

CLAIMS 1 to 11 are replaced by claims filed on 23 July 1996.

I claim as my invention:

1. A method for producing moldable thermoplastic polymer foam beads, comprising the steps of:

5 mixing a composition comprising a thermoplastic polymer in an extruder to form a melt;

injecting a blowing agent into the melt at a rate effective to produce a predetermined foam density in the melt when the melt is extruded;

0 extruding the melt in a first pressure zone into nonfoamed, foamable polyolefinic beads;

adjusting the temperature of the beads to a suitable and effective foaming temperature; and

5 expelling the beads into a second pressure zone of lower pressure than the first pressure zone, thus causing the beads to expand into foamed beads.

2. The method of claim 1, wherein the thermoplastic polymer comprises a crosslinkable, silane-modified polyolefin.

3. The method of claim 2, wherein the composition further comprises a silanol condensation catalyst.

5 4. The method of claim 1, wherein the composition is crosslinkable.

0 5. The method of claim 3, further comprising the step of: exposing the beads to moisture to induce silane crosslinking in the beads.

6. The method of claim 1, wherein the thermoplastic polymer comprises a polyolefin and a chemical crosslinking agent.

5 7. The method of claim 6, further comprising the step of:

adjusting the temperature of the beads to induce crosslinking in the polyolefin.

8. The method of claim 1, wherein the thermoplastic polymer is a polyolefin resin comprising a polymer selected from the group consisting of polyethylene, polypropylene, polybutene-1 and polyisobutene.

9. Moldable thermoplastic polymer beads made in accordance with claim 1, wherein the thermoplastic polymer is a foamable thermoplastic polymer.

10. Moldable thermoplastic polymer foam beads made in accordance with claim 9, wherein the thermoplastic polymer is crosslinked.

11. Moldable thermoplastic polymer foam beads made in accordance with claim 5, wherein the polyolefin comprises polystyrene.

12. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the thermoplastic polymer is a polyolefin resin comprising a polymer selected from the group consisting of: ethylene, propylene, butene-1 and isobutene.

13. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the thermoplastic polymer is a polyolefin resin comprising a polymer selected from the group consisting of:

medium density polyethylene, low density polyethylene, linear low density polyethylene, polypropylene, polybutylene, and homopolymers and copolymers of olefin monomers having from 2 to about 8 carbon atoms.

14. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the thermoplastic polymer

comprises a copolymer of ethylene and a monomer selected from the group consisting of:

vinyl acetate, acrylic polymers, methyl acrylic acid, and ionomer salts of methyl acrylic acid.

15. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the thermoplastic polymer comprises low density polyethylene.

16. Moldable thermoplastic polymer foam beads made in accordance with claim 15, wherein the thermoplastic polymer comprises a mixture of non-linear low-density polyethylene and linear low-density polyethylene.

17. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the thermoplastic polymer is a low density polyethylene having a density of about 0.917 to 0.923 g/cc.

18. The method of claim 1, wherein the blowing agent comprises an inert gas.

19. The method of claim 18, wherein the blowing agent comprises a gas selected from the group consisting of:
nitrogen, argon, neon, and helium.

20. The method of claim 1, wherein the blowing agent comprises a halogenated hydrocarbon.

21. The method of claim 20, wherein the blowing agent comprises a compound selected from the group consisting of:
trichlorofluoromethane (CFC-11);
dichlorodifluoromethane (CFC-12);
dichlorotetrafluoroethane (CFC-114);
difluorotetrachloroethane (CFC-122);
chlorodifluoromethane (HCFC-22); 1,1-dichloro 2, 2, 2-trifluoroethane (HCFC-123); 1-chloro-1, 2, 2, 2

tetrafluoroethane (HCFC-124); 1, 1, 2, 2, 2,-
pentafluoroethane (HCFC-125); 1, 2, 2, 2, -tetrafluoroethane
(HFC-134a); 1,1-dichloro 1-monofluoroethane (HCFC-141b);
1,-chloro-1,1,-difluoroethane (HCFC-142b); 1, 1,-
difluoroethane (HFC-152a); ethyl chloride; methyl bromide;
carbon tetrachloride; chloroform; ethylene dichloride;
methylene chloride; 1,1,2-trichloro-1,2,2-trifluoroethane;
and methyl chloride.

22. The method of claim 1, wherein the blowing agent
comprises a compound selected from the group consisting of:

acetylene, ammonia, butadiene, butane, butene, carbon
dioxide, nitrous oxide, cyclopropane, dimethylamine, 2-2-
dimethyl propane, ethane, ethylene, n-butane, isobutane,
isobutylene, methane, monomethylamine, propane, propylene
and trimethylamine.

