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(54) Title: POLYMER–FLUOROCARBON COMPOSITION

(57) Abstract

Polymers having a shore number hardness of 10 to 90 are modified with a fluorocarbon additive to impart wear resistance.

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TITLE

POLYMER-FLUOROCARBON COMPOSITION

BACKGROUND OF THE INVENTION

Technical Field

This invention relates to a polymer-fluorocarbon composition of matter comprising a polymer having a Shore A scale hardness in the range of from about 10 to about 90 and from 1% to 10% of a fluorocarbon additive and to a method for preparing said composition.

DESCRIPTION OF RELATED ART

Fluorocarbon additives are used to improve the processability of polymers and/or enhance the performance of articles fabricated from such compositions.

U.S. Patent No. 5,061,759 relates to rubber compositions vulcanizable by means of peroxides and containing processing-coadjuvating additives which are perfluoropolyethers in amounts ranging from 0.5% to 1% of the rubber composition. The additives improve processability in extrusion and give better detachability of a vulcanized article from a molding die without adversely affecting the vulcanizing system or the properties of the vulcanized article. The only articles referred to are test pieces for use in evaluating physical properties.

Japanese Patent Application Pub. No. 60-104161 relates to an abrasion resistant molding material comprising "hard" thermosetting or thermoplastic resins and from 1% to 10% of a fluorinated oil uniformly adhered to, impregnated or dispersed in the molding material. Suitable fluorinated oils include perfluoropolyethers (such as, hexafluoropropylene oxide oligomers), and perfluorocarbons (such as, tetrafluoroethylene oligomers). The molding material is used to make improved wear resistant sliding components for electrical contact switches, electromagnetic switches and the like.

U.S. Patent No. 5,143,963 and U.S. Patent No. 5,286,773 relate to a composition of matter formed by melt blending a thermoplastic polymer and from

0.01% to less than 1% of a fluorocarbon additive and to a method of forming the composition. The fluorinated additive is a fluorocarbon oil, gum or grease including fluorinated hydrocarbons and fluorinated hydrocarbon polyether oils. The compositions are said to enhance and accelerate molding and extrusion operations for films and fibers. The basic bulk mechanical, physical and chemical properties of the thermoplastic polymers are retained or even enhanced. Due to the concentration of the fluorocarbon additive at the surface of articles made from the composition the articles acquire fluorocarbon-like surface properties. The composition is said to be useful for medical products e.g., vascular grafts, mammary or ocular implants, electronic equipment, electro-optical or electro-mechanical components and as molds for precision parts for such devices.

U.S. Patent No. 4,481,333 describes a thermoplastic composition which comprises mixtures of vinyl chloride polymers and chlorinated polyethylene and which contain up to 0.4% of finely divided fluorocarbons, such as polytetrafluoroethylene, polytrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride and fluorinated polyethers e.g., perfluorovinylpolyether. The composition has a markedly improved processability, particularly when shaped into articles by extrusion. The use of such compositions for making shaped articles such as slabs, tubes, and sheeting is described.

U.S. Pat. No. 4,505,982 relates to a shaped article exhibiting good long term thermal stability, comprising a thermoplastic heat resistant polymer mixed with from 20% to 80% of at least one fluorocarbon. The fluorocarbon can be polyvinylidene fluoride, polyvinyl fluoride or copolymers with tetrafluoroethylene, perfluorovinyl ethers and the like. Uses in films, fibers and threads are described.

There is a continuing need to improve performance in use, simplify production and improve cost effectiveness for articles made from polymers. An object of the present invention is to make available a novel composition of matter from which articles having improved performance and cost effectiveness can be fabricated.

Admixture of a polymer and a fluorocarbon and the use of such a composition to form an article greatly increases the longevity or permanence of any

beneficial effects compared to the commonly applied fluorocarbon surface treatment of a preformed article.

SUMMARY OF THE INVENTION

It now has been found that a novel composition of matter comprising a thermoplastic or thermoset polymer or mixed polymers having a Shore A scale hardness in the range of from about 10 to about 90 and from 1% to 10%, of an additive consisting of a fluorocarbon or mixture of fluorocarbons, said additive having a lower surface energy than that of said polymer, can be used to fabricate an article having enhanced properties, the concentration of fluorocarbon being substantially higher at the surface of said article than the nominal bulk concentration.

Another aspect this invention relates to a method for making said composition of matter by mixing the components.

