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(54) Title: IONOMERS OF LOW MOLECULAR WEIGHT COPOLYMER AMIDES

(57) Abstract

The ionomer salt of low molecular weight copolymer reaction product of a copolymer acid of an α-olefin and an unsaturated carboxylic acid, and at least one amino acid compound, and a cation containing material. The unsaturated carboxylic acid is preferably an α,β-ethylenically unsaturated carboxylic acid. The present invention includes a method of preparing the ionomer. The ionomer has excellent compatibility with other polymers, particularly polyamides. The ionomer is useful in a method to flush water from pigments.

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IONOMERS OF LOW MOLECULAR WEIGHT COPOLYMER AMIDES

BACKGROUND OF THE INVENTION

FIELD OF INVENTION

This invention is in the field of low molecular weight olefin copolymers; more particularly, this invention relates to the salts, i.e., ionomers, of low molecular weight copolymers of an α-olefin and an unsaturated carboxylic acid, preferably an α,β-ethylenically unsaturated carboxylic acid having up to 100 percent of the carboxylic acid groups reacted with at least one amino acid. The ionomer is useful for flushing pigments.

DESCRIPTION OF RELATED ART

The process of flushing pigments is reviewed in Great Britain Patent No. 915,453, and by Apps, Printing Ink Technology, Chemical Publishing Co., Inc., NY, pp.498-500 (1959). Flushing is a process to prepare pigment dispersions in which the pigments remain finely divided and in a suitable form for further processing such as incorporation into polymeric compositions and inks.

During the manufacture of pigments an aqueous mass of pigment is produced. The removal of all of the water can result in the pigments agglomerating. Some of the water is removed leaving the finely divided pigment as a wet cake. The aqueous mass of pigment is mixed with a polyolefin usually of low molecular weight. The mixture is coagulated and the aqueous phase is removed, typically by heating the composition, optionally in a vacuum. The pigment is dispersed in the low molecular weight polymer which can optionally be pulverized.

Low molecular weight polyethylene waxes are used to flush pigments. The flushed pigments are useful in polymeric compositions used for fibers, molding compounds, extrusion compounds, sheets, film, and the like. Flushed pigments have been used in compositions based on polyethylene, polyvinylchloride, ABS, polyamides, and polycarbonates, among other.

Low molecular weight olefinic copolymers, particularly low molecular weight ethylene copolymers, are described in U. S. Patent No. 3,658,741. This patent discloses homogeneous copolymers of ethylene and various comonomers including unsaturated acids and their derivatives, such as esters and amides. Examples of the derivatives include methyl acrylate, methyl methacrylate, ethyl acrylate, and dimethylaminoethyl methacrylate.

U. S. Patent No. 4,381,378 discloses a method for the preparation of low molecular weight copolymer salts from low molecular weight copolymer acids of α-olefins and α,β-ethylenically unsaturated carboxylic acids. Preferred copolymers are copolymers of ethylene and acrylic acid.

U. S. Patent Nos. 4,412,040 and 4,603,172 disclose low molecular weight copolymer salts for use as lubricants and dispersion aides in plastics. The disclosed salts include salts of low molecular weight copolymers of α-olefins and α,β-ethylenically unsaturated carboxylic acids. Preferred copolymers are copolymers of ethylene and acrylic acid.

U. S. Patent Nos. 3,388,186 and 3,465,059 disclose polyamide compositions. The compositions are made by grafting amino acids or lactams onto a backbone chain containing recurring ethylenic units and reactive sites, such as carboxyl radicals of acid, ester or salt

groups, and particularly acrylic acid esters. The proportion of the copolymer backbone to the polyamide graft can vary between 2 and 90 percent. The copolymers disclosed for use as part of the backbone chain have a number average molecular weight of at least about 13,700 in U. S. Patent No. 3,388,196; and at least 10,000 in U. S. Patent No. 3,465,059.

U. S. Patent No. 3,634,543 discloses nucleated graft polymers of polycaprolactam on carboxy containing copolymeric backbone. The graft polymer is prepared by polymerization of caprolactam in the presence of a copolymer of an olefin and an unsaturated carboxylic acid.

U. S. Patent No. 4,035,438 discloses an impact resistant mixture of polyethylene; a graft polymer of an ethylene/acrylic acid copolymer or ethylene/methacrylic acid copolymer as a graft substrate and grafted polymerized units of ε-caprolactam; and polycaprolactam. The copolymers for use as graft substrates are those which contain 1 to 10 mol percent of (meth)acrylic acid, preferably from 30 percent to 70 percent in the form of the sodium salt.

SUMMARY OF THE INVENTION

It is desirable to have a low molecular weight copolymer having structural groups which enhance compatibility with other polymers, particularly other polymers having a higher molecular weight than the low molecular copolymer. The present invention is an ionomer of a low molecular weight copolymer with carboxyl groups reacted with at least one amino acid compound or salt thereof. The amide containing ionomer has improved compatibility with polymers such as polyamides.

