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(54) **Title:** SUPPORTED CRYSTAL NUCLEATING AGENT FOR POLYPROPYLENE

(57) **Abstract:** Methods for producing low cost alpha nucleants in-situ in a molten polypropylene by reacting particles of an insoluble non-nucleating dispersed phase metal salt or oxide with a soluble organic compound are disclosed, wherein the reactive product of these two components is an alpha nucleant which coats the dispersed phase particles. Alpha nucleants may be produced in-situ produced alpha nucleants. Polypropylene articles having higher levels of crystallinity can be prepared using conventional nucleants.

SUPPORTED CRYSTAL NUCLEATING AGENT FOR POLYPROPYLENE**BACKGROUND****TECHNICAL FIELD**

[0001] The present disclosure relates to nucleating agents, and specifically to crystal nucleating agents that can be used to produce, for example, polypropylene molded or extruded parts.

TECHNICAL BACKGROUND

[0002] Crystal nucleating agents are widely used in polypropylene processes to increase the rate of crystallization from the melt, and to increase the level of crystallinity in molded and extruded parts. Using nucleating agents can be beneficial, providing shorter cycle times during molding and higher strength and stiffness properties in a molded part. Certain nucleating agents can also improve the clarity and/or reduce the haze of a polypropylene part by producing crystalline aggregates known as spherulites. Such spherulites can be much smaller than the wavelength of visible light, leading to a reduction in light scattering that can result in haziness. These nucleating agents are typically either heterogeneous particles dispersed in molten polypropylene or compounds that dissolve in molten polypropylene and then crystallize out at temperatures higher than the temperature at which the polypropylene crystals start to develop.

[0003] Polypropylene can crystallize in one or more of three different crystalline forms known as the alpha, beta, and gamma forms. The alpha phase is the most common and most stable form of polypropylene. Most conventional crystal nucleating agents nucleate only the alpha form of polypropylene. The beta phase is less common and less thermodynamically stable, but beta crystalline polypropylene has been used to make novel products such as microporous oriented films. Beta phase polypropylene can also have higher ductility and impact strength than alpha phase polypropylene. Beta phase polypropylene has also been used to improve the properties of and lower the cost of making pressure pipe, thermoformed products, and geogrids that are used to reinforce roadbeds. The gamma form of polypropylene does not have significant commercial interest.

[0004] Alpha nucleating agents are widely used to improve the physical properties and processing characteristics of polypropylene. These nucleating agents can initiate growth of alpha spherulites from molten polypropylene as it cools during the fabrication of molded or extruded parts. Such nucleation can accelerate the solidification process, leading to shorter cycle times

and higher productivity. In addition, rapid formation of polymer crystals can lead to higher levels of crystallinity in a molded part. Also, properties that depend on the level of crystallinity, such as tensile strength and modulus, can also be higher in nucleated polypropylene. Another benefit of alpha nucleating agents is that by decreasing the size of the spherulites in the final molded or extruded part, the amount of light scattering can be decreased such that the final parts have improved clarity and reduced haze.

[0005] Many compounds are used as conventional alpha nucleants, including carboxylic acid metal salts such as sodium benzoate, lithium benzoate, aluminum 4-tertiary butyl benzoate, phosphate metal ester salts such as sodium bis (4-tertiary butyl phenyl) phosphate, or sodium 2,2'-methylenebis (4,6-di-tertiary butyl phenyl) phosphate and compounds such as polyalcohol derivatives (e.g. dibenzylidene sorbitol, bis (methyl benzylidene) sorbitol or bis (dimethyl benzylidene sorbitol). The phosphate metal ester salts and the sorbitol based nucleants can be more powerful than inexpensive nucleants such as sodium benzoate and lithium benzoate. The more powerful nucleants can provide more rapid crystallization, resulting in higher tensile strength, modulus, and better clarity compared to that of the less powerful alpha nucleants.

[0006] Sodium benzoate (NaBz) is the most commonly used alpha nucleant due to its low cost, but it does not provide ideal polypropylene parts. The clarity of parts produced using NaBz can suffer from the relatively large particle size of NaBz and the difficulty of dispersing NaBz in molten polypropylene. Both particle size and dispersibility can affect nucleation performance, since finer particle size can produce more nucleating particles at a given loading level of nucleant, and nucleation is a surface phenomenon that only takes place at the surface of the nucleating particle. Sodium benzoate particles are somewhat sticky and tend to agglomerate, making it difficult to disperse and to feed pure NaBz into a compounding extruder.

[0007] It would be desirable to boost the efficiency of inexpensive alpha nucleants so that the cycle time reduction and physical property improvements of the expensive nucleants can be achieved at a lower cost. If the effectiveness of sodium benzoate as an alpha nucleant could be improved, then it might be possible to use sodium benzoate in a wider range of applications and also save on nucleant cost. It would also be desirable to further boost the nucleation efficiency of more expensive alpha nucleants so that they could be used at lower addition levels, reducing the cost of nucleated polypropylene parts.

[0008] Thus, there remains a need for continued improvement in nucleating agents. These needs and other needs are satisfied by the compositions and methods of the present disclosure.

SUMMARY

[0009] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, this disclosure, in one aspect, relates to nucleating agents, and specifically to crystal nucleating agents that can be used to produce, for example, polypropylene molded or extruded parts.