A further aspect relates to compounding and fabricating said composition into an article of a desired shape by an appropriate procedure such as molding or extrusion.

DETAILED DESCRIPTION OF THE INVENTION

The composition of this invention comprises a thermoplastic or thermoset polymer or mixed polymers having a Shore A scale hardness in the range of from about 10 to about 90 and an additive consisting of a fluorocarbon or mixture of fluorocarbons the proportion of the latter ranging from 1% to 10% bulk concentration by weight of the amount of polymer, said fluorocarbon additive having a lower surface energy than that of said polymer.

Another aspect this invention relates to an article formed from said composition of matter, wherein the concentration of fluorocarbon is substantially higher at the surface of said article than the nominal bulk concentration.

In a further aspect this invention relates to a method for preparing said composition of matter and compounding and fabricating said composition into an article of a desired shape.

Typical articles prepared in accordance with this invention that have superior properties, such as squeak resistance and wear resistance, compared to those currently available.

By "squeak resistant" it is meant that the articles tendency to generate sound (i.e., to squeak), when moved relative to a contacting surface; in its intended use, is reduced or preferably eliminated. By "wear resistance" it is meant that articles made in accordance with the invention have longer useful lives than articles made with the same polymer, but not containing the fluorocarbon additive.

Amongst other articles, the composition may be used in the manufacture of gaskets and blades. As used herein the term "gasket" includes (1) articles inserted between two relatively hard surfaces to cushion their contact, and (2) articles that contact against a hard surface to form a seal, such as weather-stripping or lubricant seals; and the term "blade" includes articles that move across a hard surface to remove a substance, such as windshield wipers and squeegees.

Typical applications include weather-stripping, window lace, vehicle sealing system such as foamed door seals, windshield wipers, panel gaskets, spark plug and distributor boots, wear pads, bumpers suspensions, oriented bumpers, tail-light assemblies, engine mountings and gaskets, belts for vehicle engine and accessory systems, gears and bearings, window hardware components, conveyer line sections, gaskets for other purposes such as in fluid handling equipment, constructional engineering and architectural applications, luggage straps and buckles, footwear, particularly footwear for athletic purposes, parts for domestic and commercial appliances and the like.

Polymer Resins

Thermoplastic or thermosetting polymer resins or mixtures of the two types of polymer resins, having a Shore A scale hardness in the range of from about 10 to about 90, as measured by ASTM method D-2240-91, are used in the compositions of this invention. Although there is some question about the reliability of Shore A scale hardness values measured in the range of from 90 to

100, polymers with such hardness values should be considered to be within the purview of this invention. Polymers falling within definition of this invention are often called "soft" polymers.

Thermoplastic polymer resins are those resins which are softened by heat, even in the finished product. Thermosetting polymer resins are converted to infusible material during the fabrication process and thus the finished product is no longer susceptible to complete melting. Polymer resins are used in the form of molding granules or powders which can contain other compounding additives and which are usually mixed along with fluorocarbon additives under precisely controlled conditions. Thermoplastic polymer resins, having a Shore A scale hardness in the range of from about 10 to about 90, which are used in a composition of this invention can include, but are not necessarily limited to: cellulosics such as cellulose acetate, cellulose acetate butyrate, cellulose acetate proprionate, fluoropolymers, polyamides, polybutylene, polyethylenes, chlorinated polyethylenes, ethylene acid copolymers, ethylene-ethyl acrylates, ethylene-methyl acrylates, ethylene-vinyl acetates, ethylene vinyl alcohol copolymers, ionomers, polymethylpentene, ethylene-propylene copolymers, polypropylene impact copolymers, polypropylene random copolymers, styrene-butadiene copolymers, styrene-ethylene/butylene-styrene, polyvinyl chloride, chlorinated polyvinyl chloride, vinylidene chloride homopolymers and copolymers, thermoplastic elastomers such as styrene block copolymers, polyolefin blends, elastomeric alloys, thermoplastic urethanes, polyesters, copolyesters, styrene butadiene block copolymers, styrene-isoprene block copolymers, polyamides, polyether-polyamide block copolymers. Thermoplastic random, block or graft copolymers are suitable for making a composition or article of this invention. Blends and alloys of two or more thermoplastic polymers can be used in the practice of this invention.