The preferred ionomer salt is derived from a low

molecular weight copolymer acid of an α-olefin and an unsaturated carboxylic acid, preferably an α,β-ethylenically unsaturated carboxylic acid. The acid copolymer has a number average molecular weight of from about 500 to about 6,000. Preferably, the low molecular weight copolymer acid is a copolymer of ethylene and acrylic acid or methacrylic acid, having a number average molecular weight of from about 1,000 to about 3,500. The copolymer acid has preferably from about 0.8 to about 35, and preferably from 5 to 25 weight percent of the comonomer acid with a corresponding amount of α-olefin.

Up to 100, preferably from about 10 to 100, and more preferably from about 50 to 100 percent, of the carboxylic acid groups are reacted with at least one amino acid compound or salt thereof. The amino acid (or salt thereof) has an amine end group and a carboxylic acid (or carboxylic acid salt) end group. The amine end group reacts with the carboxyl end group of the copolymer acid to form an amide group at the reaction site. There is from about 0.1 to about 50, preferably about 0.1 to about 40, more preferably about 0.5 to about 30, and most preferably about 5 to 25 weight percent based on the weight of the copolymer reaction product of the amide chain derived from the amino acid compound or salt thereof. The amide chain can be from about 10 to about 30 or about 0.1 to about 10 weight percent of the reaction product depending on the desired properties.

The average amide chain length reacted at each carboxyl site is preferably from about 1 to about 250, preferably 1 to 200, with specific embodiments including amide chain lengths of from 1 to 10, and 1 to 5 amide groups. There can be longer amide chain

lengths of from 100 to 250 amide groups. Preferably, there are sufficient amide grafts, of sufficient length to confer improved compatibility of the copolymer reaction product and another polymer, preferably polyamide. For the purpose of the present invention amino acid compounds include cyclic amides, i.e., lactams which can be hydrolyzed to form an amino acid compound. A preferred amino acid compound has the formula $H_2NCH_2(CH_2)_nCOOH$ where n is from 0 to 12, and more preferably from 4 to 8. The most preferred amino acid is amino caproic acid or its lactam, caprolactam.

The term ionomer is consistent with the definition in Billmeyer, Textbook of Polymer Science, 2 ed., Wiley-Interscience, a Div. of John Wiley & Sons, Inc., page 390 (1971), and comprises the salt of the terminal carboxylic acid groups on the amide chain, as well as residual carboxylic acid groups on the acid copolymer, and a cation from a cation containing compound. Preferred cations are from Groups IA, IIA, IIB, IIIA and the transition elements of the Periodic Table of Elements, with sodium, zinc, magnesium, and calcium being most preferred.

Up to 100 percent, preferably 1 to 100, more preferably, 25 to 100, most preferably 50 to 100 percent of the total carboxylic acid groups in the reaction product are neutralized with a cation from a cation containing compound. Preferably, the cation is a metallic cation having a valence of from 1 to 3. Preferably, the copolymer acid is first reacted with at least one amino acid compound, and the reaction product is neutralized to form an ionomer. The carboxyl groups on the amino acid are neutralized by the cation of the cation containing compound to form the ionomer. Additionally, carboxylic acid groups which did not

react with the amino acid can also be neutralized. Alternatively, the amino acid can be neutralized with the cation containing compound prior to being reacted with the copolymer acid.

The method of the present invention comprises neutralizing up to 100, preferably 25 to 100, and more preferably 50 to 100 percent of the total carboxylic acid groups on the reaction product. Preferably, this is conducted above the melting point of the copolymer reaction product, and more preferably at from 140°C to 250°C.

The preferred method of preparing the above recited ionomer of the copolymer reaction product comprises the steps of heating the copolymer of the α-olefin and the unsaturated carboxylic acid, preferably the α,β-ethylenically unsaturated carboxylic acid, to from about 110°C to about 300°C, preferably about 150°C to about 275°C, and more preferably about 200°C to about 275°C; adding a sufficient amount of at least one amino acid compound to react with up to 100 percent of the carboxylic acid groups; and conducting reaction of the copolymer and the acid. Preferably, the copolymer acid is preheated to from 110°C to 200°C and more preferably, 125°C to 175°C. The reaction is preferably conducted under an inert atmosphere, such as nitrogen or argon, or under a vacuum.

The present invention also includes a polymer composition and a pigmented composition. The polymer composition comprises at least one first polymer, preferably a polyamide and the above recited ionomer. The pigment composition comprises a pigment, at least one second polymer comprising the above-recited ionomer, and optionally, at least one first polymer. The first polymer and the ionomer being different.

Uniformity of the blend is conferred by compatibility of the ionomer and the first polymer. The uniformity leads to improved melt processing, such as extruded strand integrity.

The ionomer salt of the present invention is useful in a method of flushing a pigment of the type wherein water in an aqueous mass of pigment is flushed with a low molecular weight polymer. The improvement comprises flushing the aqueous mass of pigment with at least one ionomer of the present invention resulting in a pigmented composition.

The pigmented composition of the present invention can be used in a wide variety of compositions where the pendant amide chains on the reaction product enhance compatibility. A particularly useful composition is a composition comprising the pigmented composition and a polyamide polymer. Such compositions have excellent uniformity of pigment distribution. More importantly, the pigmented composition results in a polyamide composition with uniform pigment distribution evidenced by uniform and enhanced color. The color is actually enhanced by more complete pigment dispersion.

