^\circ$  C.) by the final weight.

Stability of concentrated dispersion: Approximately 100 ml. of concentrated dispersion was added to a graduated cylinder which was tightly capped and stored on a shelf at room temperature (20–25° C.). Periodically, the height (in ml.) of the liquid in the cylinder was recorded along with the height of the interface level. The latter is the level between the clear nearly solid-free supernatant layer and the lower dispersion layer. The interface level provides a measure of the extent of settling and thus the storage stability of the dispersion. An interface level of 100 means no separating into layers has occurred and the dispersion was storage stable.

Film forming: Films of polytetrafluoroethylene approximately 4 inches by 6 inches by 4 mil thick were prepared using a semi-circular drum 4.5 inches in diameter which was covered with a sheet of 7 by 9 inch aluminum foil (0.005" thick) crimped over the edges of the drum. The foil was free of creases and bulges and conformed to the shape of the drum. A coating of polytetrafluoroethylene was made on the foil by turning the drum slowly and evenly through a 100 ml. sample of the dispersion being tested which was contained in a plastic trough. The foil was immersed in the dispersion to a depth of about one eighth of an inch. The total time any one part of the foil is in the dispersion was about 5 seconds. The foil was then removed from the drum and heated 5 minutes at  $100^\circ$  C. and subsequently for 4 minutes at  $380^\circ$  C. Six coats were made in this manner. The foil was then dissolved away from the aluminum foil over a period of about one hour using a strong aqueous solution of sodium hydroxide and the resultant film of polytetrafluoroethylene was then washed thoroughly in demineralized water.

In the following examples, parts and percents are by weight unless otherwise indicated.

#### EXAMPLE 1

In this example, the starting aqueous dispersion of negatively charged polytetrafluoroethylene particles contained 35 percent by weight polymer solids based on the weight of dispersion, and the average particle diameter was 0.21 micron. The surfactant initially added was  $\text{CH}_3(\text{CH}_2)_n\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OH}$ , wherein  $n$  is 4 to 6, having a cloud point of  $38^\circ$  C., this surfactant is available as "Plurafac A-16." The general concentration procedure involved the addition of 8 percent (based on the weight of polymer solids) of this nonionic surfactant to the dispersion and sufficient ammonium hydroxide to adjust the pH of the dispersion from a starting pH of about 3 to a pH of about 10. The resultant dispersion was stirred with mild agitation for several minutes and then heated at  $35^\circ$  C. followed by siphoning off of the resultant clear supernatant layer. The time between the

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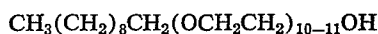
beginning of heating after stirring and the measurement of the extent of concentration was 30 minutes. The percent solids in the concentrated dispersion was 62 percent based on the weight of the concentrated dispersion and its "Plurafac A-16" content was 3 percent.

A 100 ml. sample of this dispersion was tested for storage stability and after 22 days at room temperature, the interface level had fallen to 74 ml.

To another 100 ml. sample was added 3 percent by weight of  $\text{CH}_3(\text{CH}_2)_x\text{CH}_2(\text{OCH}_2\text{CH}_2)_y(\text{OC}_3\text{H}_7)_z\text{OH}$ , wherein  $x$ ,  $y$  and  $z$  have the following average values; 10-11, 12-13, and 4-5, respectively. This surfactant has a cloud point of 65° C. and is available as DN-65. After 22 days, the interface level of the dispersion fell only to 97 ml. and after 78 days, only to 93 ml.

The experiment of the preceding paragraph was repeated except that the "Plurafac A-16" concentration was reduced from 3 to 2.8 percent by weight and the DN-65 concentration was increased to 3.2 percent by weight. The interface level for the dispersion fell only to 98 ml. after 110 days of storage at room temperature.

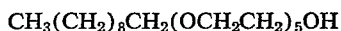
To still another 100 ml. sample of the dispersion was added 3 percent by weight of



which has a cloud point of 97.5° C. The interface level for the dispersion fell only to 98 ml. after 22 days of storage at room temperature.

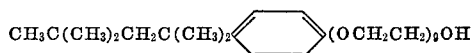
### EXAMPLE 2

The general procedure of Example 1 was repeated except "Alfonic" 1012-60 was the initial nonionic surfactant. Thus surfactant has the formula



and 1.3 percent by weight of this surfactant is present in the concentrated dispersion layer. This surfactant has a cloud point of 35° C. The surfactant added after siphoning off the supernatant layer was 8.7 percent by weight of DN-65.

Another sample containing 10 percent by weight of the compound



available as "Triton" X-100, was concentrated and stabilized in the same manner. The polymer solid content of each dispersion was  $55.5 \pm 1.3$  percent by weight.

Films were formed of each of these concentrated dispersions in accordance with the film-forming procedure described herein. The film for the "Triton" X-100 dispersion was 4.6 mils thick and for the other dispersion was 4.0 mils thick. The first mentioned film had yellowness indices of 21.09 (by transmittance) and 39.04 (by reflectance against a white background), whereas the film prepared from the dispersion concentrated according to the present invention exhibited values of 18.22 and 17.21, respectively. The yellowness indices were measured according to ASTM method D-1925-63T (27) entitled "Yellowness Index of Plastics."

