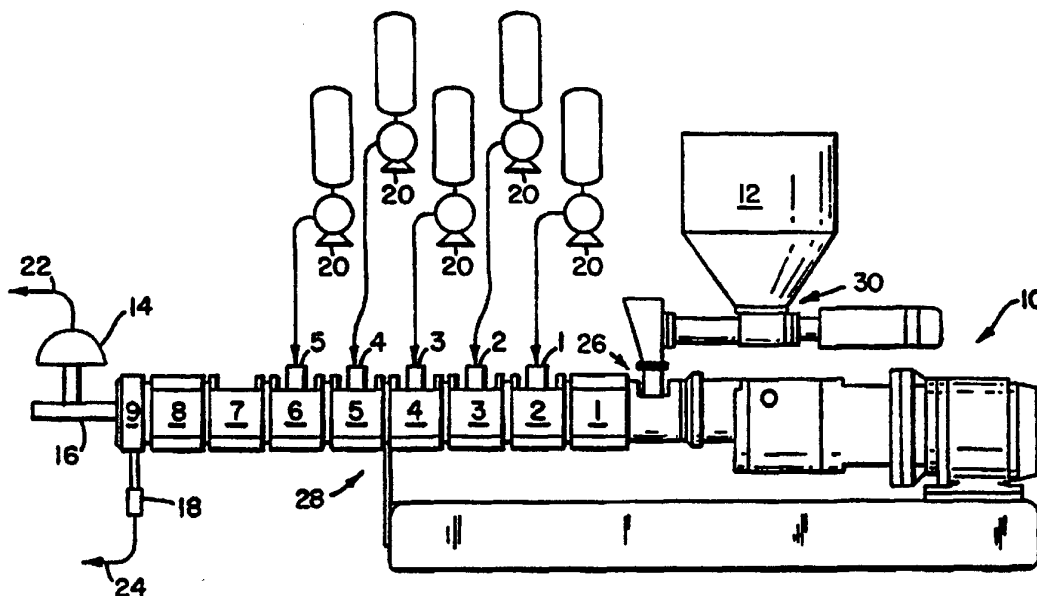




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(54) Title: LOW MOLECULAR WEIGHT GRAFTED RANDOM ETHYLENE/PROPYLENE COPOLYMER OF HIGH ACID NUMBER AND METHOD FOR PREPARATION THEREOF



(57) Abstract

Disclosed is a dispersible low molecular weight grafted random ethylene/propylene copolymer that forms very stable aqueous dispersions. The random ethylene/propylene copolymer used to prepare the grafted random ethylene/propylene copolymer contains at least 0.5 but less than 7 weight percent ethylene randomly distributed in polypropylene. The grafted random ethylene/propylene copolymer of high acid number is produced by the reactive extruding of reactants in a screw extruder.

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LOW MOLECULAR WEIGHT GRAFTED RANDOM ETHYLENE/PROPYLENE
COPOLYMER OF HIGH ACID NUMBER AND METHOD FOR PREPARATION
THEREOF

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Field of the Invention

The present invention relates to new low molecular weight highly grafted random ethylene/propylene copolymers of high acid number containing low amounts of ethylene capable of forming stable aqueous dispersions. The present invention also relates to a process of producing the dispersible low molecular weight grafted random ethylene/propylene copolymers in a screw extruder.

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Background of the Invention

Grafting of high and low molecular weight polymers has been reported often in the literature, see for example, the polymer text book "Polymer Chemistry" by M. P. Stevens (Addison-Wesley), 1975, PP196-202. Maleation is one type of grafting. For example, maleation of polypropylenes progresses easily to higher acid numbers with free radical initiation (see U.S. Patents 3,414,551, 3,480,580, 3,481,910, 3,642,722, 3,746,676, 3,932,368 and 4,613,679). The molecular weight of the products of such reactions are lower than that of the starting polypropylene due to accompanying degradation reactions. On the other hand, direct maleation of polyethylenes results in cross-linking which increases the molecular weight of the polymer, see for example, "Journal of Applied Polymer Science", 44, 1941, N. G. Gaylord et al (1992); and U.S. Patents 4,026,967, 4,028,436, 4,031,062, 4,071,494, 4,218,263, 4,315,863, 4,347,341, 4,358,564, 4,376,855, 4,506,056, 4,632,962, 4,780,228, 4,987,190, and 5,021,510]. Free radical initiated maleation of polypropylenes and polyethylenes

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in continuous processes is limited to very low levels of grafting and low acid numbers such as below 4 percent grafting. U.S. Patent 4,762,890 discloses the grafting of polymers in a twin screw extruder. This technique is effective for high molecular weight polymers; however, the grafting is only up to 2 weight percent. U.S. Patent 4,639,495 discloses the grafting using peroxide initiators however, the percent grafting is only obtainable up to 3 weight percent.