[0010] In one aspect, the present disclosure provides an alpha nucleated polypropylene resin comprising an alpha-nucleating agent produced by an in-situ reaction between a dispersed particle and a second chemical that dissolves in a molten polypropylene.

[0011] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the dispersed particle is non-nucleating.

[0012] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the dispersed particle comprises a metal salt, a metal oxide, or combination thereof.

[0013] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the dispersed particle comprises sodium carbonate, sodium bicarbonate, lithium carbonate, or a combination thereof.

[0014] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the second chemical comprises an organic mono- or dicarboxylic acid.

[0015] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the second chemical comprises benzoic acid.

[0016] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the polypropylene comprises a homopolymer, impact copolymer, random copolymer of polypropylene, or a combination thereof, where a co-monomer comprises ethylene, butene, octane, or a combination thereof.

[0017] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein the dispersed particle has an average particle size less than about 10 micrometers.

[0018] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein a ratio of the dispersed particle to the second chemical is from about 2:1 to about 200:1.

[0019] In another aspect, the present disclosure provides an alpha nucleated polypropylene resin, wherein at least a portion of the surface of the dispersed particle reacts with the second chemical to produce an alpha nucleating salt which coats at least a portion of the surface of the dispersed particle.

[0020] In another aspect, the present disclosure provides a method for preparing a supported alpha nucleating agent, the method comprising contacting a dispersed particle and a second chemical in molten polypropylene.

[0021] In another aspect, the present disclosure provides a method for preparing a supported alpha nucleating agent, wherein a dispersed particle and a second chemical are contacted such that an in-situ reaction takes place between at least a portion of the surface of the dispersed particle and the second chemical to produce an alpha nucleant coating on the surface of the dispersed particle.

[0022] In yet another aspect, the present disclosure provides an alpha nucleated masterbatch that contains between 5% and 70% of a non-nucleating dispersed phase compound that has been reacted in-situ with a dissolved organic compound in the polypropylene melt such that the particles of the dispersed phase are coated with an alpha nucleating salt of the dispersed phase particle and the dissolved organic compound.

DESCRIPTION

[0023] The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

[0024] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0025] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

[0026] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0027] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a ketone” includes mixtures of two or more ketones.

[0028] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0029] As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance can or can not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not. For example, the phrase “optionally substituted alkyl” means that the alkyl group can or can not be substituted and that the description includes both substituted and unsubstituted alkyl groups.

[0030] Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds can not be

explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific aspect or combination of aspects of the methods of the invention.

[0031] References in the specification and concluding claims to parts by weight, of a particular element or component in a composition or article, denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0032] A weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0033] A residue of a chemical species, as used in the specification and concluding claims, refers to the moiety that is the resulting product of the chemical species in a particular reaction scheme or subsequent formulation or chemical product, regardless of whether the moiety is actually obtained from the chemical species. Thus, an ethylene glycol residue in a polyester refers to one or more -OCH₂CH₂O- units in the polyester, regardless of whether ethylene glycol was used to prepare the polyester. Similarly, a sebacic acid residue in a polyester refers to one or more -CO(CH₂)₈CO- moieties in the polyester, regardless of whether the residue is obtained by reacting sebacic acid or an ester thereof to obtain the polyester.

[0034] The term “alkyl group” as used herein is a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl, hexyl, heptyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like. A “lower alkyl” group is an alkyl group containing from one to six carbon atoms.

[0035] The term “alkoxy” as used herein is an alkyl group bound through a single, terminal ether linkage; that is, an “alkoxy” group may be defined as -OR where R is alkyl as defined above. A “lower alkoxy” group is an alkoxy group containing from one to six carbon atoms.

[0036] The term “alkenyl group” as used herein is a hydrocarbon group of from 2 to 24 carbon atoms and structural formula containing at least one carbon-carbon double bond. Asymmetric structures such as (AB)C=C(CD) are intended to include both the E and Z isomers. This may be presumed in structural formulae herein wherein an asymmetric alkene is present, or it may be explicitly indicated by the bond symbol C.

[0037] The term “alkynyl group” as used herein is a hydrocarbon group of 2 to 24 carbon atoms and a structural formula containing at least one carbon-carbon triple bond.

[0038] The term “aryl group” as used herein is any carbon-based aromatic group including, but not limited to, benzene, naphthalene, etc. The term “aromatic” also includes “heteroaryl group,” which is defined as an aromatic group that has at least one heteroatom incorporated within the ring of the aromatic group. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorus. The aryl group can be substituted or unsubstituted. The aryl group can be substituted with one or more groups including, but not limited to, alkyl, alkynyl, alkenyl, aryl, halide, nitro, amino, ester, ketone, aldehyde, hydroxy, carboxylic acid, or alkoxy.

[0039] The term “cycloalkyl group” as used herein is a non-aromatic carbon-based ring composed of at least three carbon atoms. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, etc. The term “heterocycloalkyl group” is a cycloalkyl group as defined above where at least one of the carbon atoms of the ring is substituted with a heteroatom such as, but not limited to, nitrogen, oxygen, sulphur, or phosphorus.

[0040] The term “aralkyl” as used herein is an aryl group having an alkyl, alkynyl, or alkenyl group as defined above attached to the aromatic group. An example of an aralkyl group is a benzyl group.

[0041] The term “hydroxyalkyl group” as used herein is an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above that has at least one hydrogen atom substituted with a hydroxyl group.

