



(51) International Patent Classification:

C08L 23/10 (2006.01) *C08J 3/22* (2006.01)
C08L 83/04 (2006.01) *C08J 5/18* (2006.01)
C08L 23/26 (2006.01)

(21) International Application Number:

PCT/US2013/050534

(22) International Filing Date:

15 July 2013 (15.07.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/672,143 16 July 2012 (16.07.2012) US

(71) Applicant: **POLYONE CORPORATION** [US/US];
33587 Walker Road, Avon Lake, Ohio 44012 (US).

(72) Inventors: **ALRIC, Jerome**; 3 rue du Beauregard, F-95660 Champagne sur Oise (FR). **WAELE, Jerome**; 43 rue des Potelots, F-60000 Saint Martin le Noeud (FR). **AUVRAY, Fabien**; 3 rue des Tilleuls, F-95300 Pontoise (FR).

(74) Agents: **HORNICKEL, John H.** et al.; Polyone Corporation, 33587 Walker Road, Avon Lake, Ohio 44012 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

(54) Title: POLYPROPYLENE COMPOUNDS HAVING NON-MIGRATORY SLIP PROPERTIES

(57) Abstract: A masterbatch having epoxy-functionalized silicone as a slip additive, the polypropylene compound that the silicone-containing masterbatch has been let down into, and the plastic articles and films from such compounds having improved slip properties are disclosed. The improved slip properties are evidenced by (1) essentially no migration of the slip additive 12 weeks after manufacturing, (2) a dynamic coefficient of friction value of less than 0.4 and a static coefficient of friction 0.6 or less within the first day of manufacturing according to the ASTM D1894-01 method, and (3) less than 15% change in the dynamic and static coefficient of friction values between the first day of manufacturing and 20 days after manufacturing.



WO 2014/014832 A1

POLYPROPYLENE COMPOUNDS
HAVING NON-MIGRATORY SLIP PROPERTIES

CLAIM OF PRIORITY

[0001] This application claims priority from U.S. Provisional Patent Application Serial Number 61/672,143 bearing Attorney Docket Number 12012004 and filed on July 16, 2012, which is incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to masterbatches using epoxy-functionalized silicone as a slip additive, polypropylene compounds that these silicone-containing masterbatches have been let down into, and plastic articles produced from such compounds having improved slip properties compared to a non-reactive silicone slip additive and essentially no slip additive migration, as determined by measurements of the static and dynamic coefficients of friction (COF) values according to the ASTM D1894-01 method.

BACKGROUND OF THE INVENTION

[0003] Plastic has taken the place of other materials in a variety of industries. Because plastic can be engineered to not shatter, rust or rot, plastic articles have replaced glass, metal and wood articles in many applications. For example, in the food and packaging industries, plastic has replaced glass to minimize breakage, reduce weight, and reduce energy consumed in manufacturing and transport.

[0004] Additives are often added to a plastic to facilitate the processing of that material. Commonly used additives are slip agents, which act as an internal lubricant for the polymer during processing. For instance in film processing, slip additives lessen friction between the polymer film and high speed processing and packaging equipment.

[0005] Slip additives often function by migrating (i.e. “blooming”) to the surface of the polymer, where they provide a coating that reduces the surface’s coefficient of friction. Because the additive is concentrated at the surface where it is needed for processing, less slip additive is required in the polymer material overall.

[0006] Typically variants of fatty acids are used as slip additives, because they are immiscible within, and chemically inert to, the polymer matrix, making them more likely to be migratory. For example, many commonly used slip additives, such as erucamide, oleamide, stearamide, behenamide, oleyl palmitamide, stearyl erucamide, ethylene bis-oleamide, N,N'-Ethylene Bis(Stearamide) (EBS), are highly migrant (i.e. migration occurs within hours of the film formation).

[0007] However, there is also loss of slip additive, due to additive migration or transfer from the polymer material. “Additive migration” represents the slip additive migrating from the sliding layer of the film containing slip additive, to another film layer. “Additive transfer” represents the slip additive transferring to another substrate (for example transferring to another section of the film when it is rolled). Therefore, films and other articles with migratory slip additives experience diminished slip properties over time or exposure to higher temperatures.