Grafted polyolefins are suitable for use as compatibilizing agents and adhesion promoters between polymers and fillers. The increased acid number and percent grafting of polyolefins would improve these properties but yet would not render them useful in emulsions. This is true for continuously extruder grafted polypropylene, since even at high acid number, this type of homopolypropylene is not dispersible or emulsifiable in water.

In light of the above it would be very desirable to produce highly grafted polypropylene compositions capable of forming stable aqueous dispersions or emulsions.

Summary of the Invention

The process for the production of a dispersible low molecular weight grafted ethylene/propylene copolymer according to the present invention comprises:

- (a) mixing, at an elevated temperature of 160 to 300°C, in an extruder 0.1 to 20 weight percent of a free radical initiator, 0.1 to 30 weight percent of an ethylenically unsaturated polycarboxylic acid, anhydride or ester thereof and the remainder of a random ethylene/propylene copolymer containing at

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least 0.5 but less than 7 weight percent ethylene, and

(b) extruding the resultant molten grafted random ethylene/propylene copolymer.

5 The present invention is also directed to a composition that comprises a grafted random ethylene/propylene copolymer containing 0.5 to less than 7 weight percent ethylene and at least 5 weight percent grafted maleic anhydride having an acid number of at
10 least 28. This composition can also be incorporated into an aqueous dispersion that is stable.

Brief Description of the Drawing

15 Fig. 1 illustrates a preferred screw extruder apparatus for the production at elevated pressures of the dispersible low molecular weight grafted ethylene/propylene copolymer of high acid number.

Detailed Description of the Invention

20 The applicants have unexpectedly discovered a dispersible low molecular weight grafted random ethylene/propylene copolymer of high acid number. Applicants have unexpectedly discovered that by the random incorporation of a minor amount of ethylene into
25 polypropylene, a dispersible grafted random ethylene/propylene copolymer of high acid number can be produced in a grafting reaction. This grafted copolymer is able to form a stable aqueous dispersion. This is unexpected since a homopolypropylene produced in the
30 same manner, even at the same high acid number, does not form a stable aqueous dispersion.

35 The aqueous dispersions of the low molecular weight grafted random ethylene/propylene copolymers are very stable and are useful in adhesion promotion, floor polishes, and coupling aids.

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As discussed above the process for the production of a dispersible low molecular weight grafted ethylene/propylene copolymer according to the present invention comprises :

- 5 (a) mixing, at an elevated temperature of 160 to 300°C, in an extruder 0.1 to 20 weight percent of a free radical initiator, 0.1 to 30 weight percent of an ethylenically unsaturated polycarboxylic acid, anhydride or ester
10 thereof and the remainder of a random ethylene/propylene copolymer containing at least 0.5 but less than 7 weight percent ethylene, and
- 15 (b) extruding the resultant molten grafted random ethylene/propylene copolymer.

The process according to the present invention is conducted at an elevated temperature of 160 to 300°C. This elevated temperature is preferably 170 to 280°C, more preferably 170 to 250°C, with an elevated
20 temperature of 175 to 230°C being most preferred. At temperatures much below 160°C the polymer is too resistant to flow. At temperatures much above 300°C most peroxide half lives are too short to be useful.

In the process according to the present invention
25 the free radical initiator is preferably a peroxide, more preferably a dialkyl peroxide. Suitable examples of dialkyl peroxides include ditertiary butyl peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide, p-methane peroxide, 2,5-dimethyl-2,5-ditertiary butyl
30 peroxyhexene, and p-methane hydroperoxide with ditertiary butyl peroxide being most preferred. The peroxides are generally more preferred, particularly ditertiary butyl peroxide due to availability and superior performance.

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In the process according to the present invention the amount of free radical initiator is 0.1 to 20 weight percent, preferably 1 to 20 weight percent, more preferably 5 to 15 weight percent, with a weight percent of free radical initiator of 1 to 14 weight percent being most preferred. Amounts much below 0.1 weight percent free radical initiator are not sufficient to activate the graft monomer to induce grafting of the polyolefin. Amounts much above 20 weight percent free radical initiator are simply excess and tend to degrade the polyolefin excessively.

In the process according to the present invention the ethylenically unsaturated polycarboxylic acid, anhydride, or esters thereof is present in a concentration of 0.1 to 30 weight percent, preferably 1 to 25 weight percent, more preferably 5 to 25 weight percent, with a weight percent of 7 to 20 being most preferred. As with the free radical initiator, the ethylenically unsaturated polycarboxylic acid, anhydride or ester thereof should not be much below 0.1 weight percent otherwise, sufficient grafting of the polyolefin is not obtained. Amounts much above 30 weight percent are excess and do not significantly increase the performance properties of the products.

Examples of suitable ethylenically unsaturated polycarboxylic acid, anhydride or esters include the acid, anhydride or esters of the group consisting of maleic, citraconic, fumaric, 2-methylmaleic, 2-chloromaleic, 2-methoxycarbonylmaleic, 2,3-dimethylmaleic, and 2,3-dichloromaleic, with maleic anhydride being most preferred.