[0042] The term “alkoxyalkyl group” is defined as an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above that has at least one hydrogen atom substituted with an alkoxy group described above.

[0043] The term “ester” as used herein is represented by the formula —C(O)OA , where A can be an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

[0044] The term “carbonate group” as used herein is represented by the formula —OC(O)OR , where R can be hydrogen, an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above.

[0045] The term “carboxylic acid” as used herein is represented by the formula —C(O)OH .

[0046] The term “aldehyde” as used herein is represented by the formula —C(O)H .

[0047] The term “keto group” as used herein is represented by the formula —C(O)R , where R is an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above.

[0048] The term “carbonyl group” as used herein is represented by the formula C=O .

[0049] The term “ether” as used herein is represented by the formula AOA_1 , where A and A_1 can be, independently, an alkyl, halogenated alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl group described above.

[0050] The term “sulfo-oxo group” as used herein is represented by the formulas $\text{—S(O)}_2\text{R}$, $\text{—OS(O)}_2\text{R}$, or $\text{—OS(O)}_2\text{OR}$, where R can be hydrogen, an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above.

[0051] Each of the materials disclosed herein are either commercially available and/or the methods for the production thereof are known to those of skill in the art.

[0052] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

[0053] As briefly described above, the present disclosure provides crystal nucleating agents that can, in various aspects, impart improved properties to a molded or extruded polypropylene part.

[0054] In one aspect, it would be advantageous to provide a cost-effective alpha nucleant with improved efficiency, such that cycle time can be reduced and one or more physical properties can be improved. In another aspect, an improved sodium benzoate nucleant can be useful in a wide range of applications and reduce nucleant cost. It would also be advantageous to improve the nucleation efficiency of more expensive alpha nucleants so that they could be used at lower addition levels and reduce the final cost of a nucleated polypropylene part.

[0055] For beta nucleation, researchers have shown that by coating a nano-sized calcium carbonate particle with pimelic acid, it is possible to produce a supported calcium pimelate on the surface of the calcium carbonate particles. Calcium pimelate is known to be a very effective beta-nucleating agent in polypropylene. Such a supported beta nucleant can be produced using lower levels of expensive pimelic acid and can provide high activity and high selectivity for the beta nucleation of polypropylene. This approach, however, also has several drawbacks including the need for a difficult and expensive step of coating calcium carbonate particles with pimelic acid using solvents such as acetone. In addition, nano-sized calcium carbonate should be prepared using precipitated calcium carbonate, which is much more expensive than the more commonly used ground calcium carbonate. Finally, the nano-particle size of these supported nucleating particles can lead to a low bulk density for the nucleating agent and difficulties in dispersing the nucleant in polypropylene.

[0056] In one aspect, the effectiveness of the calcium pimelate salt as a beta nucleant could be dramatically improved by producing the calcium pimelate in-situ in a polypropylene melt by incorporating both calcium carbonate and pimelic acid into the melt. In one aspect, and while not wishing to be bound by theory, the pimelic acid can react, for example, at the surface of the calcium carbonate particles, to produce a coating of calcium pimelate which can function as a beta nucleant. Thus, in such an aspect, the calcium pimelate nucleant is supported on the calcium carbonate particles. In another aspect, by producing calcium pimelate in-situ, significantly lower

levels of calcium pimelate can be necessary to provide strong beta nucleation, as all or substantially all of the calcium pimelate resides on the surface of the calcium carbonate particles. In a further aspect, dispersion of the nucleant can then be determined by the dispersion of the calcium carbonate, which is readily dispersed in polypropylene with a small particle size. In one aspect, the required concentration of calcium pimelate can be reduced by at least a factor of 10, for example, a factor of at least 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, or 50.

[0057] In another aspect, the methods of the present invention can provide an improvement in nucleation ability as measured by the crystallization temperature, T_c , in the cooling cycle of a DSC scan (differential scanning calorimetry). In such an aspect, the higher the T_c value, the more rapid the crystallization of polypropylene. With traditional beta nucleants such as quinacridones, T_c values are typically never higher than about 124 C, based on a DSC cooling rate of 10 °C per minute. In one aspect, an in-situ generated calcium pimelate, as prepared in accordance with the various methods of the present disclosure can provide a T_c values of up to about 130 °C.

[0058] In one aspect, the methods of the present disclosure can be used to produce alpha nucleants in-situ, using a two-component system, so that the alpha nucleants are supported on non-nucleating particles. In another aspect, the in-situ nucleants can be inexpensive and easy to disperse in molten polypropylene. In another aspect, the support particles for the inventive alpha nucleants can comprise one or more inorganic salts, such as, for example, salts that are not soluble in molten polypropylene and/or which are easy to disperse in molten polypropylene to give small particles and uniform particle size dispersion. In another aspect, the second component can be an organic molecule, such as, for example, an organic acid, that is soluble in the molten polypropylene, and which can react with the support particles during, for example, standard extrusion compounding.

[0059] In an exemplary aspect, a dispersion of sodium bicarbonate and/or sodium carbonate in molten polypropylene, together with dissolved benzoic acid. In another aspect, sodium bicarbonate can be combined with benzoic acid. In one aspect, a low level of benzoic acid and an excess of sodium bicarbonate can provide a coating of sodium benzoate on sodium bicarbonate particles, wherein the dispersed particles can function as an alpha-nucleating agent. In such an aspect, the resulting dispersion of sodium benzoate coated particles of sodium bicarbonate can function as a strong alpha-nucleating agent. Since both sodium bicarbonate and

benzoic acid are inexpensive components, this in-situ produced alpha nucleant can be inexpensive to produce.