DETAILED DESCRIPTION OF THE INVENTION

The present invention includes an ionomer salt of a copolymer reaction of a low molecular weight copolymer of an unsaturated acid and an α-olefin, and an amino acid compound resulting in a copolymer having pendant amide chains, including polyamides, and a method to make the ionomer. The present invention also includes a polymer composition, and a pigmented composition which comprise the ionomer, as well as compositions which comprise the pigmented composition. The present invention further includes a method of flushing pigments with the ionomer.

Copolymer acids useful to make the ionomer of the present invention include the copolymer of an α-olefin and an unsaturated carboxylic acid, preferably an α,β-ethylenically unsaturated carboxylic acid or derivative thereof. These copolymers are of low molecular weight, having a number average molecular weight of from about 500 to about 6,000, and preferably about 1,000 to about 3,500. Useful and preferred copolymers include homogeneous copolymers of ethylene disclosed in U. S. Patent No. 3,658,741, the disclosure of which is hereby incorporated by reference.

The α-olefin preferably has from 2 to 8 carbon atoms and is most preferably ethylene or propylene. There is at least about 50, preferably from about 50 to about 99.5, more preferably, about 65 to about 99.2, and most preferably from about 80 to about 98 mol percent of the α-olefin, which is most preferably ethylene.

The unsaturated carboxylic acid or derivatives thereof includes such compounds disclosed in U. S. Patent No. 3,658,741. Useful carboxylic acids include both monocarboxylic and polycarboxylic acids and derivatives thereof, including esters and anhydrides, which are capable of reacting with the amino acids recited below. Useful carboxylic acids or derivatives thereof include unsaturated monocarboxylic acid containing from 3 to 6 carbon atoms and dicarboxylic acids containing from 4 to 8 carbon atoms. Specific examples of unsaturated acids copolymerizable with ethylene include acrylic acid, methacrylic acid, ethacrylic acid, itaconic acid, crotonic acid, maleic acid and fumaric acid. Also useful are acid halides, amides and esters including acrylyl chloride and

acrylamide. Esters which can be used include methyl acrylate, methyl methacrylate, ethyl acrylate and dimethylaminoethyl methacrylate. Also useful are monoesters of dicarboxylic acids, such as methyl hydrogen maleate, methyl hydrogen fumarate, ethyl hydrogen fumarate, and maleic anhydride. Particularly preferred compounds include α,β-ethylenically unsaturated acids and derivatives thereof.

A preferred copolymer acid is a copolymer of ethylene and an α,β-ethylenically unsaturated mono-carboxylic acid having 3 to 6 carbon atoms. A most preferred α,β-ethylenically unsaturated mono-carboxylic acid is acrylic acid. Most preferred is ethylene acrylic acid copolymer which has an acid number in the range from about 1 to about 180, with an acid number from about 40 to 160 being preferred, and an acid number from about 40 to 120 being most preferred. The acid number is determined by the number of milligrams of potassium hydroxide needed to neutralize one gram of acid. The number average molecular weight is from about 500 to about 5000, and preferably from about 1000 to about 3500. Table I below characterizes preferred ethylene acrylic acid copolymers.

TABLE I

Copolymer Acid	Softening Pt. (ASTM E-28) °C	°F	Hardness dmm (ASTM D-5)	Density g/cc D-1501	Brookfield Viscosity @140°C cps	Acid No. mg KOH/g	Wt% Acrylic
A	108	226	2.0	0.93	500	40	5
B	101	215	4.0	0.93	650	75	9.4
C	92	198	11.5	0.93	650	120	15

The copolymer acids are available from Allied-Signal Inc. as A-C®540(A); A-C®580(B) and A-C®143(C).

The low molecular weight copolymer acids can be prepared by any suitable method such as described in above referenced U. S. Patent No. 3,658,741. Of particular interest in U. S. Patent No. 3,658,741 is the passage beginning at column 7, line 36 through column 8, line 6. In accordance with this process, the ethylene desirably constitutes at least 65% by weight of the monomer feed and the comonomer from 1.0% to 35% of the feed, preferably 2 to 20% by weight of the feed. Under specific conditions of vapor phase polymerization the ratios by weight of the monomers in the feed and in the product are substantially constant. The ratio of comonomer between feed and product are at most only minor such that products obtained by the invention contain a major portion of ethylene and generally 0.8% to 35% by weight of the comonomer, preferably 2.0% to 20% by weight of the comonomer. The ratio of comonomer in the product to comonomer in the feed is preferably within the range of 0.7:1 to 1.8:1.

The acid copolymers useful in the present invention are of low molecular weight ranging generally between about 500 to about 6000 number average molecular weight, preferably between about 1000 to about 3500 number average molecular weight, as measured by a vapor pressure osmometer. The copolymers also desirably have a Brookfield viscosity not exceeding about 2000 centipoises at 140°C., preferably between about 200 to about 1200 centipoises at 140°C. Of special interest are the copolymers of ethylene and acrylic or methacrylic acid containing from about 1% to about 20% by weight acrylic acid or methacrylic acid in the copolymer, preferably about 3.5% to about 12%, and

further characterized by a number average molecular weight between about 1500 to about 3500, acid number between about 10 to about 200, preferably about 20 to about 130, and hardness (0.1 mm penetration) between 0.5 to 30, preferably 1 to 10 when tested at room temperature about 25°C (77°F.) according to ASTM D-5 using a needle with a load of 100 grams for 5 seconds.