23. The method of claim 1, wherein the blowing agent
comprises a hydrocarbon.

24. The method of claim 23, wherein the blowing agent
comprises a compound selected from the group consisting of:

isopentane, pentane, hexane, heptane, octane, pentene,
4-methyl pentene, and hexene.

25. The method of claim 1, wherein the blowing agent
comprises an ester.

26. The method of claim 1, wherein the blowing agent
comprises an ether.

27. The method of claim 26, wherein the blowing agent
comprises diethyl ether.

28. The method of claim 1, wherein the blowing agent
comprises an alcohol.

29. The method of claim 28, wherein the blowing agent is selected from the group consisting of methanol and ethanol.

30. The method of claim 1, wherein the blowing agent comprises a ketone.

31. The method of claim 30, wherein the blowing agent is selected from the group consisting of acetone and methyl ethyl ketone.

32. The method of claim 1, wherein the physical blowing agent comprises a heat activated chemical blowing agent.

33. The method of claim 32, wherein the heat activated chemical blowing agent is selected from the group consisting of:

azodicarbonamide; p-toluene sulfonyl hydrazide; dinitrosopentamethylene; mixtures of sodium bicarbonate and citric acid; gypsum; hydrated aluminas such as aluminum trihydrate; and sodium borohydrate.

34. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the foam beads have a density in the range of from about 0.5 to about 40 pcf.

35. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the foam beads have a density in the range of from about 1.5 to about 2.5 pcf.

36. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the thermoplastic polymer comprises a crosslinkable, silane-modified polyolefin having one or more silane groups selected from the group consisting of:

- (1,2-epoxyethane) ethyltrimethoxy silane;
- (1,2-epoxyethane) propyltrimethoxy silane;
- (1,2-epoxyethane) ethyltriethoxy silane;

- (1,2-epoxyethane) propyltriethoxy silane;
- (1,2-epoxyethane) ethylmethyldimethoxy silane;
- (1,2-epoxyethane) propylmethyldimethoxy silane;
- (1,2-epoxyethane) ethyl-tris-(ethoxymethoxy) silane;
- (1,2-epoxyethane) propyl-tris-(ethoxymethoxy) silane;
- (1,2-epoxypropane) ethyltrimethoxy silane;
- B-(3,4-epoxycyclohexane) ethyltrimethoxy silane;

and the sulfur and nitrogen analogues of these groups.

37. Moldable thermoplastic polymer foam beads made in accordance with claim 3, wherein the silanol condensation catalyst comprises at least one compound selected from the group consisting of:

organotin compounds, including organotin esters such as dibutyltin dilaurate, stannous acetate, and stannous octanoate or stannous caprylate; lead naphthenate; zinc caprylate; iron 2-ethylhexanoate; cobalt naphthenate; titanate acid esters; titanium chelate compounds, including tetrabutyl titanate, tetranonyl titanate and bis(acetylacetonitrile)diisopropyl titanate; amines, including ethylamine, hexylamine, dibutylamine or pyridine; inorganic acids, including hydrochloric acid and phosphoric acid; fatty acids, including stearic acid, linoleic acid and octylic acid, and their metal salts; and zinc salts of higher aliphatic or alicyclic carboxylic acids, including zinc stearate, zinc octanoate, zinc laurate, and zinc naphthenate.

38. Moldable thermoplastic polymer foam beads made in accordance with claim 3, wherein the silanol condensation catalyst comprises a mixture of at least one organotin compound and the zinc salt of a higher carboxylic acid.

39. The beads of claim 38, wherein the organotin compound is selected from the group consisting of:

dibutyltin dilaurate, dibutyltin maleate dibutyltin diacetate, triallyl cyanurate, and triallyl isocyanurate.

5 40. The beads of claim 39, wherein the amount of the organotin compound in the mixture ranges from 0.05 to 10 percent based on the total weight of the mixed silanol catalyst, and is limited to not more than 5 percent based on the total weight of the mixed silanol catalyst.

10 41. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the chemical crosslinking agent comprises at least one compound selected from the group consisting of:

15 organic peroxides, including benzoyl peroxide, dichlorobenzoyl peroxide, lauroyl peroxide, t-butyl peracetate, t-butyl peroxy-2-ethyl hexanoate, t-butyl peroxy isobutyrate, t-butyl peroxy benzoate, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexane, 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexyne-3, di-t-butyl peroxide, 2,5-
20 di(peroxybenzoate)hexyl-3, 1,3-bis(t-butyl-peroxyisopropyl)benzene; and azo compounds, including azobisisobutyronitrile and dimethyl azodiisobutyrate.