The amount of polyolefin present in the present invention is the amount that remains after the other components are calculated but is preferably 70 to 98 weight percent, more preferably 70 to 95 weight percent,

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with a weight percent of 75 to 90 being most preferred. At concentrations much below 70 weight percent polyolefin the grafting is not as efficient, whereas at concentrations much above 98 weight percent there is not sufficient free radical initiator or grafting comonomer to significantly graft the polyolefin.

The random ethylene/propylene copolymer treated according to the present invention to form the novel grafted random ethylene/polypropylene copolymer of high acid number contains at least 0.5 but less than 7 weight percent ethylene, preferably at least 0.8 to 6.5 weight percent, more preferably 1 to 6 weight percent, with a weight percent of ethylene of 2 to 6 being most preferred. Random ethylene/propylene copolymers containing less than 0.8 weight percent ethylene behave too much like propylene in the grafting process and degrade to a significant extent. Random ethylene/propylene copolymers containing 7 or more weight percent ethylene be have too much like polyethylene in the reactive grafting process and tend to crosslink. It is the concentration of ethylene within this unexpectedly narrow range, randomly distributed in the ethylene/propylene copolymer, that permits the production of a grafted ethylene/propylene copolymer of high acid number that forms stable dispersions. It is completely unexpected that the random addition of a few minor percent of ethylene into polypropylene could have such a dramatic effect on the quality of the emulsion or dispersion made from the reactively processed or grafted material.

The process of producing the grafted random ethylene/propylene copolymer according to the present invention is preferably conducted in a screw extruder having a pressurized control valve to maintain an elevated pressure in the barrel due to the low viscosity

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of the grafted copolymer. This preferred process and apparatus are disclosed and claimed in the application identified by attorney docket number 68621 and filed the same date herewith. The preferred apparatus used according to the process of the present invention comprises a screw extruder having a heated elongated chamber or barrel containing a screw feed means, a feed opening at the first end of said chamber, and a pressure control valve at the second end of said chamber having a means to maintain the pressure within said chamber at 30 to 400 psig, and a means to permit molten polymer to exit the chamber, wherein said screw means operates so as to feed material from said feed opening to said pressure control valve and wherein said chamber has a plurality of injection ports along said chamber for injecting material into said chamber.

This process is preferably conducted in a screw extruder as illustrated in Figure 1, more preferably a twin screw extruder. Injection ports 1, 2, 3, 4, and 5 are located along the barrel or chamber 28 of screw extruder 10. Feed hopper/feed apparatus 12, feeds particulate polyolefin via a calibrated conveying means 30 into screw extruder 10 to a throat or feed opening 26 at a first end of the chamber 28. The polyolefin then proceeds in the molten state through zones 1, 2, 3, 4, 5, 6, 7, 8, and 9 out of the die opening 16 past the pressure control valve 14 out of the second end of chamber 28. The ethylenically unsaturated carboxylic acid, anhydride or ester thereof such as maleic anhydride, is pumped into and through one or more of the injection ports 1, 2, 3, 4, or 5 into the zones of the chamber 28 by reagent injection pumps 20. In this same manner, the free radical initiator, usually peroxide such as ditertiary butyl peroxide, is fed through one or more of the injection ports in a 50/50 solution of

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peroxide to hydrocarbon solvent by reagent injection pumps 20. In the examples the amount of the hydrocarbon solvent is not counted when calculating the amount of peroxide. The elevated pressure of 30 to 400 psig is maintained in the chamber 28 of the extruder 10 by means of the pressure control valve 14 that is actuated by the current to pneumatic (IP) converter (not shown) by measuring the pressure within zone 9 with the pressure transducer 18 with connection 24 to a pressure indicator. The pressure is controlled by a standard controller.

Another key element of the preferred process of the present invention is the use of reverse kneading blocks in the screw extruder apparatus (not shown) close to the throat or feed opening of the extruder. These kneading blocks serve as a physical barrier to the pressured extruder additives (eg volatile solvent, peroxide, or maleic anhydride). These kneading blocks prevent the volatile reactants from entering the throat of the extruder. The reverse kneading blocks appear to be more effective than reverse conveying elements at forming a barrier for the pressured volatile reactants. Since resin grade ethylene/propylene copolymers are used as feeds, the viscosity of the melt stream is sufficient for the reverse kneading blocks to adequately prevent the blow by of the reactants out of the feed throat.

With the use of the preferred apparatus having the pressurized grafting process, the resulting molten grafted ethylene/propylene copolymer can have a very low viscosity as it exits the chamber through the die of the extruder. This viscosity can be below 3000 cP at 190°C. It is this low viscosity ethylene/propylene copolymer that requires the pressure control valve and pressure control mechanism to maintain the reactants in the extruder. This apparatus and process is very useful for

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the efficient production of highly grafted ethylene/propylene copolymers to high acid number polymers that have low viscosities. The molten grafted ethylene/propylene copolymer preferably has a viscosity of less than 2000 cP at 190°C, more preferably less than 1000 cP at 190°C, with a viscosity of less than 600 cP at 190°C being most preferred.