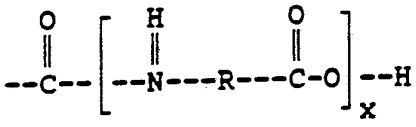
In accordance with the present invention up to 100, preferably from about 50 to about 100 and more preferably about 10 to about 30 percent of the carboxylic acid groups are reacted with from about 0.1 to about 50, preferably, 0.1 to 40, more preferably about 0.5 to about 30, and most preferably about 5 to about 25 weight percent based on the weight of the reaction product of at least one amide chain derived from at least one amino acid compound. There can be from about 10 to about 30, or about 0.1 to about 10 weight percent of at least one amide derived from at least one amino acid. For the purpose of the present invention amino acid compounds include: amino acids, and cyclic amides, i.e., lactams which can be hydrolyzed to form amino acids; and derivatives thereof.

Preferably, the amino acid compound is an amino acid monomer which has the formula $H_2NCH_2(CH_2)_nCOOH$ where n is from 0 to 12, and more preferably from 4 to 8; or an amino acid oligomer or polymer derived from this monomer. The most preferred amino acid monomer is amino caproic acid or its lactam, caprolactam.

Also useful amino acid compounds are derivatives of the amino acids including esters, or lactams of the amino acids. Specific examples of useful amino acids include ϵ-amino-caproic acid; 11-aminoundecanoic acid; 12-aminododecanoic acid; esters, amides and lactams of

monoamino-monocarboxylic acids, such as ϵ-caprolactam; ethyl ϵ-aminocaproate; lauryl lactam; ethyl-11-aminoundecanoate; 11-aminoundecanoamide, and the like. The amino acid can be a polyamide, such as, polycaprolactam. Alternatively, the polyamide can be a polyamide of the type made from a diamine and a dicarboxylic, such as poly(hexamethylene adipamide), i.e., nylon 66.

The reaction between the amino acid compound and the acid copolymer results in grafts having the formula



wherein x is from at least 1, and preferably 1 to 250, and R can comprise at least 2 methylene groups and preferably from 4 to 8 methylene groups; or be the radical of a diacid/diamine polyamide.

The average amide chain length reacted at each carboxyl site is preferably from about 1 to about 250, preferably 1 to 200, with specific embodiments including amide chain lengths of from 1 to 10, and 1 to 5 amide groups. There can be longer amide chain lengths of from 100 to 250 amide groups. Preferably, there are sufficient amide grafts, of sufficient length to confer compatibility of the copolymer reaction product and another polymer, preferably polyamide. For the purpose of the present invention amino acid compounds include cyclic amides, i.e., lactams which can be hydrolyzed to form an amino acid compound. A preferred amino acid compound has the formula $H_2NCH_2(CH_2)_nCOOH$ where n is from 0 to 12, and more preferably from 4 to 8. The most preferred amino acid is amino caproic acid or its lactam, caprolactam.

The copolymer reaction product useful in the present invention is characterized by an acid number of from about 10 to about 200, preferably about 25 to about 150, and most preferably about 25 to about 75 where the acid number is the number of milligrams of KOH used to neutralize one gram of sample. The copolymer reaction product has a Brookfield viscosity at 140°C of from about 500 to about 5,000, preferably about 500 to about 2,000, and more preferably about 500 to about 1,500. The Mettler drop point according to ASTM D-3104 can be at least about 90°C, and can be from about 90°C to about 150°C.

The present invention includes methods to make the ionomer. The preferred method is to neutralize the reaction product of a copolymer acid and an amino acid. Alternatively, the amino acid can first be neutralized with a cation containing compound and the copolymer acid can be neutralized with the salt of the amino acid.

In the preferred method of the present invention, the preparation of the above recited copolymer reaction product comprises the steps of heating a copolymer of α-olefin and an α,β-ethylenically unsaturated carboxylic acid to from about 110°C to about 300°C, preferably about 150°C to about 275°C, and more preferably about 200°C to about 275°C; adding a sufficient amount of at least one amino acid compound to react with up to 100 and preferably 50 to 100 percent of the carboxylic acid groups; and conducting the reaction of the copolymer and the amino acid compound. Preferably, the copolymer acid is preheated to from about 110°C to about 200°C and more preferably, about 125°C to about 175°C prior to reaction with the amino acid compound.

The reaction is preferably conducted under an inert atmosphere, such as nitrogen or argon, or under a vacuum. The reaction pressure is not critical and is preferably conducted at about 1 atmosphere. The reaction can be conducted continuously or in batches.