[0060] In a similar manner, lithium carbonate can be produced in-situ by blending an excess of lithium carbonate with benzoic acid into molten polypropylene, so that lithium benzoate forms on at least a portion of the surface of the dispersed lithium carbonate particles.

[0061] In still other aspects, high performance alpha nucleating agents, such as phosphate ester salts, can be produced by the in-situ reaction of a dissolved ester compound with a dispersed particle of an insoluble sodium salt in molten polypropylene. In such an aspect, the active nucleating agent would be present as a coating on the dispersed sodium salt particle. Lower levels of active nucleating agent would be needed to achieve strong alpha nucleation in the polypropylene.

[0062] Thus, in one aspect, the present invention provides methods to produce a supported alpha nucleating in-situ by reacting an insoluble dispersed compound with a soluble compound in the molten polypropylene. In such an aspect, a chemical reaction can take place between the dissolved compound and the dispersed compound to produce an active alpha nucleating agent on at least a portion of the surface of the dispersed particle. In one aspect, for an in-situ produced sodium benzoate alpha nucleant, the dispersed particle can comprise sodium bicarbonate. In another aspect, the dissolved compound can comprise benzoic acid. In another aspect, for a lithium benzoate alpha nucleant, the dispersed particle can comprise lithium carbonate and the dissolved compound can comprise benzoic acid. In still other aspects, an alpha nucleant can comprise a mixture of two or more individual alpha nucleants that can be formed, for example, in-situ.

[0063] In another aspect, a method is disclosed for modifying at least a portion of the surface of dispersed, non-nucleating particles in a polypropylene matrix so that these particles become alpha nucleating agents. Such a method comprises reacting the dispersed particles with a dissolved organic compound, such as benzoic acid, in the molten polypropylene so that a layer of an alpha nucleant salt, such as sodium benzoate and/or lithium benzoate, forms on the surface of the dispersed particles. In one aspect, these salts are known to be effective alpha-nucleating agents, and since the dispersed particles are coated with these agents, the dispersed particles will become alpha-nucleating agents.

[0064] A further object of this invention is to provide articles that are molded or extruded from any of the alpha-nucleated polypropylene compositions described herein.

[0065] In another aspect, the efficiency of an alpha nucleant produced by the in-situ reaction of a dissolved organic compound such as benzoic acid with a metal salt such as sodium bicarbonate or lithium carbonate, can be improved so that more rapid crystallization of the polypropylene part occurs when compared to that of simply dispersing the pure alpha nucleant in the polypropylene resin.

[0066] In various aspects, the types of polypropylene that can be useful in the inventive compositions described herein can include polypropylene homopolymer and copolymers of propylene and ethylene, for example random and heterophasic (or impact) copolymers. In another aspect, other polypropylene compositions can be used alone or in combination with any of the compositions recited herein. In another aspect, the inventive polypropylene compositions can comprise one or more impact modifiers such as ethylene-propylene-diene monomer copolymers (EPDM), copolymers of ethylene with higher alpha-olefins (such as ethylene-octene copolymers), polybutadiene, polyisoprene, styrene-butadiene copolymers, hydrogenated styrene-butadiene copolymers, styrene-isoprene copolymers, and hydrogenated styrene-isoprene copolymers. In another aspect, the inventive polypropylene compositions can further comprise polymer additives known in the art, including but not limited to hindered phenolic antioxidants, phosphorus based secondary antioxidants (*e.g.* phosphites and phosphonites), thioethers, hydroxylamines, nitrones, amine-N-oxides, alkylated diphenylamines, acid neutralizers (metal soaps, metal oxides, and the like as well as mixtures), metal deactivators, ultraviolet absorbers, hindered amine light stabilizers, benzoate light stabilizers, lubricants, anti-scratch additives, pigments, flame retardants, fluorescent whitening agents, and many others. These additional polymer additives are described in "Plastic Additives Handbook", 5th ed., H. Zweifel, Ed., Hanser Publishers, Munich, 2001, which is incorporated herein by reference. The additional polymer additives may be incorporated into the polymeric materials as part of the additive mixtures of the present invention or as separate components.

[0067] In another aspect, various types of polypropylene-based resins can be used as the starting base resin. The propylene-based polymers, as referred to herein, contain at least one propylene unit. The polymer may be a homopolymer of polypropylene, a random or block copolymer of propylene and another α -olefin or a mixture of α -olefins, or a blend of a polypropylene homopolymer and a different polyolefin. For the copolymers and blends, the α -olefin may be

polyethylene or an α -olefin having 4 to 12 carbon atoms. In one aspect, the α -olefin contains containing 4 to 8 carbon atoms, such as butene-1 or hexene-1. In the case of copolymers, it is desirable that at least 50 mol% of the copolymer is formed from propylene monomers. In one aspect, the copolymer may contain up to 40 mol%, and up to 50 mol%, of ethylene or an α -olefin having 4 to 12 carbon atoms, or mixtures thereof. Blends of propylene homopolymers with other polyolefins, such as high density polyethylene, low density polyethylene, or linear low density polyethylene and polybutylene can be used herein.