The elevated pressure maintained in the extruder by way of the pressure control valve and feed back mechanism is maintained at a pressure of at least 30 psig, preferably 30 to 400 psig, more preferably 50 to 400 psig, even more preferably 75 to 200 psig with a pressure of 100 to 175 psig being most preferred. At pressures much below 30 psig too much of the reactants blow past the pressure control device or valve out the die and are not maintained in the chamber with the polyolefin to react to a significant extent at high efficiencies. At pressures much above 400 psig and sometimes 200 psig, depending upon kneading block temperature and polymer type, volatile reactants back up in the throat. With the judicious choice of kneading block temperature and configuration this can be avoided.

The process according to the present invention produces a novel highly grafted random ethylene/propylene copolymer of high acid number having greater than 5 weight percent comonomer grafted thereon and an acid number that is relatively high, higher than 28. The amount of grafted comonomer is preferably greater than 7 weight percent, with a weight percent of grafted comonomer of greater than 10 being most preferred. The acid number also corresponds to the amount of grafting, 5 weight percent equaling an acid number of 28. The higher the amount of grafting and the higher acid numbers are more preferred, thus, an acid number greater than 35 is more preferred, with an acid

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number greater than 44 being most preferred. Low acid numbers and low grafting percent of comonomer below what is stated is less preferred in that the desired property of emulsifiability producing a stabilized emulsion is dramatically affected. The upper amounts of grafting and acid number can be as high as is practical and are only limited by the capacity of the apparatus, such as the extruder.

Emulsions produced from the grafted random ethylene/propylene copolymer of the present invention contain (1) 10 to 30 weight percent of the grafted copolymer, (2) a minor amount up to 15 weight percent of a surfactant, and (3) 60 to 90 weight percent water.

The terms dispersion and emulsion are used interchangeably herein; however, if the grafted random ethylene/propylene copolymer is considered a solid then the term dispersion may be more appropriate.

The grafted random ethylene/propylene copolymer waxes produced according to the present invention are formed into emulsions according to the preferred process comprising mixing at an elevated temperature under neutral or basic conditions 10 to 30 weight percent of the grafted random ethylene/propylene copolymer wax, a minor amount up to 15 weight percent of a surfactant, and 60 to 90 weight percent water for a period of time sufficient to produce an emulsion of the grafted random ethylene/propylene copolymer wax.

The temperature at which the emulsion is prepared is preferably between 160 and 180°C, more preferably between 165 and 178°C with a temperature of 170 to 175°C being most preferred. The emulsion is prepared at neutral or basic pH. However, it is preferred that the pH be between 7 and 10, preferably between 9 and 10, with a pH between 9.5 and 9.7 being most preferred.

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The emulsions prepared according to the present invention generally contain 10 to 30 weight percent grafted random ethylene/propylene copolymer wax, preferably 20 to 27 weight percent, with a weight percent of grafted random ethylene/propylene copolymer wax of 21 to 23 weight percent being most preferred. Amounts of grafted random ethylene/propylene copolymer wax much above 30 weight percent and much below 10% are not as useful in applications.

The amount of surfactant used in the emulsions of the present invention can be as high as 15 weight percent but is preferably between 5 and 10 weight percent with a weight percent of 6 to 8 being more preferred. Amounts much over 15 weight percent are not needed to render the amount of grafted random ethylene/propylene wax dispersible in the water. However, minor amounts below 3 weight percent do not adequately disperse the grafted random ethylene/propylene wax. Any surfactant that forms a dispersion or emulsion of the present system would be useful herein. Examples of suitable surfactants include Igepal CO-630, Igepal CO-710, nonylphenyl, and ethoxylated alcohols such as Tergitol 15-S-9 and Tergitol 15-S-12.

The amount of water generally varies, depending upon the desired concentration, but is generally between 60 and 90 weight percent, preferably between 65 and 80 weight percent, with a weight percent of 70 to 79 weight percent water being most preferred. A base is generally added to the emulsion to render the aqueous solution basic. Amounts of base generally range from below 1 to 3 weight percent and are generally selected from standard bases such as tertiary amines and potassium hydroxide. Amounts of base can range from 0.05 to 3 weight percent, but are preferably 0.75 to 1.5 weight

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percent, more preferably 0.8 to 1.2 weight percent, with 1 weight percent base being most preferred.

The emulsion can also contain other ingredients such as bleaching agents or whitening agents such as sodium metabisulfite in concentrations as high as 0.34 weight percent. The bleaching agent is preferably in the range of 0.1 to 0.34 weight percent, more preferably 0.15 to 0.34 with an amount of bleaching agent of 0.29 to 0.31 being most preferred. The bleaching agent or whitening agent is generally not needed. However, minor amounts often do decrease the color.

