

AQUEOUS DISPERSIONS OF OLEFIN COPOLYMERS

This invention relates to an aqueous dispersion of an olefin copolymer. These dispersions may be film-forming at room temperature and can have excellent physical and mechanical properties.

5 Aqueous dispersions of polyolefins are known in the art, although none are reported to have been derived from polyolefins having molecular weights above 40,000. For example, in U.S. Patent 3,734,686, Douglas et al. discloses a mechanically stable aqueous emulsion of polyethylene particles having an average molecular weight ranging from 7,000 to 40,000. These dispersions are taught to be useful for treating carpets.

10 In U.S. Patent 3,418,265, McClain teaches that aqueous film-forming ethylene polymer latexes containing ethylene polymer particles of submicron size can be prepared by dispersing in water an ethylene polymer and a water-soluble block copolymer of ethylene oxide and propylene oxide. No examples of stable dispersions of ethylene polymers having a molecular weight above 27,000 are reported.

15 Many of the polyolefin latexes previously described are actually not purely polyolefinic, but rather contain polar groups, such as acids or halides. Since the film-forming properties of these so-called polyolefin latexes are often adversely influenced by the presence of these polar substituents, it would be desirable to prepare latexes derived from higher molecular weight polyethylenes that did not contain polar groups. It would be of further value if these latexes were film-forming at room temperatures.

The present invention is a film-forming, artificial latex comprising an aqueous dispersion of a copolymer of ethylene and a C₃-C₂₀ alpha-olefin, the olefin polymer being characterized by having:

- 25 a) an absence of polar groups;
b) a polydispersity index from about 1.5 to about 2.5;
c) an I₁₀/I₂ of at least 6;
d) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear
30 olefin polymer having the same I₂ and polydispersity index;
e) a weight average molecular weight of at least 45,000; and
f) a density of about 0.85 to about 0.9 g/cm³.

35 In another aspect, the present invention is a film-forming, aqueous dispersion comprising a copolymer of ethylene and a C₃-C₂₀ alpha-olefin having a narrow molecular weight distribution, a random distribution of comonomer units along the polymer backbone, and a homogeneity index of at least 75.

It has surprisingly been discovered that film-forming latexes can be prepared from these olefin polymers in the absence of polar substituents.

The olefin polymer used to prepare the aqueous dispersion of the present invention is from a family of olefin polymers, which are described in U.S. Patents 3,645,992; 5,272,236; and 5,278,272. The class of olefin polymers described in U.S. Patent 3,645,992, hereinafter referred to as the Elston olefin polymer, is characterized by being a copolymer of ethylene and at least one other alpha-olefin having four or more carbon atoms, such as 1-butene, 1-hexene, 1-octene, and 1-octadecene. Interpolymers, such as ethylene-octene-butene or ethylene-octene-propylene are also suitable for the preparation of the aqueous dispersions of the present invention. The Elston olefin polymer is further characterized by a narrow molecular weight distribution and a homogeneity index of at least 75 as described in the '992 patent.

The olefin polymers described in U.S. Patents 5,272,236 and 5,278,272 (collectively referred to as substantially linear olefin polymers) are ethylene- C_3 - C_{20} alpha-olefin copolymers characterized by having 1) high melt elasticity; 2) high processability; 3) a polydispersity index of less than 3.5; 4) 0.01 to 3 long chain branches per 1000 carbon atoms along the polymer backbone; and 5) a melt flow index that is essentially independent of the polydispersity index. The olefin polymer of the '236 patent is further characterized as having a critical shear stress rate at onset of gross melt fracture of greater than 4×10^6 dyne/cm²; and the olefin polymer of the '272 patent is further characterized by having a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having the same I_2 and M_w/M_n .

The substantially linear olefin polymers from which the aqueous dispersions are prepared can be homopolymers of C_2 - C_{20} olefins, such as ethylene, propylene, 4-methyl-1-pentene, or they can be interpolymers of ethylene and at least one C_3 - C_{20} alpha-olefin, and/or a C_2 - C_{20} acetylenically unsaturated monomer and/or a C_4 - C_{18} diolefin. Preferred monomers include C_2 - C_{10} alpha-olefins, especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene and 1,4-hexadiene.

The substantially linear olefin polymers have 0.01, preferably 0.3, to 3, and preferably 1 long chain branch per 1000 carbon atoms along the polymer backbone. Long chain branching is defined herein as a chain length of at least 6 carbon atoms, above which the length cannot be distinguished by carbon NMR spectroscopy. The long chain branch can be as long as the polymer backbone.

The polydispersity index of the substantially linear olefin polymers (that is, the molecular weight distribution, or the ratio weight average molecular weight to the number average molecular weight (M_w/M_n)), is preferably from 1.5 to 2.5. The melt flow index (that is, the I_{10}/I_2) of the substantially linear olefin polymers is at least 5.63, preferably at least 6, more preferably at least 7, and is essentially independent of the polydispersity index, in contrast to

conventional polyolefins which show a dependence of the melt flow index on the polydispersity index. This property is illustrated in Figure 2 of the '236 patent.

The preparation of the substantially linear olefin polymers is described in detail in the '236 patent.

5 The density of the olefin polymer disclosed in the '272 patent is preferably from 0.85 g/cm³, more preferably from 0.86 g/cm³, to 0.90 g/cm³, more preferably to 0.88 g/cm³.

The weight average molecular weight of the substantially linear olefin polymers used to prepare the aqueous dispersion is preferably at least 45,000 amu, more preferably at least 60,000 amu. The molecular weights are measured as described in U.S. Patent 5,278,272,
10 column 5, line 56 to column 6, line 20. The olefin preferably contains no polar groups, such as acetate, ester, ether, amine, alcohol, acrylic, methacrylic, halogen, nitrile, nitro, sulfate, phosphate, or mercaptan groups; and there is preferably no post-modification step to add polar groups.