[0008] Consequently, if for example there is an interval before further processing, those polymer materials containing traditional migratory slip additives may require cold storage. Slip performance may also decrease when exposed to high processing temperatures. Finally, migratory slip additives are not suitable for applications that require consistent slip properties over the useful life of the article, such as for release films and permanent anti-slip coatings.

[0009] High molecular weight (HMW) non-reactive silicone gums have been found to migrate more slowly (over days versus hours). However, the

trade off is reduced slip properties, represented by higher COF values, and limited long-term stability.

SUMMARY OF THE INVENTION

[00010] What the art needs is a slip additive for polypropylene-based compounds that is non-migratory, has improved slip properties compared to non-reactive silicone slip additives, and that exhibits good stability over time.

[00011] In one embodiment of the invention is a masterbatch for polypropylene, comprising: (a) polypropylene carrier; (b) epoxy functionalized polysiloxane; (c) functionalized polyolefin; and (d) optionally, other additives. The functionalized polyolefin contains a maleic anhydride (MAH) group and acts as a grafting agent for the epoxy functionalized polysiloxane.

[00012] In one embodiment of the invention a polypropylene compound of the masterbatch described above is let down into a polypropylene resin. Because the functionalized polyolefin is miscible with polypropylene, when its MAH group reacts to the epoxy group on the polysiloxane, the functionalized polyolefin becomes an anchor that immobilizes the slip additive in the polypropylene matrix.

[00013] Another embodiment of the invention is a plastic article produced from the polypropylene compound or directly from the masterbatch. The article may be shaped from injection molding, blown film extrusion, or calendered into sheets.

[00014] Another embodiment of the invention is a film produced from the polypropylene compound. The film may include other layers having the same or different ingredients forming a laminate. The laminate may be a coextruded multilayer structure. The laminate may have a core layer and a skin layer contacting the surface of the core layer.

[00015] In another aspect of the invention, the skin layer of the laminate has a dynamic COF value of 0.4 or less and a static COF value of 0.6 or less

measured within 1 day after manufacturing, according to the ASTM D1894-01 method.

[00016] Another aspect of the invention is a laminate in which there is essentially no migration of the slip additive into another layer of the film 12 weeks after manufacturing.

[00017] The following embodiments explain some attributes of the invention.

EMBODIMENTS OF THE INVENTION

[00018] Polypropylene

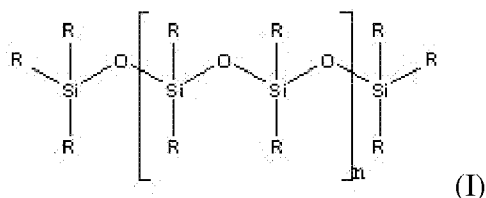
[00019] Polypropylene is an economical material that offers a combination of outstanding physical, mechanical, thermal, and electrical properties not found in other thermoplastics. For purposes of this invention, polypropylene is the polymer carrier for the masterbatch formulation and also serves as the matrix for the polymer compound forming the final plastic article. Polypropylene is intended to cover the homopolymer of propylene as well as various copolymers of propylene. The copolymers can be random copolymers or block copolymers wherein the blocks themselves may be either homopolymers or random copolymers.

[00020] There are numerous commercial manufacturers of polypropylene, including LyondellBasell, ExxonMobil, Ineos, Flint Hills Resources, Formosa, Continental Chemical, Sunoco Chemicals, Braskem, Total, Mitsui Chemical and Chisso Chemical Corporation.

[00021] Polyorganosiloxane

[00022] Siloxanes can have branched or unbranched backbones consisting of alternating silicon and oxygen atoms -Si-O-Si-O-, with side chains R attached to the silicon atoms. Polymerized siloxanes with organic side chains are commonly known as silicones or as polysiloxanes, as represented generally

by the following structure:



[00023] The organic side chains confer hydrophobic properties while the -Si-O-Si-O- backbone is purely inorganic. It is preferred for the invention that “n”, the number of repeating Si-O groups in the molecule backbone, is an integer from 1 to 1500.

[00024] Polysiloxanes may be modified by a reactive functional group, such as a hydroxyl group, an alcohol group, a carboxyl group, an isocyanate group, a silanol group, a blocked polyisocyanate group, a primary amine group, a secondary amine group, an amide group, a carbamate group, a urea group, a urethane group, a vinyl group, an unsaturated ester group, a maleimide group, a fumarate group, an anhydride group, a hydroxy alkylamide group, or an epoxy group. The polysiloxanes for the invention include at least one epoxy group.