The following examples are intended to illustrate the present invention but are not intended to limit the reasonable scope thereof.

Examples

Comparative Example 1

A 100 melt flow rate crystalline polypropylene, available as Tenite P9-018 from Eastman Chemical Company (Eastman) was fed to a 43 L/D 25 mm co-rotating twin-screw extruder (see Figure 1) at the rate of ten pounds/hour. Ditertiarybutyl peroxide was fed into zones 2, 4, 5, and 6 at the rates of 0.25, 3.0, 2.5 and 2.5 pph relative to polymer feed respectively. Molten maleic anhydride was fed into zone 3 at the rate of 20 pph. The temperature of zone 1 was 240°C while zones 2, 7 and 8 were 220°C. All other zones were at 210°C. The screw speed was set at 300 rpm and the back pressure control valve was set at 125 psi. The product at these conditions had a 69.7 acid number and a viscosity at 190°C of 843 cP. This is an 82.4 percent conversion of maleic anhydride. A nonionic pressure emulsion consisting of 40 g of grafted polymer, 12 g of Igepal CO-630, 6.5 g KOH and 137 ml of water was prepared at

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175°C in a 300 ml Parr autoclave. After cooling with ice water the contents of the reactor was poured out to reveal a heavy residue on the reactor walls. The liquid phase was filtered through cheese cloth and bottled.

5 After a week a heavy cream was present.

Example 2

10 An ethylene/propylene random copolymer (available as Tenite P5-006 from Eastman) containing 2.3 weight percent ethylene and having a melt flow rate of 7 g/10 minutes was maleated at 220°C on a 43 L/D 25 mm twin-screw extruder (see Figure 1) at 10 lbs/hr and 250 rpm. The zone 1 temperature was 250°C, zone 2 temperature was 240°C and zone 3 temperature 230°C. The remaining 5
15 zones were set to 220°C. Maleic anhydride was fed to zone 3 at a rate of 20 pph. Ditertiarybutyl peroxide was fed to zones 2, 4, 5, and 6 at rates of 0.25, 3.0, 3.0 and 3.0 pph with a back pressure of 125 psi. The product had a 60.6 acid number. The viscosity was 1,418
20 cP at 190°C. The ring and ball softening point (RBSP) was 150°C. This is a 71.7 percent conversion of maleic anhydride. A nonionic pressure emulsion consisting of 40 g of grafted copolymer, 12 g of Igepal CO-630, 5.6 g of KOH and 138 g of water was made at 175°C as in
25 Example 1. The emulsion was homogeneous and left no residue on the reactor walls. After 2 months no cream or grit had formed in the emulsion.

Example 3

30 A random ethylene propylene copolymer containing 5.5 weight percent ethylene and having a melt flow rate of 0.5 (available as Tenite P5-001 from Eastman) was maleated to 45.7 acid number in a 43 L/D 25 ml co-rotating twin-screw extruder (see Figure 1). Barrel
35 zone 1 temperature was 250°C, zone 2 was 240°C, zone 3

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was 230°C and zones 4, 5, and 6 were 200°C. Zones 7, 8, and 9 temperatures were 220°C. Copolymer was fed at 10 pounds/hour and maleic anhydride was fed at 11 pph into zone 3. Ditertiarybutyl peroxide was fed into zones 2, 4, 5 and 6 at 0.25, 2.3, 2.3 and 2.3 pph respectively. The screw speed was 200 rpm and the back pressure control valve was set at 150 psi. The product viscosity was 1,520 cP and RBSP was 139°C. The acid number of 45.7 represents a 93.0 percent conversion of maleic anhydride. The nonionic pressure emulsion was made from 40 g of copolymer, 12 g of CO-630, 4.3 g of KOH and 131 g of water at 175°C as in Example 1. The emulsion was free of solid matter and homogeneous. The emulsion was unchanged after one month.

15

Example 4

A random ethylene propylene copolymer containing 3.2 weight percent ethylene (available as Tenite P5-011 from Eastman) was maleated at the rate of 10 pounds/hour at 250 rpm and 150 psi back pressure on a 43 L/D 25 mm twin-screw extruder (see Figure 1). The temperature of zone 1 was 250°C, zone 2 was 240°C, and zone 3 was 230°C. Zones 4, 5, and 6 temperatures were 200°C while zones 7, 8, and 9 temperatures were 220°C. Maleic anhydride was fed to zone 3 at the rate of 11 pph. Ditertiarybutyl peroxide was fed to zones 2, 4, 5, and 6 at the rate of 0.25, 1.6, 1.6 and 1.6 pph respectively. The product had an acid number of 41.4, a viscosity of 1,073 cP at 190°C and a RBSP of 143°C. The maleic anhydride conversion was 89.8 percent. The nonionic pressure emulsion was prepared at 165 C from 40 grams of wax, 12 grams of Igepal CO-630, 3.9 grams of KOH and 130 mls of water. The emulsion left only a trace of solid in the reactor and was stable for at least three weeks.