The copolymer reaction product is then neutralized by a suitable cation containing compound. The cation containing compound can be added directly to the copolymer reaction product. The cation containing material is preferably added in the form of an aqueous slurry and/or solution to enhance dispersion in the copolymer reaction product. The neutralization reaction is preferably conducted at a temperature above the melt temperature of the copolymer reaction product. Preferably, the neutralization reaction is conducted at from 140°C to 250°C, and more preferably form 175°C to 225°C. The reaction is preferably conducted at about 1 atmosphere. The reaction can be conducted continuously or in batches. The reaction is conducted until a desired degree of neutralization is attained. Preferred neutralization times are from 0.5 to 10, and more preferably from 1 to 5 hours, with 2 to 4 hours being most preferred. Preferably, the reactor has a means, such as a condenser, to remove water introduced into the reactor with the reactants, as well as water formed during the reaction.

Reaction additives to help facilitate the reaction can be added. A particularly preferred additive is acetic acid, preferably glacial acetic acid is added to help speed the reaction and make a more uniform ionomer. The acetic acid converts metal oxides, and\or hydroxides to more soluble acetates. This helps to speed the reaction and reduce agglomerates of the metal compound. Preferably, there is at least 0.1, and more

preferably from 0.1 to 1.0, and most preferably 0.2 to 0.5 percent of the reaction additive based on the weight of the copolymer reaction product. In a most preferred embodiment an aqueous slurry of the cation containing compound is combined with the reaction additive, i.e., acetic acid, and this slurry added to a reactor containing molten polymer.

Alternatively, the amino acid compound can be first neutralized with the cation containing compound. The formed amino acid metal salt can then be reacted with the copolymer acid in under the same conditions recited above for the reaction product of the copolymer acid and the amino acid.

Cations having valences of 1 to 3 can be used to neutralize the copolymer acid. Preferably, metallic cations are derived from a group of metals which can be chosen from Groups IA, IIA, IIB, IIIA and the transition elements of the Periodic Table of Elements to be used in this process. Metal cations which are preferred are sodium, potassium, magnesium, calcium, barium, zinc and aluminum cations, with sodium, zinc, calcium and magnesium cations being most preferred. Cation containing materials can be metal salts including: oxides, hydroxides, acetates, methoxides, oxylates, nitrates, carbonates and bicarbonates. Metallic salt containing materials which are illustrated in the examples discussed below include calcium hydroxide, calcium acetate, magnesium oxide and zinc acetate.

The copolymer acid can be neutralized up to 100 percent; it is perferred to neutralize the copolymer reaction product to from 15 to 100 percent, and more preferably from 25 to 100 percent neutralization of tne

total carboxylic acid groups using the process of the present invention. Carboxyl groups in the amide chain ends, as well as residual carboxyl groups on the copolymer acid, can be neutralized.

The most preferred ionomer is the ionomer of the reaction product of copolymer acid B of Table I neutralized to between about 15 and about 100 percent with sodium, zinc, magnesium or calcium cations.

The properties of the ionomer of the present invention will depend upon the starting materials, and reaction conditions as recited above. However, the ionomers of the present invention have the following typical properties. The acid number of the ionomer is lower than that of the copolymer acid. Depending on the length of the amide chain, the acid number of the ionomer can be from 5 to 25 percent lower than the copolymer acid. Typical ranges of acid number are from about 8 to about 200, preferably about 25 to 150, and more preferably from about 25 to 75, where the acid number is defined as above. The ionomer has a Brookfield Viscosity at 190°C of from 5,000 to 5,000,000, preferably 25,000 to 3,000,000, and more preferably 50,000 to 2,000,000. The ionomer has a Mettler Drop Point (ASTM D-3104) of from 90°C to 200°C, and preferably from 100°C to 150°C. For certain applications, such as dispersing pigments in polyamides, it is desirable to maintain the moisture content as low as possible, preferably below 0.5, and more preferably below 0.1 percent based on the weight of the ionomer.

The present invention also includes a polymer composition comprising at least one first polymer, and at least one second polymer comprising the above-recited ionomer. The polymer composition comprises up

to 99 percent and preferably from 1 to 99 percent of at least one first polymer and a corresponding amount of the reaction product. The reaction product can lubricate the first polymer consistent with polymer lubrication recited in U. S. Patent No. 4,412,040. The first polymer is different from the second polymer.

The first polymers include but are not limited to polyamides, such as nylon 6, nylon 66, nylon 4, nylon 11, nylon 12 and like; polyolefins, such as polyethylene and polypropylene; styrene based polymers, such as polystyrene; polyesters, such as polyethylene terephthalate and polybutylene terephthalate; ABS (copolymers of acrylonitrile, butadiene and styrene); polycarbonates; phenolic resins.

The present invention includes a pigment composition comprising from about 1 to about 50, preferably from about 5 to about 40, and more preferably from about 15 to about 35 weight percent of above-recited copolymer reaction product; from about 1 to about 50, and more preferably from about 5 to about 40 weight percent of a pigment; and from 0 to 98 weight percent of the first polymer. The pigment composition is useful in polymer compositions for molded and extruded goods, films and fibers, inks and the like. The ionomer by virtue of improved compatibility with the first polymer improves pigment dispersion consistent with improved dispersion properties recited in U. S. Patent No. 4,603,172.