Thermosetting polymer resins having a Shore A scale hardness in the range of from about 10 to about 90, used in a composition of this invention can include, but are not necessarily limited to: polybutadiene, natural rubbers, silicones, silicone epoxy, polyesters, ethylene-propylene diene terpolymers (e.g., EPDM rubber), ionomers (e.g., Surlyn®), polyurethanes, segmented polyurea/urethanes, reaction injection molded (RIM) urethanes, styrene butadiene rubber, nitrile

butadiene rubber. Thermosetting resins are also meant to include thermoplastic resins which have been cross-linked to a high enough degree such that molten reprocessing is no longer possible without severe property losses. Blends and alloys of two or more thermosetting polymers can also be used in the practice of this invention.

Mixtures of thermoplastic and thermosetting polymers, such as EPDM rubber "alloys" with polypropylene (Santoprene®) and with PVC (Alcryn®) are also suitable for this invention.

Additives for Polymer Resins

The polymer resins used in the compositions and articles of this invention usually also contain one or more conventional resin compounding ingredients, such as, but not necessarily limited to: organic or inorganic fillers, reinforcing agents, colorants, thermal stabilizers, antioxidants, antiozonants, antistatic agents, antimicrobial agents, plasticizers, lubricants, antifogging agents, coupling agents, flame retardants, foaming agents, fragrances, heat stabilizers, impact modifiers, mold release agents, titanates, ultraviolet stabilizers, thermally conductive fillers, electrically conductive fillers, curing agents, cross-linking agents, catalysts, and the like. Especially important for this invention are those compounding additives, e.g.. plasticizers and impact modifiers, which have the effect of reducing the base polymer hardness to a Shore A scale hardness range of from about 10 to about 90.

Fluorocarbon Additives

Suitable fluorocarbon additives are oils, gums or greases comprising fluorinated hydrocarbons or fluorinated hydrocarbonpolyethers having six or more carbon atoms, including linear, branched and cyclic compounds. Examples of suitable compositions are perfluoroalkylpolyethers, (e.g., Krytox®, Fomblin®, Demnum® and Aflunox®), perfluoropolyethylene oxide, perfluoropolypropylene oxide, polytetrafluoroethylene (e.g., Teflon®) perfluoropolyethylene-polypropylene, perfluoropolybutadiene, polyvinylidene fluoride, perfluorocarbons and fluorohydrocarbons including ethers containing functional group(s) such as but not limited to alcohols, amines, amides, esters, nitriles, thiols, acids, acid halides,

including chlorine, bromine and iodine. Higher molecular weight homologous linear and branched fluorohydrocarbons and fluorinated cyclic hydrocarbons may also be used, as well as partially fluorinated additives, such as those more than 50% fluorinated, preferably more than 75% fluorinated. For example, polychlorotrifluoroethylenes, polytetrafluoroexetanes, or other highly fluorinated compounds may be selected..

Fluorocarbon or mixed fluorocarbon additives which are compounded with the polymer resins preferably have a surface energy substantially lower than that of the polymers. Generally it is preferred that a fluorocarbon have a surface energy at least 5 dynes/cm lower than the surface energy of the polymer with which it is compounded. The amount of fluorocarbon compounded with a suitable polymer resin is from 1% to 10% bulk concentration by weight of the amount of polymer. In an article formed from a composition of the invention the beneficial effects of the fluorocarbon additive are markedly evident toward the lower end of the range, due to the concentration at the surface being much higher than the nominal bulk concentration. At bulk loading levels of 1% and 10% the concentration of fluorocarbon in a surface layer 10nm thick is respectively above about 80% and up to about 99%.

The optimum amount of fluorocarbon additive will vary with the selected polymer, processing conditions, and intended use, and is readily determined by routine experimentation. The amount selected will generally be below the maximum level that can be retained by that particular polymer to avoid housekeeping problems that would be created by higher levels of addition not assimilated into the polymer.

Surface Concentration of Fluorocarbon Additives

The relationship between the surface concentration and the nominal bulk loading of fluorocarbon additives in a polymer can be ascertained by measuring the former using the ESCA analytical procedure on a test specimen, "poker chip", comprising a polymer compounded with perfluoroalkyl-polyether oil,(Krytox®). This procedure, which quantitatively analyses the atomic concentration of elements

in a surface layer about 5 to 10 nanometers (nm) thick, is calibrated by applying a film of Krytox® oil to a glass slide and determining the level of fluorine in the film. This amount of fluorine, about 65% corresponded to 100% coverage, with Krytox® oil. By determining the fluorine level in the surface layer of a PVC "poker chip" the level of Krytox® oil in the surface layer is ascertained. At a bulk loading of 1.0% Krytox® TM oil in PVC having a Shore A scale hardness of 84 the concentration in a surface layer 10 nm thick is found to be 88%. The level of Krytox® is clearly much higher in the surface layer than in the bulk of the sample and at a bulk loading of 10% the surface concentration approaches 99% and can be more. The degree to which fluorocarbon surface enrichment occurs depends upon the particular polymer and fluorocarbon components of a composition and the procedures used to mix them and fabricate an article of this invention.