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Example 5

A random ethylene propylene copolymer having a 1.9 melt flow rate containing 2.3 weight percent ethylene (available as Tenite P5-006 from Eastman) was maleated at the rate of 10 pounds/hour with a screw speed of 200 rpm (in the same extruder used in all the examples). Barrel zone 1 was at 250°C, zone 2 was at 190°C, zone 3 was at 230°C and zones 4 through 8 were at 220°C. Ditertiarybutyl peroxide was injected into zones 3, 5, 6, and 7 at the rates of 0.25, 3.0, 3.25 and 3.25 pph respectively. Molten maleic anhydride was injected into zone 4 at the rate of 16.6 pph. The back pressure control device was set to 145 psi. The product had a viscosity of 670 cP at 190°C and an acid number of 70. The maleic anhydride conversion was 97.7 percent. The nonionic pressure emulsion was made from 40 g of copolymer, 12 grams of CO-630, 6.5 g of KOH and 130 g of water as above. The emulsion was homogeneous and stable for at least 5 weeks.

Comparative Example 6

An 11 melt flow rate crystalline polypropylene available from Eastman Chemical as Tenite P4-007, was fed to a 43 1/d 25 mm co-rotating twin screw extruder at a rate of ten pounds/hour. The pressure control device was not used and the pressure at the exit die of the extruder was less than 25 psig. Ditertiarybutyl peroxide was fed into zones 2, 3, 4, and 6 at the rate of 0.5, 1.5, 1.0 and 5.3 pph relative to the polymer feed respectively. Molten maleic anhydride was fed into zone 5 at a rate of 10 pph. The temperatures of zone 1 was 240°C while zones 2 through 8 were 230°C. The screw speed was set at 200 rpm. The product made at these conditions had a 25 acid number and a viscosity at 190°C of 500 cp. This is a 48 percent conversion of maleic

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anhydride. All attempts to prepare a nonionic direct pressure emulsion were unsuccessful.

Example 7

5 An ethylene propylene random copolymer (available as Tenite P5-006 from Eastman (2.3% ethylene) was extruder grafted with maleic anhydride without using the back pressure control valve. Extruder pressure measured at the die was 25 to 30 psig. Polymer feed rate was 9
10 pounds per hour and screw speed was 250 rpm.. Zone 1 and 2 temperatures were at 200°C and zones 3 through 8 were at 220°C. Ditertiarybutyl peroxide was fed into zones 3, 5, 6 and 7 at the rate of 0.25, 2.5, 2.5 and 2.0 pph. Maleic anhydride was fed into zone 4 at the rate of 11
15 pph. The product after the first pass through the extruder had a viscosity of 848 cPs and an acid number of 34.9. This is a 63 percent conversion of maleic anhydride. A nonionic emulsion was made as above at 165°C from 40 grams of wax, 12 grams of Igepal CO-630,
20 3.9 grams of KOH and 141 mls of water. The resulting mixture was lumpy and not homogeneous. It did not emulsify. This material was not usable in an emulsion but was less brittle than the homopolypropylene and is useful as a melt blended brittle compatibilizing agent.

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Comparative Example 8

A crystalline polypropylene (available as Tenite P4-026 from Eastman) with a melt flow rate of 1.2 grams/10 minutes, was extruder grafted with maleic anhydride at 150 psi back pressure, 250 rpm screw speed
30 on a 43 L/D twin screw extruder at the rate of 10 pounds/hour. Extruder zones 1, 2 and 8 were at 200°C and zones 3 through 7 were at 220°C. Maleic anhydride was injected into zone 4 at the rate of 14 pph.
35 Ditertiarybutyl peroxide was injected into zones 3, 5, 6

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and 7 at the rates of 0.25, 3.0, 3.0 and 3.0. The product had an acid number (after devolatilization) of 59 and a viscosity of 503 cps at 190°C. This is a 93.9 percent conversion of maleic anhydride. A nonionic pressure emulsion was prepared as above at 165°C using 5 40 g of wax, 12 g of Igepal CO-630, 5.47 g of KOH and 133 ml of water. The emulsion separated after three days.

10 Example 9

An ethylene/propylene random copolymer (available as Tenite P5-006 from Eastman) containing 2.3 weight percent random ethylene was extruder grafted under similar conditions as in Example 8 above. All 15 temperatures and ditertiarybutyl peroxide feed rates were the same. The screw speed was 250, back pressure was 150 psig and the polymer feed rate was 10 pounds per hour. The maleic anhydride feed rate was 15 pph. The product had a viscosity of 725 cps at 190°C an acid 20 number of 61.1. This is a 92.7 percent conversion of maleic anhydride. The nonionic pressure emulsion of the wax was made as above at 165°C from 40 grams of wax, 12 grams of Igepal CO-630, 5.7 grams of KOH and 134 mls of water. The emulsion was stable for at least 7 days.