25 42. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the silane-crosslinked polyolefin foam beads comprise low density polyethylene produced by extrusion foaming with a blowing agent selected from the group consisting of hydrocarbons, halogenated hydrocarbons, carbon dioxide, and inert gases, wherein said
30 foam comprises a silanol condensation catalyst, and wherein the silane crosslinking is produced by exposure of said foam beads to moisture, the density of said foam thereafter being in the range of from about 1.2 to about 5 pcf.

35 43. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the beads are crosslinked

until they are sufficiently heat stable to be molded by application of heat and pressure.

44. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the composition further comprises at least one antistatic agent.

45. The beads of claim 44, wherein the antistatic agent is an anionic surfactant.

46. The beads of claim 45, wherein the antistatic agent comprises at least one compound selected from the group consisting of:

alkyl sulfates, alkyl sulfonates, alkyl benzene sulfonates, sulfosuccinates, esters of aliphatic alcohols, esters of phosphoric acid, and esters of phosphates;

47. The beads of claim 44, wherein the antistatic agent is a cationic surfactant.

48. The beads of claim 47, wherein the antistatic agent comprises one or more compounds selected from the group consisting of:

primary amine salts, secondary amine salts, tertiary amine salts, quaternary ammonium compounds, and pyridine derivatives.

49. The beads of claim 44, wherein the antistatic agent is a nonionic surfactant.

50. The beads of claim 49, wherein the antistatic agent comprises at least one alkylene oxide adduct of a compound selected from the group consisting of:

aliphatic alcohols, fatty acids, alkyl phenols, alkyl naphthols, polyhydric alcohols, aliphatic amines, aliphatic amides, polyethylene glycol, and block copolymers of polyethylene glycol and polypropylene glycol.

51. The beads of claim 49, wherein the antistatic agent comprises at least one compound selected from the group consisting of the monoesters and diesters of:

polyoxyethylene alkyl ethers, polyoxyethylene alkylaryl ethers, phosphoric acid, polyoxyethylene alkylene ester sulfates, and polyoxyethylene alkyl phenol ether sulfates.

52. The beads of claim 44, wherein the antistatic agent is an amphoteric surfactant.

53. The beads of claim 52, wherein the antistatic agent comprises at least one compound selected from the group consisting of:

alkyl betaene derivatives and imidazoline derivatives.

54. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the composition further comprises a stability control agent.

55. The beads of claim 54, wherein the stability control agent comprises at least one compound selected from the group consisting of:

partial esters of long chain fatty acids with polyols; higher alkyl amines; fatty acid amides; and olefinically unsaturated carboxylic acid copolymers.

56. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the composition further comprises a cell size control agent.

57. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein the composition further comprises a nucleating agent.

58. The beads of claim 56, wherein said cell size control agent is selected from the group consisting of:

mixtures of an acidic alkali metal salt of citric acid and a carbonate or bicarbonate which reacts with the acidic alkali metal salt at the extrusion temperature.

5 59. Moldable thermoplastic polymer foam beads made in accordance with claim 1, wherein said composition further comprises at least one flame retardant agent.

10 60. The beads of claim 59, wherein said flame retardant agent comprises a halogenated organic compound.

61. The beads of claim 60, wherein said flame retardant agent comprises a compound selected from the group consisting of:

15 brominated and chlorinated organic compounds.

62. The beads of claim 61, wherein said flame retardant agent contains at least 50 percent by weight of bromine or chlorine.

20 63. The beads in accordance with claim 59, wherein the flame retardant agent comprises at least one compound selected from the group consisting of:

25 chloroparaffin, 1,2,5,6,9,10-hexabromocyclododecane, tetrabromodibenzalacetone, pentabromophenylallylether, pentabromomonochloro cyclohexane, 1,1,2,3,4,4-hexabromobutene-2,2,5-bis(tribromomethyl)-1,2,3, -thiadrazol, 2,4,6-tris-(tribromomethyl)-1,3,5,-triazine, tetrabromoethane, bromotrichloromethane, 1,2,5,6-tetrabromohexane, hexabromo-benzene, pentabromophenol, penta-bromodiphenylether, tris (dibromopropyl)-phosphate, octabromo cyclohexadecane, octabromodiphenol oxide, 2,4,6-tribromophenol, decabromodiphenyl oxide, bis(tribromophenoxy)ethane, and bromonaphthalene.