[0068] In one aspect, the propylene-based polymer has a melt flow rate (MFR) sufficiently high for facile and economical production of the injection molded or extruded parts, but not so high as to produce a molded part with undesirable physical properties. In one aspect, the MFR should be in the range of from about 0.5 decigrams/minute to about 200 decigrams/minute (dg/min), for example, about 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 25, 50, 75, 100, 125, 150, 175, or 200; or from about 2.0 dg/min to about 100 dg/min, for example, about 2, 3, 4, 5, 6, 7, 8, 9, 10, 13, 16, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55, 57, 59, 61, 63, 65, 67, 69, 71, 73, 75, 77, 79, 81, 83, 85, 87, 89, 91, 93, 95, 97, 99, or 100 dg/min, as measured by ASTM-1238. In one aspect, it can be disadvantageous for the MFR of the resin to exceed about 200 dg/min. In such an aspect, the molded part can become brittle or have reduced tensile strength. When the MFR is less than 0.5 dg/min, difficulties can be encountered in extruding or molding the part due to the high melt viscosity. In another aspect, it can also be possible to blend polypropylene-based polymers of different melt flow rates to obtain a final average MFR that is in the desired range.

[0069] In one aspect, the propylene-based polymer is a polypropylene homopolymer or blend thereof. In a further aspect, the propylene-based polymer comprises polypropylene. In a further aspect, the propylene-based polymer comprises a random or block copolymer selected from the group consisting of copolymers of propylene and ethylene, copolymers of propylene and an α -olefin with 4 to 12 carbon atoms, copolymers of polypropylene and a mixture of α -olefins with 4 to 12 carbon atoms, and copolymers of propylene and ethylene and one or more α -olefins with 4 to 12 carbon atoms.

[0070] In another aspect, the propylene-based polymer can optionally be admixed with one or more additives, including lubricants, antioxidants, ultraviolet absorbers, radiation resistance agents, antistatic agents, coupling agents, coloring agents, such as pigments and dyes, opacifiers, such as TiO₂ and carbon black. In one aspect, standard quantities of the additives are included in

the resin, although the addition of any minerals or abrasive additives should be kept to a minimum. In another aspect, care should be taken to avoid incorporation of certain fatty acid salts or Group IIA metals such as calcium stearate, since these compounds can react with the alpha nucleating agents that have been formed in-situ, and destroy or diminish their alpha nucleating ability.

[0071] In one aspect, preparation of the inventive polypropylene compositions can be carried out by known methods such as dry blending of the components followed by mixing at a temperature sufficiently high to melt the thermoplastic components. The melt blending can be carried out in any heatable container equipped with a mixer, *e.g.* in a closed apparatus such as an extruder, kneader, mixer or stirred vessel. In a specific aspect, the second step of the mineral modification process can be conducted simultaneously to the preparation of the polypropylene compositions. In such an aspect, the insoluble metal salts or oxides can be contacted and/or mixed with an organic acid and polypropylene resin in an extruder at a temperature sufficient to melt the polypropylene. The composition is extruded as a strand, solidified in a water bath, and chopped into pellets suitable for use in subsequent molding processes. In another aspect, sodium bicarbonate particles and/or lithium carbonate particles can be mixed with benzoic acid and polypropylene resin in an extruder. During this melt compounding process the benzoic acid can react *in-situ* with either the sodium bicarbonate or lithium carbonate to produce dispersed particles of the metal salts that are coated with the alpha-nucleating agents sodium benzoate and/or lithium benzoate.

[0072] In another aspect, useful articles molded from the inventive polypropylene compositions can be produced. The pellets of the inventive alpha-nucleated polypropylene compositions can be fabricated into a number of useful articles, including automotive interior, exterior, and under-the-hood parts, appliance components, and many others. The use of injection molding for the fabrication of such articles is an exemplary process and is well known in the art. During the cooling process in the mold, alpha-crystals can nucleate at the surface of the modified dispersed particles, producing a polypropylene article containing a fine grained alpha crystalline structure with a high crystallization temperature (T_c) as measured by DSC. In another aspect, the inventive articles are characterized by having a superior balance of tensile strength, stiffness, and reduced cycle time compared to articles prepared from comparable alpha-nucleated polypropylene compositions where pure or substantially pure alpha nucleant is dispersed in the polypropylene resin.

[0073] In one aspect, thermal analysis through the use of Differential Scanning Calorimetry (DSC) can be performed on extruded pellets or molded parts of the inventive composition to assess the enhanced alpha nucleation that has been achieved through the use of in-situ formed alpha nucleating agents. The parameter of most interest is the peak temperature of crystallization that is observed on the cooling scan after the sample is first heated in the DSC to a temperature that is well above the melting point of polypropylene. In a typical DSC cooling scan the molten polymer in the DSC is cooled at a controlled rate such as 10 degrees per minute. When the melt begins to crystallize heat is given off and an exothermic peak is observed in the DSC. The peak temperature (T_c) of this exotherm is an indication of the extent of nucleation of the resin. The higher the T_c value, the stronger the degree of nucleation.. For example, non-nucleated polypropylene homopolymer cooled at 10 degrees per minute generally has a T_c value that is less than 115 °C. In one aspect, if the T_c value is greater than about 115 °C, there can be some heterogeneous nucleation occurring in the polypropylene. In another aspect, if only alpha crystals are being nucleated, then on the second heat scan following this cooling scan, only a single melting peak for the alpha crystals at about 165 °C can typically be observed.