25

Example 10

The unstripped extruder material of Example 7 was granulated and reextruded. The peroxide feed rates and temperatures were the same as the first extruder pass. 30 The pressure was 7 to 10 psig. The polymer feed rate was 8 pounds per hour. At the same maleic anhydride feed rate the acid number after the second pass was 89.6 and the viscosity was 338 cPs at 190°C. This is a 65.0 percent conversion of maleic anhydride. The nonionic 35 emulsion prepared as above at 165°C from 40 grams of

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wax, 12 grams of Igepal CO-630, 8.3 grams of KOH and 141 mls of water was homogeneous and stable.

5 This method of extruder grafting, two passes through the extruder without a pressure control valve, can make the preferred novel composition, however, it is time consuming and not a very economical method of making high acid number low viscosity grafted ethylene/propylene waxes. Pressure control enables the grafting reaction to be complete in one pass.

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CLAIMS

We claim:

1. A process for the production of a dispersible low molecular weight grafted ethylene/propylene copolymer comprising:
 - (a) mixing, at an elevated temperature of 160 to 300°C, in an extruder 0.1 to 20 weight percent of a free radical initiator, 0.1 to 30 weight percent of an ethylenically unsaturated polycarboxylic acid, anhydride or ester thereof and the remainder of a random ethylene/propylene copolymer containing at least 0.5 but less than 7 weight percent ethylene, and
 - (b) extruding the resultant molten grafted random ethylene/propylene copolymer.
2. The process according to Claim 1 wherein said elevated temperature is 170 to 280°C.
3. The process according to Claim 1 wherein said concentration of said free radical initiator is 5 to 15 weight percent.
4. The process according to Claim 1 wherein said free radical initiator is a peroxide selected from the group consisting of ditertiarybutyl peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide, p-menthane peroxide, 2,5-dimethyl-2,5-ditertiary butyl peroxyhexene, and p-methane hydroperoxide.
5. The process according to Claim 4 wherein said peroxide is fed in a solvent solution.
6. The process according to Claim 1 wherein said ethylenically unsaturated polycarboxylic acid, anhydride, or ester thereof is present in a concentration of 1 to 25 weight percent.
7. The process according to Claim 1 wherein said ethylenically unsaturated polycarboxylic acid,

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anhydride, or ester thereof is selected from the acid, anhydride, or esters of the group consisting of maleic, citraconic, fumaric, 2-methylmaleic, 2-chloromaleic, 2-methoxycarbonylmaleic, 2,3-dimethylmaleic, and 2,3-dichloromaleic.

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8. The process according to Claim 1 wherein the concentration of said random ethylene/propylene copolymer is 70 to 98 weight percent.

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9. The process according to Claim 1 wherein the concentration of ethylene in said random ethylene/propylene copolymer is 0.8 to 6.5 weight percent.

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10. The process according to Claim 1 wherein said molten grafted random ethylene/propylene copolymer has a viscosity less than 3,000 cP at 190°C.

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11. The process according to Claim 1 wherein said extruder is equipped with an outlet pressure control device and said elevated temperature is higher than the atmospheric boiling point of at least one of the components, producing an elevated pressure in said extruder greater than 30 psig.

12. The process according to Claim 11 wherein said pressure is 30 to 400 psig.

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13. The process according to Claim 1 wherein said grafted random ethylene/propylene copolymer is grafted with maleic anhydride to greater than 5 weight percent.

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14. A composition comprising a grafted random ethylene/propylene copolymer containing 0.5 to less than 7 weight percent ethylene and at least 5 weight percent grafted maleic anhydride having an acid number of at least 35.

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15. The composition according to Claim 14 wherein the concentration of ethylene in said random ethylene/propylene copolymer is 0.8 to 6.5 weight percent.

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16. The composition according to Claim 15 wherein the concentration of ethylene in said random ethylene/propylene copolymer is 1 to 6 weight percent.

5 17. The composition according to Claim 16 wherein the concentration ethylene in said random ethylene/propylene copolymer is 2 to 6 weight percent.

18. The composition according to Claim 14 wherein said acid number is at least 44.

19. An emulsion composition comprising;

10 (1) 10 to 30 weight percent of the low molecular weight grafted random ethylene/propylene copolymer of Claim 14,

(2) a minor amount up to 15 weight percent of a surfactant, and

15 (3) 60 to 90 weight percent water.

20 20. The emulsion composition according to claim 19 wherein the emulsion contains 20 to 27 weight percent (1), 5 to 10 weight percent (2), and 65 to 80 weight percent (3).