Typical pigments include: titanium dioxide, zinc oxide; calcium carbonate; barite, silica and china clay; lead white; carbon black; red lead; chromate pigments; Venetian Red; Prussian blue; chromic oxide;

chrome green; cobalt blue, Phthalo blue, Phthalo green, and azo pigments.

There can be from about 0.1 to about 100 parts per hundred parts of polymer of the pigment to be dispersed. Preferably there is about 0.1 to about 50 parts of the material . Lower concentrations of from about 0.1 to about 1 part per hundred parts of polymer are useful for direct blending of low concentration materials such as colorants. Higher concentrations of from greater than about 10 parts of material can be directly introduced into the polymer. High concentrations of from about 10 to about 50 parts of material per hundred parts of polymer are useful to make master-batches, such as color concentrates, for introduction into larger quantities of the same or different polymers.

The composition can comprise conventional additives such as colorants including fillers, flame retardants, antioxidants, stabilizers, processing aids, and the like.

Typically, fillers may be selected form a wide variety of minerals, metals, metal oxides, siliceous materials, metal salts, and materials thereof. Examples of fillers include glass fibers, alumina, feldspar, asbestos, talc, calcium carbonates, clay, carbon black, quartz, novaculite and other forms of silica, kaolinite, bentonite, garnet, mica, saponite, wollastonite, etc. The foregoing recited fillers are illustrative only and are not meant to limit the scope of the fillers that can be utilized in this invention.

The ionomer of the present invention is useful in a method of flushing a pigment, of the type wherein water in an aqueous mass of pigment is flushed away

with a low molecular weight polymer. The improvement of this invention comprises flushing the aqueous mass of pigment with at least one ionomer of the present invention.

In the flushing process an aqueous pigment mass comprising finely divided pigment is in the form of a filter press cake having from about 25 to about 60, and more typically from about 30 to about 45 weight percent of pigment with a corresponding amount of water. The ionomer is added in a mixing means such as a Sigma blade mixer in amounts as recited above. Preferably, there is from about 25 to about 75, and more preferably from about 40 to about 60 percent by weight of pigment and a corresponding amount of the ionomer of the present invention. The amount of water is not included in the weight percent. The mixture is heated until the water separates from the pigment and the low molecular weight reaction product, typically at about 90°C to about 110°C, preferably, about 90°C to about 100°C, and most preferably, about 90°C to about 95°C. The process typically takes from 10 to 120 minutes and more usually 15 to 30 minutes. At this point a drop in power to the mixer will be observed. The mixing is continued for a few more minutes, typically 2 to 5 additional minutes. The water in the mixer is decanted. A vacuum can be applied to remove the balance of the water. This leaves behind a uniform blend of the pigment and the low molecular weight copolymer reaction product. The process of flushing can be conducted batchwise or continuously with filter press cake and ionomer continuously or intermittently added as the water is decanted. The process has resulted in a high quality dispersion of the pigment in the copolymer reaction product.

The flushed pigments result in pigment concentrates which can be further diluted with a first polymer of the type recited above to make pigment master batches. Such dilution can be accomplished by melt blending in a suitable melt blender, such as an extruder. The pigment master batch typically has from 40 to 80 weight percent of a first polymer and correspondingly from 20 to 60 weight percent of the pigment concentrate.

The flushed pigments in the form of pigment concentrates and in pigment master batches are useful in polymeric compositions used for fibers, molding compounds, extrusion compounds, sheets, film, and the like.

The examples set forth below illustrate the nature of the invention and the manner of carrying it out. However, the invention should not be considered as being limited to the details thereof.

EXAMPLE 1

This example illustrates the preparation copolymer reaction product useful to make the ionomer of the present invention based on an ethylene acrylic acid copolymer B of Table 1, sold by Allied-Signal Inc. as A-C® 580. This copolymer acid is reported to have an acid number of 71.9. 4361 grams of A-C® 580 were melted in a twelve liter flask. A nitrogen atmosphere was maintained at all times. The copolymer was heated to 116°C, at which time 713 gms of 6-aminocaproic acid powder was added. The mixture was continually stirred. The temperature was increased and at 149°C the evolution of water was observed. The water was allowed to distill. At 156°C water was evolving vigorously. The temperature was then maintained at 160-162°C for

three hours. After three hours at 160°C, the flask was discharged, at which point the material had an acid number of 65.1. Acid number is based on the milligrams of KOH needed to neutralize a gram of sample.

EXAMPLE 2

Pilot plant runs were made to make the copolymer reaction product useful to make the ionomer of the present invention. The copolymer acid used was A-C® 580 described above. The amino acid used was a polycaprolactam having a number average molecular weight of about 18,000, and a formic acid viscosity of about 50. Where indicated the polycaprolactam contained minor amounts of heat stabilizers. The polycaprolactam was a straight chain polymer terminated at one end with an amine group and at the opposite end with a carboxylic acid group.

A charge of 550 pounds (250 kg) copolymer acid was first premelted in a 200 gallon ($0.76m^3$) tank at 145 to 150°C under a nitrogen sweep at about 1 atm.