35 64. The beads of claim 59, wherein the flame retardant agent comprises at least one oxide of antimony.

65. ~~The method of claim 1, further comprising the step of:~~
adding at least one antistatic agent and at least one
flame retardant agent to said melt.

5 66. The method of claim 1, further comprising the step of:
crosslinking the beads by combining the polyolefin with
an additive comprising a photo-chemical crosslinking agent.

10 67. The method of claim 1, wherein the composition further
comprises at least one stability control agent.

68. The method of claim 67, in which the stability control
agent comprises a fatty acid amide.

15 69. The method of claim 67, in which the stability control
agent comprises an olefinically unsaturated carboxylic acid
copolymer.

20 70. The method of claim 67, in which the stability control
agent comprises polystyrene.

71. The method of claim 67, in which the stability control
agent comprises a partial ester of a long chain fatty acid
and a polyol.

2! 72. The method of claim 67, wherein the stability control
agent eliminates the need to pressurize the foam beads prior
to molding them.

30 73. The method of claim 67, wherein the foam beads are not
pressurized prior to molding them.

74. The method of claim 1, wherein the thermoplastic
polymer is selected from the group consisting of:

35 ethylene homopolymers, and copolymers of ethylene and
~~a copolymerizable monomer.~~

75. The method of claim 74, wherein the composition further comprises a stability control agent selected from the group consisting of:

partial esters of long chain fatty acids with polyols;
higher alkyl amines; fatty acid amides; olefinically
unsaturated carboxylic acid copolymers; and polystyrene.

76. The method of claim 75, wherein the blowing agent comprises isobutane.

77. The method of claim 76, wherein the blowing agent is a mixture of from 5%-95% isobutane on a molar basis with from 95%-5% of a physical blowing agent selected from the group consisting of:

chlorofluorocarbons and fluorocarbons having from 1 to 4 carbon atoms, boiling points between -50° and 50°C., and a permeation rate through said olefin polymer resin modified with said stability control agent of less than about 1.2 times the permeation rate of air;

a mixture comprising at least 70% isobutane and having a permeation rate through the composition of greater than about 1.2 times the permeation rate of air; and

a mixture comprising a physical blowing agent and having less than 70% isobutane, said mixture having a permeation rate through the composition of greater than about 1.2 times the permeation rate of air.

78. A method for producing moldable thermoplastic polymer foam beads, comprising the steps of:

forming in an extruder a melt comprising a thermoplastic polymer and a photo-chemical crosslinking agent;

injecting a blowing agent into the melt at a rate effective to produce a predetermined foam density in the melt when it is extruded;

extruding the melt into a first zone of pressure that is sufficiently high to prevent significant expansion of the blowing agent;

cutting the extrudate into nonfoamed, foamable beads;

conveying the beads through a photo-crosslinking apparatus to produce crosslinking of the beads;

adjusting the temperature of the beads to a suitable and effective foaming temperature; and

expelling the beads into a second zone of lower pressure that is sufficiently low to allow the beads to expand into foamed beads.

79. A method for producing a crosslinked polyolefin foam, comprising the steps of:

mixing a composition comprising a silane-modified polyolefin and a silanol condensation catalyst in an extruder to produce a melt;

injecting and mixing a blowing agent into the melt at a rate effective to produce a desired foam density once the extrudate is expanded;

extruding the molten admixture into a first zone of pressure that is sufficiently high to prevent any significant expansion of the blowing agent;

exposing the crosslinkable foamable extrudate to moisture to produce silane crosslinking in the extrudate;

adjusting the temperature of the extrudate to a suitable and effective foaming temperature; and

expelling the crosslinked extrudate into a second zone of pressure that is sufficiently low to allow the extrudate to expand into a foamed product.

80. The method of claim 79, further comprising the step of:

cutting the extrudate as it is extruded into crosslinkable, non-foamed, foamable polyolefin beads.

81. A method for producing a crosslinked polyolefin foam, comprising the steps of:

mixing a composition comprising a polyolefin and a chemical crosslinking agent in an extruder to produce a melt;

5 injecting and mixing a blowing agent into the melt to form a molten admixture, the injection occurring at a rate effective to produce a desired foam density once the extrudate is expanded;

10 extruding the molten admixture into a first zone of pressure that is sufficiently high to prevent any significant expansion of the blowing agent;

exposing the crosslinkable, foamable extrudate to sufficient temperatures to induce crosslinking in the extrudate;

15 adjusting the temperature of the extrudate to a suitable and effective foaming temperature; and

expelling the extrudate to a second zone of pressure that is sufficiently low to allow the extrudate to expand and form a foamed product.