### EXAMPLE 3

Example 2 was repeated except that the dispersion contained  $63.5 \pm 0.7$  percent by weight polymer solids, the amount of DN-65 surfactant added after concentration of one sample of the dispersion concentrated according to the present invention was 4.7 percent by weight (1.3 percent "Alfonic" 1012-60 was already present in concentrated dispersion), and the "Triton" X-100 concentration in the other sample of dispersion was 6.0 percent by weight. The film obtained from the former dispersion was 4.5 mil thick and from the latter dispersion, 4.3 mil thick. The yellowness index values were 20.69 (trans-

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mitted) and 24.23 (reflected) for the film containing "Triton" X-100 and 19.20 (transmitted) and 18.90 (reflected) for the other film.

The polytetrafluoroethylene in the aqueous dispersions of this invention can consist of the homopolymer or can be a copolymer with other copolymerizable ethylenically unsaturated monomer. For example, the homopolymer can include small amounts of co-monomer modifier, wherein the homopolymer still retains its non-melt fabricable character, such as up to two percent by weight of polymer units derived by copolymerization with tetrafluoroethylene of perfluoroalkyl- or oxyperfluoroalkyl trifluoroethylene of 3 to 10 carbon atoms, and preferably hexafluoropropylene, as disclosed in U.S. Pat. 3,142,665 to Cardinal, Edens, and Van Dyk. Larger amounts of these monomers or other monomers can be present in amounts up to 35 percent by weight to render the resultant copolymer melt fabricable. Examples of such copolymers include copolymers of tetrafluoroethylene with such monomers as hexafluoropropylene, as disclosed in U.S. Pat. 2,946,763 to Bro and Sandt, higher perfluoroalkenes such as those containing from 4 to 10 carbon atoms, perfluoro(alkyl vinyl ethers) such as perfluoroethyl or perfluoropropyl vinyl ether, disclosed in U.S. Pat. No. 3,132,123 to Harris and McCane, perfluoro(2-methylene-4-methyl-1,3-dioxolane) disclosed in U.S. Pat. 3,308,107 to Selman and Squire, and the highly fluorinated monomers in which a single hydrogen is present which does not change the fluorocarbon character of the copolymer, such monomers being for example 2-hydroperfluoroalkene containing 1 to 3 carbon atoms such as 2-hydropentafluoropropene, the omega-hydroperfluoroalkenes containing from 3 to 10 carbon atoms, and the omega-hydroperfluoro(alkyl vinyl ethers) in which the alkyl group contains from 1 to 5 carbon atoms.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for concentrating an aqueous dispersion consisting essentially of polytetrafluoroethylene particles dispersed in water, comprising adding sufficient ethoxylated aliphatic alcohol having a cloud point of no greater than 45° C. to the dispersion to form two layers upon the subsequent heating step, adding sufficient basic compound to the dispersion to increase its pH to at least 8, heating the dispersion at a temperature of no greater than 45° C. to form said two layers, separating the top and bottom layers one from the other, and adding to said bottom layer a stabilizing amount of ethoxylated aliphatic alcohol having a cloud point of at least 10° C. greater than the first-mentioned ethoxylated aliphatic alcohol and at least 50° C.

2. The process of claim 1 wherein each said ethoxylated aliphatic alcohol has the formula  $\text{ROA}_n\text{H}$  wherein  $\text{A}_n$  is the group  $(\text{C}_2\text{H}_4\text{O})_n$  or mixture of the groups  $(\text{C}_2\text{H}_4\text{O})_a$  and  $(\text{C}_3\text{H}_6\text{O})_b$ , wherein  $n$  is an integer of from 2 to 50,  $b$  is an integer of 0 to 30,  $a$  is an integer of at least 2,  $a+b$  being equal to  $n$ , and R is an aliphatic group containing from 8 to 24 carbon atoms.

3. The process of claim 1 wherein the first mentioned ethoxylated aliphatic alcohol has a cloud point of from 30 to 45° C.

4. The process of claim 1 wherein the first mentioned ethoxylated aliphatic alcohol has a cloud point of from 33 to 40° C.

5. The process of claim 1 wherein the first mentioned ethoxylated aliphatic alcohol has the formula



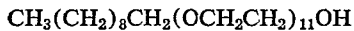
wherein  $n$  is an integer of 6 to 10 and  $m$  is an integer of 3 to 6.

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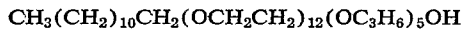
6. The process of claim 1 wherein the second mentioned ethoxylated aliphatic alcohol has a cloud point of at least 55° C.

7. The process of claim 1 wherein the second mentioned ethoxylated aliphatic alcohol has a cloud point of from 65 to 98° C. 5

8. The process of claim 1 wherein the second mentioned ethoxylated aliphatic alcohol has the formula



or



9. The process of claim 1 wherein the first mentioned ethoxylated aliphatic alcohol has a cloud point of from 33 to 40° C. and the second mentioned ethoxylated aliphatic alcohol has a cloud point of from 65 to 98° C. 15

10. The process of claim 1 wherein the amount of the first mentioned ethoxylated aliphatic alcohol added is

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from 6 to 40 percent and the amount of the second mentioned ethoxylated aliphatic alcohol added is 1 to 12 percent, based on the weight of polytetrafluoroethylene particles in the respective dispersions.

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HAROLD D. ANDERSON, Primary Examiner

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