The molten copolymer acid was fed to a 200 gallon ($0.76m^3$), stirred reactor which had a condenser to remove moisture flashing off during the formation of the reaction product. The copolymer acid was heated to about 158 to 162°C and 155 pounds (70 kg) of the polycaprolactam was gradually added. The reactor was closed and heating continued to 260°C for eight hours with agitation.

Seven batches were made using the stabilized polycaprolactam (Runs 1-7) and two batches were made using the same polycaprolactam without stabilizers (Runs 8,9). Results are reported in Table 2 below.

TABLE 2

RUN	PARTS PER 100 AC580	RxTEMP (°C)	ACID NO. (°C)	METTLER DROP POINT (°C)	BROOKFIELD VISC. @ 140°C (Cps)
1	28.2	250	54.4	96.2	1575
2	28.2	270	54.5	97.0	1730
3	28.2	260	54.3	96.8	1520
4	22.6	250	57.1	96.6	1488
5	17.0	250	60.5	96.1	1375
6	28.2	250	54.9	95.3	1562
7	28.2	260	54.5	95.6	1542
8	28.2	260	54.9	96.1	1777
9	28.2	260	55.3	96.2	1825

EXAMPLE 3

The procedure of Example 2 was repeated resulting in a reaction product having an acid number of 51.1; a Brookfield viscosity at 140°C of 1168 centipoise; and a Mettler Drop Point of 100.7°C.

The copolymer reaction product had a uniform and white appearance. The feel was that of a hard waxy material. As indicated by the relatively low Mettler Drop Point values, this material is readily melt blendable with other polymers.

EXAMPLE 4

The pilot scale Runs in Example 2 were neutralized with zinc oxide to form zinc ionomer.

The copolymer reaction product in each of the Runs of Example 2 were cooled to 220°C. An aqueous slurry of zinc oxide was prepared from zinc oxide powder, Kadox 920, supplied as a fine powder by the New Jersey Zinc Company. The slurry contained 27 pounds (12.2 kg) of zinc oxide, 243 pounds (110.2 kg) of water, and 1.1 pounds (0.5 kg) of glacial acetic acid. The slurry was charged to the reactor at a constant rate, with agitation, over a period of 3 hours. Water coming off

from the reactor was removed. The reactor was continually monitored to assure that no excessive frothing occurred. Upon completion of the addition of the zinc oxide slurry, agitation was continued and the temperature maintained at from 220°C to 224°C for three hours. This stirring period was used to dissolve the zinc oxide and to remove moisture. The desired moisture content is a maximum of 0.1%. Upon completion of the reaction the ionomer was removed. The results of Runs 1 to 9 from Example 2 converted to ionomer are summarized in Table 3 below.

TABLE 3

RUN	Rx TEMP. (°C)	BROOKFIELD VISC. @ 190°C (cps)	ASTM-D-5 DECI MM	EXTRUSION EVALUATION
1	200	47,000	0.6	Fair
2	220	240,000	.8	Very Good
3	220	220,000	1.2	Very Good-
4	220	45,500	.8	Fair
5	220	38,200	1.2	Good
6	220	180,000	.7	Good
7	220	220,000	1.2	Very Good
8	220	102,000	.9	
9	220	100,00	1.0	

EXAMPLE 5

The compatibility of the ionomer of the present invention with fiber grade nylon was indicated by its ability to be melt blended and satisfactorily extruded as a polymer composition. A mixture of 30% by weight of the ionomer Runs 1-7 of Example 2 was made with 70% by weight of fiber grade nylon 6, supplied by the Firestone Tire and Rubber Corp. as Firestone C-200, in

in pellet form. The mixture was extruded through a 1-1/4 inch, single screw Brabender extruder, having a barrel length to diameter ratio of 24 to 1, at 250°C with a 7.5 pounds per hour feed rate. The sample extrusion performance was based on the overall extrudability of a 1/8 extruded strand. The integrity, appearance, and observed melt strength were considered. Overall results are summarized in Table 3 above.

EXAMPLE 6

This example illustrated a typical pigmented composition. The pigment used was phthalocyanine (Phthalo Blue) from Sun Chemical Company, supplied as press cakes which were 30-40 weight percent pigment and a corresponding amount of water.

The amount of pigment in the press cake was determined and a mixture was made based on equal weights of the ionomer of the present invention and pigment, excluding the weight of the water.

The ionomer used was of the type made in Examples 1-3. The ionomer was heated in a Sigma Blade Mixer until it melted (about 100°C). Half of the press cake was fed into the mixer and after 15 to 20 minutes, the water from the press cake breaks (comes out of press cake) and was poured off. The balance of the press cake was added and after another 15 to 20 minutes, the balance of the water breaks and was poured off. The water initially appeared blue and as the pigment was wetted by the ionomer, the water cleared and was decanted. The mixture cooled and the pigmented composition was a brittle plastic hard wax. The composition was broken into pellet size pieces suitable for extrusion. The pigmented composition was a uniform deep blue color having 50 weight percent ionomer and 50 weight percent pigment.

EXAMPLE 7

Pigment concentrates of the type made in Example 6 were extruded with fiber grade nylon at 50 percent by weight resulting in a pigment master batch composition having 25% by weight pigment. The master batch was extruded with fiber grade nylon at levels of 0.5 and 0.25 weight percent pigment and spun into the resulting carpet fiber. The fiber was satisfactory and had uniform and excellent color quality.