[0074] Thus, in one aspect, the methods of the present disclosure comprise the production of an alpha nucleating agent in-situ in molten polypropylene by reacting a dispersed phase comprising a metal salt, oxide, or other compound that does not melt or dissolve in polypropylene, with an organic compound that dissolves in polypropylene. Exemplary metal salts can include sodium bicarbonate and lithium carbonate. An exemplary organic compound is benzoic acid. The chemical reaction to produce this in-situ alpha nucleating agent can result in the alpha nucleant coating the dispersed particles of the insoluble metal salt.

[0075] In one aspect, the insoluble metal salt component can be present at an excess as compared to the dissolved organic compound. In another aspect, the ratio of the dispersed salt to the dissolved organic compound can be in the range of from about 2:1 to about 200:1, for example, 2:1, 4:1, 6:1, 8:1, 10:1, 15:1, 20:1, 25:1, 30:1, 40:1, 50:1, 60:1, 70:1, 80:1, 90:1, 100:1, 125:1, 150:1, 175:1, or 200:1; or from about 5:1 to about 50:1, for example, 5:1, 7:1, 9:1, 11:1, 13:1, 15:1, 17:1, 19:1, 21:1, 23:1, 25:1, 27:1, 29:1, 31:1, 33:1, 35:1, 37:1, 39:1, 41:1, 43:1, 45:1, 47:1, 49:1, or 50:1.

[0076] In one aspect, since the active alpha nucleant is present as a coating on at least a portion of the particle of the dispersed metal salt in the polypropylene, the nucleating efficiency of the alpha nucleant can be significantly improved, so that very low levels of the pure alpha nucleant

are needed to produce high levels of alpha crystallinity in a molded polypropylene part, and very high crystallization temperatures (T_c) are achieved.

[0077] In another aspect, the dispersion of the alpha nucleant can be controlled by the particle size and/or particle size distribution of the dispersed metal salt. Thus, it can be advantageous to use a fine particle size compound that can be easily dispersed in the polypropylene matrix. In various aspect, the average particle size of a supported substrate can be less than about 10 micrometers, for example, less than about 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 micrometers; or less than about 5 micrometers, for example, less than about 5, 4, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 micrometers.

[0078] In another aspect, the dispersed metal salt and the organic compound can be directly blended with polypropylene using standard melt compounding equipment such as a twin screw extruder, a single screw extruder, or Farrell continuous mixer. In another aspect, it is not necessary to pre-coat the organic compound onto the surface of the supported substrate. In such an aspect, the organic compound can dissolve in the molten polypropylene during the melt compounding operation, and then react with the surface of the dispersed metal salt particles, producing a coating on the surface of this particle that represents the actual alpha nucleant. When the molten polypropylene cools, the dispersed, coated particle can cause alpha crystals to form that then continue to grow until the fully crystallized polypropylene contains high concentrations of alpha crystals.

[0079] Although it is not necessary to pre-coat the dispersed metal salt with the organic compound, the metal salt particles can be coated with the organic compound during the grinding process that is used to produce the fine metal salt particle size. In one aspect, such a pre-treatment step would eliminate the need to separately blend in the organic compound and the metal salt with polypropylene during the compounding process.

[0080] In another aspect, it can be possible to produce a masterbatch of the dispersed, coated alpha nucleating particles of the dispersed metal salt by using high concentrations of the metal salt and high concentrations of the organic compound during the melt compounding operation. Such a masterbatch can contain a high concentration of coated particles, such that it can be greatly diluted by subsequent blending of small quantities of this masterbatch with large quantities of polypropylene in order to produce an alpha nucleated polypropylene exhibiting high T_c values in the DSC and short cycle times during injection molding.

[0081] While typical aspects have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present invention.

EXAMPLES

[0082] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

EXAMPLE 1

[0083] In a first example, samples of sodium benzoate nucleated polypropylene were prepared. A comparative sodium benzoate nucleated polypropylene sample identified as 004-14-4 in Table 1 was prepared by first making a masterbatch containing 10 % sodium benzoate (NaBz) in 90 % polypropylene homopolymer having a melt flow rate of 12 g/10 minutes. This masterbatch was prepared using a co-rotating twin screw extruder at a melt temperature of about 230 °C. Then 0.6 % of this masterbatch was blended with an additional 99.4 % of polypropylene using a heated 2-roll mill at 200 °C for three minutes, after which the molten polypropylene was pressed into a plaque on a compression molding press. The final concentration of sodium benzoate in this sample was 0.06 %.

[0084] Other comparative examples, as detailed in Table 1, were prepared by directly blending the additives shown with polypropylene on the two roll mill as described above, and then plaques were pressed in a similar manner using the compression molding press.

[0085] Portions of each plaque were subjected to analysis by DSC, operating under a nitrogen purge and using heating and cooling rates of 10 °C per minute. The first heat scan started at room temperature and ran to 230 °C, followed by a cool down to room temperature and a second

heating to 230 °C. The crystallization temperature, T_c, was measured as the peak temperature of the exotherm observed on the cool down scan.