Compounding A Polymer Resin Fluorocarbon Composition

In a composition of this invention the fluorocarbon is completely or to a large degree immiscible with the polymer and other components. Sufficient mixing must be provided to disperse the fluorocarbon throughout the polymer-fluorocarbon composition. The fluorocarbon wets the processing equipment surfaces because of its low surface tension. Processing a polymer-fluorocarbon composition from the liquid state to a solid article includes an essentially non-turbulent (i.e., not well mixed) flow field and adequate quench time to allow the fluorocarbon enriched surface layer to develop. Antithetically, if the liquid state is in a highly turbulent (i.e., well mixed) flow field and instantaneously quenched to the solid state considerably less fluorocarbon surface enrichment occurs.

In order to maximize the fluorocarbon surface enrichment when the polymer-fluorocarbon composition contains other additives which remain as solids when the polymer-fluorocarbon composition is being processed as a liquid, these solid ingredients should be wetted with molten polymer or molten composition ingredients other than the fluorocarbon prior to addition of the fluorocarbon. Otherwise, the fluorocarbon having a very low surface tension would wet the solid additive surfaces resulting in decreased fluorocarbon surface enrichment for the polymer-fluorocarbon phase.

Polymer-fluorocarbon compositions where the polymer is a thermoplastic involve melting the thermoplastic polymer in order to mix with the fluorocarbon as a liquid. The molten thermoplastic polymer-fluorocarbon composition is mixed to disperse the fluorocarbon throughout the thermoplastic polymer-fluorocarbon composition. The molten thermoplastic polymer-fluorocarbon is then solidified by freezing, and when this constitutes the final article a low shear flow regime and adequate quench time is needed to allow fluorocarbon surface enrichment to occur.

Some of the possible, yet not meant to be all inclusive, processing methods for incorporating fluorocarbon into a thermoplastic polymer-fluorocarbon composition are:

1) dry mixing a polymer powder, a plasticizer, and other additives so as to wet the ingredients which remain solid during molten processing, adding the fluorocarbon last to the dry blend, and feeding to the molten mixing device;

2) dry blending all ingredients except the fluorocarbon, using this dry blend to feed the molten mixing device, and liquid injecting the fluorocarbon into the molten mixing device;

3) compounding the polymer and additives without the fluorocarbon and feeding the compounded polymer to a molten mixing device with liquid injection of the fluorocarbon into the molten mixing device.

Liquid injection of the fluorocarbon into the molten mixing device is the preferred manner of adding the fluorocarbon to the polymer-fluorocarbon composition. Some examples of molten mixing devices which can be used to mix a thermoplastic polymer-fluorocarbon composition are continuous mixers, extruders, kneaders and injection molding machines.

Thermosetting polymer-fluorocarbon compositions can be made via two different routes.

1) Involves molten processing of additives and fluorocarbon with an already formed polymer with simultaneous or subsequent curing (i.e., cross-linking) to affect its thermoset character.

2) Involves contacting monomer, additives and fluorocarbon to form the thermosetting polymer directly.

In either case, it is unlikely that the fluorocarbon will interfere with polymerization or curing reactions. In the case where molten processing of the thermosetting polymer-fluorocarbon occurs, processing could be done as for the thermoplastic polymer-fluorocarbon compositions described above. In the case of a thermosetting polymer-fluorocarbon composition when the polymer is directly formed from reactants, the fluorocarbon will need to be well mixed in the reactants as they contact each other, and will form the enriched surface layer as the thermoset polymerization occurs.

Fabrication Of An Article

An article can be formed from a novel composition of this invention by a number of conventional fabrication processes. The fabrication process will usually be determined by cost effectiveness, for example the elimination of topical application, labor costs, and/or the need to fit existing process equipment.