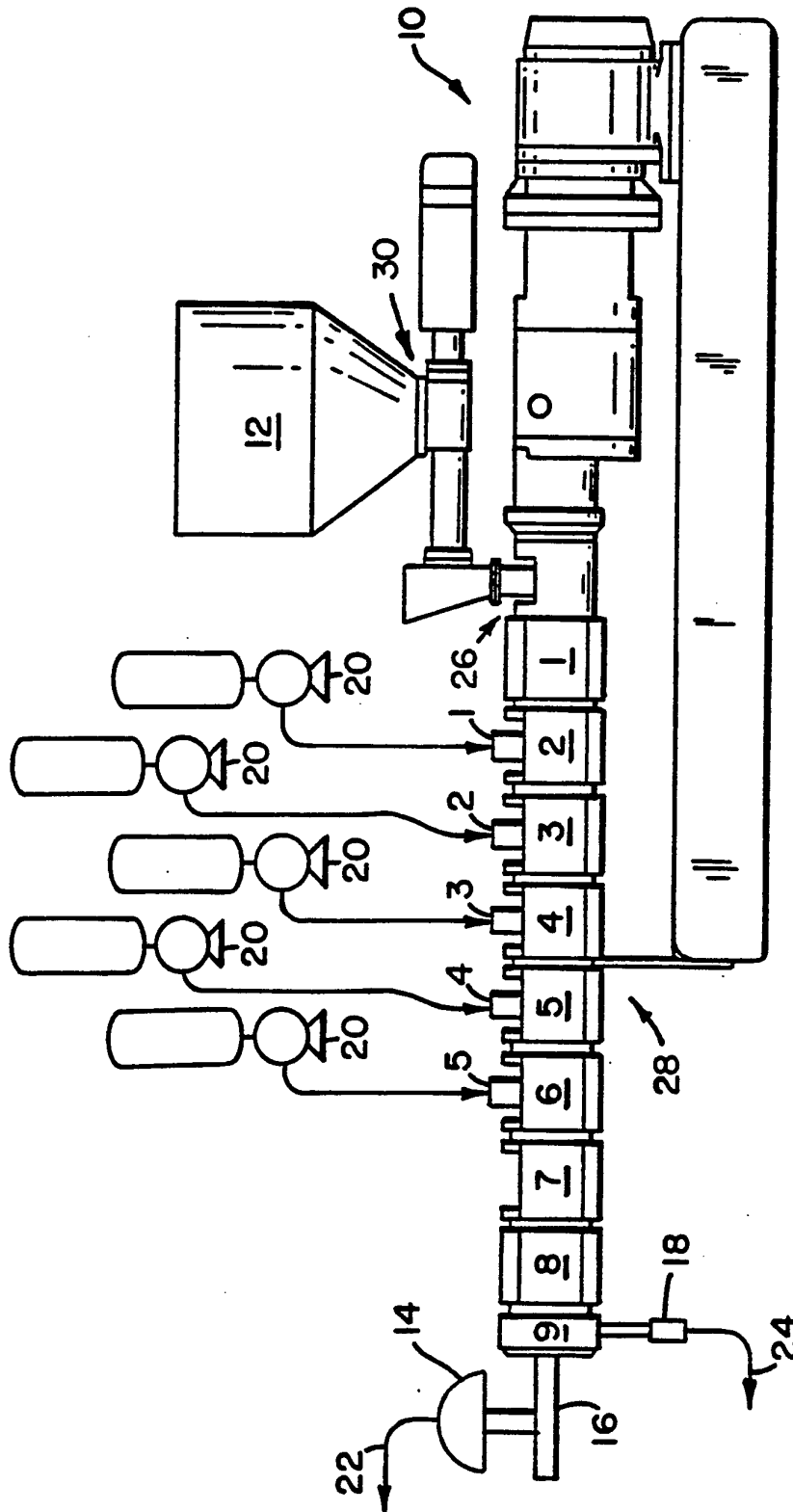


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 94/13994

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 255/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A1, 9311175 (QUANTUM CHEMICAL CORPORATION), 10 June 1993 (10.06.93), claims 1-6, p. 3, l. 27 - p. 4, l. 14; p. 6, l. 25 - p. 7, l. 8; p. 9, l. 17 - p. 10, l. 5; p. 11, l. 4 - p. 12, l. 28; p. 13, l. 20-27	1-9, 13-17
	--	
A	US, A, 4613679 (KENNETH R. MAINORD), 23 Sept 1986 (23.09.86), column 2, line 44 - column 3, line 54, claim 1	1-13
X		14-16, 18
	--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents

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"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

6 March 1995

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Name and mailing address of the International Searching Authority/Authorized officer



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/13994

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3868433 (KENNETH W. BARTZ ET AL), 25 February 1975 (25.02.75) ----- -----	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

09/02/95

International application No.
PCT/US 94/13994

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9311175	10/06/93	AU-A- 3149493 US-A- 5367022	28/06/93 22/11/94
US-A- 4613679	23/09/86	NONE	
US-A- 3868433	25/02/75	BE-A- 797701 CA-A- 992241 DE-A- 2316614 FR-A,B- 2179059 GB-A- 1428553 JP-A- 49009546 US-A- 3987122	03/10/73 29/06/76 18/10/73 16/11/73 17/03/76 28/01/74 19/10/76