[0086] TABLE 1

Sample ID	Wt.% NaBz Masterbatch	Metal Salt	Wt.% Salt	Wt.% Benzoic acid	T _c (°C)
004-14-4	0.6%	NaBz	0.06%	---	115.8
004-14-5	---	NaBz	0.12%	---	116.9
004-14-2	---	Na ₂ CO ₃	1.00%	0.05%	116.4
004-14-3	---	NaHCO ₃	1.00%	0.05%	116.9
004-14-6	---	NaHCO ₃	2.00%	0.10%	118.5

[0087] As illustrated in Table 1, all of the samples containing either sodium carbonate or sodium bicarbonate plus benzoic acid exhibited higher T_c values than sample 004-14-4, which contained a very well dispersed sodium benzoate as the alpha nucleant. This improvement in T_c occurred in spite of the fact that the samples containing the sodium carbonate or sodium bicarbonate had poor particle dispersions as evidenced by numerous white specs in the compression molded plaques. Sample 004-14-4 had the best plaque appearance in that no white specs were seen. Increasing the sodium bicarbonate and benzoic acid concentrations to 2.0% and 0.10% respectively in sample 004-14-6 led to a large rise in T_c, that was much higher than that observed when pure sodium benzoate was used at a 0.12% loading level in sample 004-14-5. These results demonstrate that producing sodium benzoate in-situ from the reaction of a sodium salt and benzoic acid can provide superior alpha nucleation compared to using pure sodium benzoate as the alpha nucleant.

EXAMPLE 2

[0088] In a second example, polypropylene samples were prepared using lithium benzoate or a combination of lithium carbonate and benzoic acid. These samples were prepared by blending either lithium benzoate (LiBz) or a combination of lithium carbonate plus benzoic acid with polypropylene using a 2-roll mill under the same conditions as described above for Example 1. The compositions of the blends and the T_c values are shown in Table 2 below:

[0089] TABLE 2

Sample ID	Metal Salt	Wt.% Metal	Wt.% Benzoic	T _c (°C)
-----------	------------	------------	--------------	---------------------

		Salt	Acid	
004-19-1	LiBz	0.12%	---	117.0
004-19-2	Li ₂ CO ₃	2.0%	0.10%	120.5

[0090] The data in Table 2 demonstrate that producing the LiBz nucleant in-situ in sample 004-19-2 can provide a dramatically higher Tc value as compared to using pure lithium benzoate.

Example 3

[0091] In a third example, nucleated polypropylene samples were prepared using a 1" single screw extruder. The sodium benzoate (NaBz) containing samples were prepared by blending pure sodium benzoate, available from Sigma Aldridge or Adeka Palmarole Company, with a polypropylene reactor powder resin using an addition level of 0.12 %. In the case of the Sigma Aldridge product, the sodium benzoate was first ground to a fine powder using a mortar and pestle. The Adeka Palmarole sodium benzoate, identified as NA-08, was already in the form of a fine powder so it was used without further treatment.

[0092] For the sample prepared using sodium bicarbonate and benzoic acid, the benzoic acid was first ground to a fine powder using a mortar and pestle. The sodium bicarbonate was already in the form of a fine powder, so it was used without further treatment. 1.0% of sodium bicarbonate was dry mixed with 0.10% of benzoic acid, and this mixture was melt blended with polypropylene reactor powder in the extruder. The composition of these samples and the DSC crystallization temperature data are detailed below in Table 3.

[0093] TABLE 3

Sample ID	Nucleant	Metal Salt	Wt. % Salt	Wt. % Benzoic Acid	Tc (°C)
004-21-1	0.12% NaBz (Sigma Aldridge)	NaBz	0.12%	---	124.1
004-21-5	0.12% NaBz (Adeka Pal.)	NaBz	0.12%	---	126.4
004-21-2	---	NaHCO ₃	1.0%	0.10%	128.6

[0094] As demonstrated by the data in Table 3, production of sodium benzoate in-situ from a blend of sodium bicarbonate plus benzoic acid can provide stronger nucleation and a higher crystallization temperature (Tc) compared to the results obtained by dispersing pure sodium benzoate into the polypropylene.

Example 4

[0095] In a fourth example, nucleated polypropylene samples were prepared using a 1" single screw extruder. Lithium benzoate (LiBz) containing samples were prepared by blending pure lithium benzoate, available from either Sigma Aldridge or Adeka Palmarole Company, with a polypropylene reactor powder resin using an addition level of 0.12 %. In the case of the Sigma Aldridge product, the lithium benzoate was first ground to a fine powder using a mortar and pestle. The Adeka Palmarole lithium benzoate was already in the form of a fine powder so it was used without further treatment.

[0096] For the sample prepared using lithium carbonate and benzoic acid the benzoic acid was first ground to a fine powder using a mortar and pestle. The lithium carbonate was already in the form of a fine powder, so it was used without further treatment. 1.0% of lithium carbonate was dry mixed with 0.10% of benzoic acid, and this mixture was melt blended with polypropylene reactor powder in the extruder. The composition of these samples and the DSC crystallization temperature data are given in Table 4.

[0097] Table 4

Sample ID	Nucleant	Metal Salt	Wt. % Salt	Wt. % Benzoic Acid	Tc (°C)
004-21-3	0.12% LiBz (Sigma Aldridge)	LiBz	0.12%	---	122.0
004-21-6	0.12% LiBz (Adeka Pal.)	LiBz	0.12%	---	126.8
004-21-4	---	Li ₂ CO ₃	1.0%	0.10%	129.7

[0098] As demonstrated by the data in Table 4, producing the lithium benzoate in-situ from a blend of lithium carbonate plus benzoic acid gives stronger nucleation and a higher crystallization temperature (Tc) compared to the results obtained by dispersing pure lithium benzoate into the polypropylene.