The latexes of the substantially linear olefin polymers are prepared in the
15 presence of a stabilizing and an emulsifying amount of a suitable surfactant. A preferred surfactant is a sulfate of an ethoxylated phenol represented by the formula:
$$X-\phi-O-(CH_2-CH_2-O)_n-SO_3^-Z^+$$
wherein X is a C₆-C₁₈ linear or branched alkyl group, preferably octyl, nonyl, or lauryl, more preferably octyl or nonyl, most preferably nonyl; ϕ is phenylene, preferably p-phenylene; n is
20 from 4 to 32, preferably from 4 to 12; and Z is sodium, potassium, or ammonium, preferably ammonium. Some of the preferred sulfates of ethoxylated alkylphenols are commercially available, for example, poly(oxy-1,2-ethanediyl) alpha-sulfo- ω (nonylphenoxy) ammonium salt.

Aqueous dispersions of the substantially linear olefin polymers can be prepared by any suitable technique, including those described in U.S. Patents 3,360,599; 3,503,917;
25 4,123,403; and 5,037,864. It has surprisingly been discovered that a film having a substantially uniform thickness across a substrate or form can be prepared from the aqueous dispersion described hereinabove. The film is further characterized by an absence of cracking or foramina. Finally, the film has useful physical properties, such as a high tensile strength, and can be formed at room temperature, and in the absence of polar substituents.

30 The film can be prepared by any suitable means such as casting, coagulating, or spraying. If films are prepared by coagulation, it is generally preferred to use fatty acid based surfactants, such as the sodium salt of oleic acid.

The following examples are for illustrative purposes only and are not intended to limit the scope of the invention.

35 Example 1 - A Cast Film of an Ethylene-1-Octene Latex

An artificial latex was prepared from ENGAGE™ CL 8002 ethylene-octene elastomer (Trademark of The Dow Chemical Company), which has a melt index of 1, a density of 0.87 g/cm³, an I₁₀/I₂ of 7.8, a weight average molecular weight of 129,800, and a M_w/M_n of

2.2. To a 2-liter reactor vessel was added 612 g of the ethylene-octene copolymer solution containing 61 g of the copolymer in 551 g of cyclohexane; 3.06 g of RHODAPEX™ CO 436 surfactant (Trademark of Rhone Poulenc); and 288 g of water. These ingredients were emulsified using a Gifford-Woods homogenizer by mixing at nominally 10,000 rpm for 10 minutes. 0.2 g of DF37 defoamer (obtained from Air Products) was added to reduce the foam. The cyclohexane solvent was removed from the emulsion by rotary evaporation at 80°C. The resulting artificial latex was concentrated to 30 percent solids by applying a partial vacuum to the latex with continued heating.

The particle size of the latex, which is analyzed using a Coulter Counter Multisizer IIe, was found to be 0.9 microns, with 74 percent of the particles being less than 1.25 microns.

20 mL of the latex was poured on a clean glass substrate, and spread uniformly using a draw bar. The latex was allowed to air dry at room temperature. As the latex dries, a coherent film was formed. The film, still on the substrate, was annealed at 60°C for 5 minutes to drive off any remaining water, then allowed to cool to room temperature. The resultant film had a tensile strength of 1600 psi, 100 percent modulus of 270 psi, and a percent elongation of 1270 percent.

Example 2 - A Cast Film of an Ethylene-1-Octene Latex

An artificial latex was prepared as described in Example 1 from an ethylene-octene copolymer having a melt index of 11, a density of 0.887 g/cm³, an I₁₀/I₂ of 7.8, a weight average molecular weight of 60,000, and an ethylene/octene ratio of 2.1:1, and prepared according to the teachings of the '272 patent. The resultant film had a tensile strength of 2200 psi, 100 percent modulus of 460 psi, and a percent elongation of 1300 percent.

CLAIMS:

1. A film-forming, artificial latex comprising an aqueous dispersion of a copolymer of ethylene and a C₃-C₂₀ alpha-olefin, the olefin polymer being characterized by having:
- 5 a) an absence of polar groups;
b) a polydispersity index from about 1.5 to about 2.5;
c) an I₁₀/I₂ of at least 6;
d) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear
10 olefin polymer having the same I₂ and polydispersity index;
e) a weight average molecular weight of at least 45,000; and
f) a density of about 0.85 to about 0.9 g/cm³.
2. The film-forming, artificial latex of Claim 1 wherein the copolymer has a density of about 0.86 to about 0.88.
- 15 3. The film-forming, artificial latex as in Claim 1 or 2 wherein the copolymer is an ethylene-1-octene, ethylene-1-butene, ethylene-1-hexene, or ethylene-4-methyl-1-pentene copolymer.
4. The film-forming, artificial latex of any of Claims 1 to 3 wherein the copolymer is an ethylene-1-octene copolymer.
- 20 5. The film-forming, artificial latex of any of Claims 1 to 4 wherein the dispersion is stabilized with a sulfate of an ethoxylated phenol represented by the formula:
$$X-\phi-O-(CH_2-CH_2-O)_n-SO_3^-Z^+$$

wherein X is a C₆-C₁₈ linear or branched alkyl group; ϕ is phenylene; n is from 4 to 32; and Z is sodium, potassium, or ammonium.
- 25 6. The film-forming, artificial latex of any of Claims 1 to 5 that is film-forming at room temperature.
7. A film-forming, artificial latex comprising an aqueous dispersion of a copolymer of ethylene and a C₃-C₂₀ alpha-olefin having a narrow molecular weight distribution, a random distribution of comonomer units along the polymer backbone, and a
30 homogeneity index of at least 75.