While exemplary embodiments of the invention have been described, the true scope of the invention is to be determined from the following claims.

What is claimed is:

1. An ionomer of a copolymer reaction product of (A) and (B) where:

(A) is a copolymer acid of an α-olefin and an unsaturated carboxylic acid having a number average molecular weight between 500 and 6,000 and, c h a r a c t e r i z e d in that;

(B) is the reaction product of an amino acid compound wherein the amino acid compound is derived from an amino acid monomer of the formula $H_2NCH_2(CH_2)_nCOOH$ where n is from 0 to 12,

where up to 100 percent of the carboxylic acid groups of (A) are reacted with (B), and

where (B) constitutes up to 50% of the sum total of the weights of (A) and (B), and

where the copolymer reaction product of (A) and (B) is up to 100 percent neutralized with at least one cation selected from the group of metallic cations having a valence of 1 to 3.

2. The ionomer of claim 1 further c h a r a c t e r i z e d in that:

the α-olefin of (A) is ethylene or propylene.

3. The ionomer of claim 1 further c h a r a c t e r i z e d in that:

(B) is derived from an amino acid monomer which is aminocaproic acid or caprolactam.

4. The ionomer of claim 1 further c h a r a c t e r i z e d in that:

the carboxylic acid of (B) is an α,ß-ethylenically unsaturated carboxylic acid selected from; acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid or mixtures thereof.

5. The ionomer of any preceeding claim further characterized in that:
the amino acid compound (B) has an average chain length at each carboxyl site of 1 to 250 amino acid monomer units.

6. The ionomer according to preceeding claim 1 or 5 characterized in that:
the amino acid is a polyamide.

7. The ionomer according to claim 1, 5 or 6 characterized in that:
the cation is a metallic cation selected from the group consisting of Groups IA, IIA, IB, IIIA and the transition elements of the Periodic Table of Elements.

8. The ionomer according to claim 1 characterized in that:
the cation is a metallic cation selected from the following group of compounds: metallic oxides, metallic hydroxides, metallic oxylates, metallic acetates, metallic bicarbonates, metallic methoxides, metallic nitrates.

9. A composition which includes an ionomer according to any preceeding claim and which further includes a pigment.

10. The ionomer according to any of preceeding claims 1 - 8 used to flush an aqueous mass of pigment.

11. The ionomer reaction product according to any preceeding claim produced by a process which includes the process steps of:

adding a sufficient amount of (B) to react up to 100 percent of the carboxylic acid groups of (A),

reacting the sufficient amount of (B) with (A) to form a copolymer reaction product therefrom,

neutralizing up to 100 percent of the carboxylic acid groups of the copolymer reaction product with at least one metallic cation selected from the group consisting of: Groups IA, IIA, IB, IIIA of the Periodic Table of Elements, the transition elements of the Periodic Table of Elements, one or more metallic cations selected from the following group of compounds: metallic oxides, metallic hydroxides, metallic oxylates, metallic acetates, metallic bicarbonates, metallic methoxides, metallic nitrates.

12. The ionomer according to claim 10 which is made by a process which further includes the process step of:

conducting the neutralization of the up to 100 percent of the carboxylic acid groups at a process temperature higher than the melting temperature of the copolymer reaction product.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/07359

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 F 8/44, C 08 L 23/26, C 09 B 67/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 F; C 08 L; C 09 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP, A1, 0342244 (DU PONT - MITSUI POLYCHEMICALS CO., LTD.) 23 November 1989, see the whole document	1-8
Y		9-12
	--	
Y	GB, A, 915453 (THE GEIGY COMPANY LIMITED) 16 January 1963, see the whole document	9-10
	--	
Y	US, A, 4381376 (ALBEE, JR. ET AL) 26 April 1983, see the whole document	11-12
	--	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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

"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

IV CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
27th March 1991	22. 04. 91
International Searching Authority	**Signature of Authorized Officer**[14]
EUROPEAN PATENT OFFICE	Natalie Weinberg

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	Chemical Abstracts, volume 102, no. 4, 28 January 1985, (Columbus, Ohio, US), see page 38, abstract 25581c, & JP,, 59157122 (Mitsui Polychemicals Co.,Ltd.) 1984 --	1-8
X	Chemical Abstracts, volume 106, no. 4, 26 January 1987, (Columbus, Ohio, US), Hirasawa, Eisaku et al: "Heat-resistant adhesion and melt rheology of the polymer complex between ionomer and polyamide oligomer", see page 22, abstract 19352v, & Nihon Reoroji Gakkaishi 1986, 14(3), 113- 122 --	1-8

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/07359

SA 43379

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/02/91
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0342244	23/11/89	AU-D-	2729988	14/06/89
		WO-A-	89/04853	01/06/89
GB-A- 915453	16/01/63	CH-A-	391293	00/00/00
		NL-C-	124227	00/00/00
		NL-A-	264614	00/00/00
US-A- 4381376	26/04/83	CA-A-	1183864	12/03/85
		EP-A-B-	0054761	30/06/82