20 82. The method of claim 81, further comprising the step of: cutting the extrudate as it is extruded to form crosslinkable, non-foamed, foamable polyolefin beads.

83. A method for producing moldable thermoplastic polymer foam beads, comprising the steps of:

mixing a composition comprising a thermoplastic polymer in an extruder to form a melt;

30 injecting a blowing agent into the melt at a rate effective to produce a predetermined foam density in the melt when it is extruded;

extruding the melt into nonfoamed, foamable polyolefinic beads;

cooling the beads to a low enough temperature to prevent their expansion;

35 shipping the non-expanded beads to a remote location; and

adjusting the temperature of the beads at the remote location to a suitable and effective foaming temperature.

5 84. The method of claim 83, further comprising the step of:
placing the beads into a zone of lower pressure that will cause them to expand into foamed beads.

10 85. The method of claim 83, wherein the beads are maintained in a cooled state when they are shipped to the remote location.

15 86. The method of claim 1, further comprising the step of:
adjusting the temperature of the beads to a temperature suitable for inducing crosslinking.

87. The method of claim 5, further comprising the step of:
adjusting the temperature of the beads to a temperature suitable for inducing silane crosslinking.

20 88. The method of claim 11, wherein the polyolefin comprises a blend or copolymer of polystyrene and one or more polymers.

89. The method of claim 1, wherein the thermoplastic polymer comprises a blend or copolymer of at least two polymers selected from the group consisting of:

30 polystyrene; ethylene; propylene; butene-1; isobutene; medium density polyethylene; low density polyethylene; linear low density polyethylene; polypropylene; polybutylene; homopolymers and copolymers of olefin monomers having from 2 to about 8 carbon atoms; and the copolymers of ethylene and a monomer selected from the group consisting of vinyl acetate, acrylic polymers, methyl acrylic acid, and ionomer salts of methyl acrylic acid.

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90. The method of claim 1, wherein the blowing agent comprises a combination of at least two blowing agents selected from the group consisting of:

nitrogen; argon; neon; helium;
trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); dichlorotetrafluoroethane (CFC-114); difluorotetrachloroethane (CFC-122); chlorodifluoromethane (HCFC-22); 1,1-dichloro 2, 2, 2-trifluoroethane (HCFC-123); 1-chloro-1, 2, 2, 2 tetrafluoroethane (HCFC-124); 1, 1, 2, 2, 2, -pentafluoroethane (HCFC-125); 1, 2, 2, 2, -tetrafluoroethane (HFC-134a); 1,1-dichloro 1-monofluoroethane (HCFC-141b); 1,-chloro-1,1,-difluoroethane (HCFC-142b); 1, 1,-difluoroethane (HFC-152a); ethyl chloride; methyl bromide; carbon tetrachloride; chloroform; ethylene dichloride; methylene chloride; 1,1,2-trichloro-1,2,2-trifluoroethane; methyl chloride; acetylene; ammonia; butadiene; butane; butene; carbon dioxide; nitrous oxide; cyclopropane; dimethylamine; 2-2-dimethyl propane; ethane; ethylene; n-butane; isobutane; isobutylene; methane; monomethylamine; propane; propylene; trimethylamine; isopentane; pentane; hexane; heptane; octane; pentene; 4-methyl pentene; hexene; diethyl ether; methanol; ethanol; acetone; methyl ethyl ketone; azodicarbonamide; p-toluene sulfonyl hydrazide; dinitrosopentamethylene; mixtures of sodium bicarbonate and citric acid; gypsum; hydrated aluminas such as aluminum trihydrate; and sodium borohydrate.

91. The method of claim 66, wherein the additive further comprises a catalyst.

92. The method of claim 1, further comprising the step of: providing retention means for improving the retention of the blowing agent in the foam beads, thereby eliminating the need to pressurize the foam beads prior to molding them.

93. The method of claim 92, wherein the retention means is a solubility enhancer that is blended or copolymerized with the thermoplastic polymer.

5 94. The method of claim 93, wherein the solubility enhancer is a natural or synthetic rubber.

95. Moldable thermoplastic polymer foam beads made in accordance with claim 93.

10 96. The method of claim 93, wherein the foam beads are not pressurized prior to molding them.

15 97. The method of claim 78, wherein the melt further comprises a catalyst.