In turn, the fabrication process used to make the polymer-fluorocarbon article will determine the nature of the polymer and fluorocarbon feedstocks to the process. If the fabrication process involves little or no mixing, e.g., compression molding, then a pre-compounded polymer-fluorocarbon composition would best serve as the feedstock. However, if the fabrication process employs a molten mixing device with sufficient mixing, the process feeds could be a post-compounded polymer-fluorocarbon composition, polymer with fluorocarbon liquid injection, or blends of polymer and a precompounded polymer-fluorocarbon composition.

If the polymer-fluorocarbon article is comprised of a polymer foam, then the maximum outer surface enrichment by the fluorocarbon will be obtained if the fluorocarbon surface enrichment largely occurs prior to the foam expansion and freezing step. Conversely, if the foamed polymer-fluorocarbon composition is processed molten as an expanded foam the fluorocarbon, due to its low surface

tension, would enrich the surfaces of the interior foam cells decreasing enrichment of the outer surface of the article.

Some examples of polymer-fluorocarbon article fabrication processes include, but are not limited to: extrusion, injection molding, injection blow molding, extrusion blow molding, calendaring, pultrusion, reactive injection molding, and reactive extrusion.

Migration of the fluorocarbon towards the surface of the article also occurs during the fabrication step so that the concentration of fluorocarbon is much greater at the surface than the nominal bulk concentration. The high concentration of fluorocarbon additive near the surface gives rise to fluorocarbon-like surface properties such as, lower friction, hydrophobicity, chemical inertness and non-adherent surfaces. These properties result in performance improvements such as decreased wear and noise reduction. An important additional benefit which derives from mixing the fluorocarbon component with polymer and other additives prior to or during fabrication is the greater longevity of performance compared with that obtained with post applied surface coatings.

Some examples of polymer-fluorocarbon articles which can be formed from the novel composition of this invention include, but are not limited to: fibers, rods, tubes, sheets, profiles, and intricately shaped parts such as, vehicle weather-stripping, window lace, windshield wiper blades, panel gaskets, spark plug and distributor boots, sealing joints between flanges, such as gaskets for engines, for lines which carry gases or liquids, pumps, reaction vessels and the like, engine drive belts, contact switches, magnetic switches, seal caps or boots for lubricated joints, wear pads, wire harness connectors and spark plug caps, bumper suspensions, oriented bumpers, tail light assemblies, window hardware components and articles used in architectural applications, footwear, particularly footwear for athletic purposes, conveyer line sections parts of domestic and commercial appliances and the like.

In many applications articles, such as those described above are subjected over extended periods to vibration, sudden change in direction of movement, sliding surfaces in contact and similar conditions which result in the production of

undesirable noises e.g., squeaks, and excessive wear. Articles made using the compositions and procedures of this invention show improved performance in these respects over prolonged periods of use.

WHAT IS CLAIMED IS:

1. A composition of matter comprising a polymer resin having a Shore A scale harness in the range of from 10 to 90 and from 1% to 10% of a fluorocarbon additive, said additive having a lower surface energy than that of said polymer.

2. An article fabricated from the composition of claim 1 wherein the concentration of fluorocarbon additive is higher at the surface of said article than the nominal bulk concentration.

3. An article comprising a polymer having a Shore A scale hardness in the range of from 10 to 90 and a fluorocarbon additive having a nominal bulk concentration in the range of from 1% to 10% by weight based on the polymer, said additive having a lower surface energy than that of said polymer, the concentration of said fluorocarbon in an outer layer of said article having a thickness of 10 nanometers being respectively between 80% to 99% by weight.

4. An article of claim 3 wherein the polymer is from a thermoplastic resin.

5. An article of claim 3 wherein the polymer is from a thermosetting resin.

6. An article of claim 3 wherein the polymer is from a polyvinyl resin.

7. An article of claim 3 wherein the polymer is from a polyurethane resin.

8. A squeak resistant article of claims 3, 6 and 7.

9. A wear resistant article of claims 3, 6 and 7.

INTERNATIONAL SEARCH REPORT

Interna al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/00 C08L101/00 //(C08L101/00,101:00,101:04)

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)
IPC 6 C08K C08L

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 286 773 A (STERLING ROBERT E ET AL) 15 February 1994 cited in the application see column 3, line 60 - column 4, line 68 see column 5, line 9 - line 32 see claim 1 ---	1-9
X	EP 0 113 114 A (HOECHST AG) 11 July 1984 cited in the application see claim 1 --- -/--	1-4,6,8, 9

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
26 February 1999	15/03/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 98/23113

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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