[0099] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other aspects of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

CLAIMS

What is claimed is:

1. An alpha nucleated polypropylene resin comprising an alpha-nucleating agent produced by an in-situ reaction between a dispersed particle and a second chemical that dissolves in a molten polypropylene.
2. The alpha nucleated polypropylene resin of claim 1, wherein the dispersed particle is non-nucleating.
3. The alpha nucleated polypropylene resin of any preceding claim, wherein the dispersed particle comprises a metal salt, a metal oxide, or combination thereof.
4. The alpha nucleated polypropylene of any preceding claim, wherein the dispersed particle comprises sodium carbonate, sodium bicarbonate, lithium carbonate, or a combination thereof.
5. The alpha nucleated polypropylene of any preceding claim, wherein the second chemical comprises an organic mono- or dicarboxylic acid.
6. The alpha nucleated polypropylene of any preceding claim, wherein the second chemical comprises benzoic acid.
7. The alpha nucleated polypropylene of any preceding claim, wherein the polypropylene comprises a homopolymer, impact copolymer, random copolymer of polypropylene, or a combination thereof, where a co-monomer comprises ethylene, butene, octane, or a combination thereof.
8. The alpha nucleated polypropylene of any preceding claim, wherein the dispersed particle has an average particle size less than about 10 micrometers.
9. The alpha nucleated polypropylene of any preceding claim, wherein a ratio of the dispersed particle to the second chemical is from about 2:1 to about 200:1.

10. The alpha nucleated polypropylene of any preceding claim, wherein at least a portion of the surface of the dispersed particle reacts with the second chemical to produce an alpha nucleating salt which coats at least a portion of the surface of the dispersed particle.
11. A method for preparing a supported alpha nucleating agent, the method comprising contacting a dispersed particle and a second chemical in molten polypropylene.
12. The method of claim 11, wherein the dispersed particle is non-nucleating.
13. The method of any of claims 11-12, wherein the dispersed particle comprises a metal salt, a metal oxide, or a combination thereof.
14. The method of any of claims 11-13, wherein the dispersed particle comprises sodium carbonate, sodium bicarbonate, lithium carbonate, or a combination thereof.
15. The method of any of claims 11-14, wherein the second chemical comprises an organic mono- or dicarboxylic acid.
16. The method of any of claims 11-15, wherein the second chemical comprises benzoic acid.
17. The method of any of claims 11-16, wherein the polypropylene comprises a homopolymer, impact copolymer, random copolymer of polypropylene, or a combination thereof.
18. The method of any of claims 11-17, wherein the dispersed particle has an average particle size less than about 10 micrometers.
19. The method of any of claims 11-18, wherein the ratio of the dispersed particle to the second chemical is from about 2:1 to about 200:1.
20. The method of any of claims 11-19, wherein contacting is performed using a melt mixing device.

21. The method of any of claims 11-20, wherein contacting is performed such that an in-situ reaction takes place between at least a portion of the surface of the dispersed particle and the second chemical to produce an alpha nucleant coating on the surface of the dispersed particle.
22. An alpha nucleated masterbatch that contains between 5% and 70% of a non-nucleating dispersed phase compound that has been reacted in-situ with a dissolved organic compound in the polypropylene melt such that the particles of the dispersed phase are coated with an alpha nucleating salt of the dispersed phase particle and the dissolved organic compound.
23. The alpha nucleated masterbatch of claim 22, wherein the ratio of the dispersed phase compound to the dissolved organic compound is from about 2:1 to about 200:1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/25037

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C08K 5/09 (2012.01) USPC - 524/284 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) IPC(8)- C08K 5/09 (2012.01); USPC- 524/284 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Patents and NPL (classification, keyword; search terms below) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL); search terms: nucleate, crystal, polypropylene, polyolefin, olefin, melt, molten, liquid, extrudate, mix, disperse, particle, dissolve, miscible, in situ, metal, salt, oxide		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2008/0045638 A1 (CHAPMAN et al.) 21 February 2008 (21.02.2008), para [0033], [0391], [0401]-[0423], [0566]	1-3, 11-13 ----- 22, 23
Y	US 2010/0016491 A1 (NIGA et al.) 21 January 2010 (21.01.2010), para [0047], [0267] [0273], [0279], [0280], [0288], [0292], [0294], [0298], [0301], [0303]	22, 23
Y	US 2009/0081387 A1 (SUZUKI) 26 March 2009 (26.03.2009), para [0020]-[0452]	1-3, 11-13, 22, 23
Y	US 2008/0249248 A1 (THURMAN et al.) 09 October 2008 (09.10.2008), para [0008]-[0156]	1-3, 11-13, 22, 23
Y	US 6,313,204 B1 (KOBAYASHI) 06 November 2001 (06.11.2001), col 2-16	1-3, 11-13, 22, 23
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent 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 when the document is taken alone "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		
Date of the actual completion of the international search 18 May 2012 (18.05.2012)		Date of mailing of the international search report 25 MAY 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/25037

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 4-10, 14-21
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.