[00025] Polysiloxanes are commercially available from a wide variety of manufacturers, including Dow Corning, Evonik, ICM Products and UCT Specialties.

[00026] Functionalized Polyolefin

[00027] The functionalized polyolefin plays a key role for immobilizing the slip additive in the polypropylene matrix. For the present invention, the functionalized polyolefin contains a maleic anhydride group that is highly reactive with the epoxy group on the functionalized polysiloxane.

[00028] The reaction between the epoxy group on the polysiloxane and the maleic anhydride group on the functionalized polyolefin will form either an ester or ether linkage. The ester linkage is formed as a result of the anhydride ring opening into a monoester having a carboxylic group that will then react with the epoxy group on the polysiloxane. The ether linkage is formed by a reaction between the epoxy group on the polysiloxane and a hydroxyl group

from the compound of the previously described ester-forming reaction or from the anhydride monoester. The ester-forming and ether-forming reactions for the present invention may exclude the use of a catalyst.

[00029] As a result of the polysiloxane forming a linkage to the functionalized polyolefin, the polysiloxane is consequently also anchored in the polyolefin matrix. Therefore, the more compatible the functionalized polyolefin is to the polypropylene, the better dispersed the slip additive will also be in the polypropylene matrix.

[00030] Functionalized polyolefins having a maleic anhydride group include Lotader 8200, an ethylene ethyl acrylate maleic anhydride terpolymer from Arkema; Priex 25097 and Priex 25093, maleic anhydride grafted polypropylenes from Solvay; and BHX-10016, a maleic anhydride propylene copolymer from Baker Petrolite.

[00031] Optional Additives

[00032] The polymer compounds of the present invention can include any conventional plastics additives in any combination that would not deleteriously affect the slip properties of the compound. The amount should not be wasteful of the additive or detrimental to the processing or performance of the compound. Those skilled in the art of thermoplastics compounding, without undue experimentation but with reference to such treatises as Plastics Additives Database (2004) from Plastics Design Library (www.elsevier.com), can select from many different types of additives for inclusion into the compounds of the present invention.

[00033] Non-limiting examples of optional additives include adhesion promoters; antioxidants; biocides (antibacterials, fungicides, and mildewcides), anti-fogging agents; anti-static agents; bonding, blowing and foaming agents; dispersants; fillers and extenders; smoke suppressants; expandable char formers; impact modifiers; initiators; lubricants; micas; pigments, colorants and dyes; plasticizers; processing aids; other polymers; release agents; silanes, titanates and zirconates; additional slip agents; anti-blocking agents; stabilizers;

stearates; ultraviolet light absorbers; viscosity regulators; waxes; and combinations of them.

[00034] In particular, antiblock additives are often used together with slip additives and for their complementary functions. Anti-block additives reduce adhesion or the “stickiness” between polymer layers (usually layers of the same polymer), which is created by blocking forces inherent to many polymers. Whereas slip additives decrease friction caused from moving across the surface of a polymer, antiblock additives create a microrough surface that lessens the adhesion caused by these blocking forces. Antiblock additives, like slip additives, are commonly used to improve the handling of a polymer for applications such as packaging. Preferably for this invention a nonmigratory antiblock additive, such as crosslinked poly(methyl methacrylate) or an inorganic silica, is used.

[00035] For convenience during processing and handling, the reactive silicone slip additive can be made into a masterbatch formulation, which is afterward let down into the polypropylene resin that is made into a film or other article. To have the highest concentration of slip additive, as required for example in release film applications, the masterbatch can also be processed into the film directly.

[00036] Table 1 shows the acceptable, desirable, and preferable ranges of ingredients for the masterbatch mixture. The masterbatch of the invention can comprise, consist essentially of, or consist of these ingredients in these amounts.

Table 1 Ranges of Ingredients for the Masterbatch Mixture			
Ingredient (Wt. Percent)	Acceptable	Desirable	Preferable
Polypropylene Carrier	1% - 99%	30% - 90%	45% - 81%
Epoxy functionalized polysiloxane	0.1% - 50%	5% - 20 %	5% - 10%

Table 1 Ranges of Ingredients for the Masterbatch Mixture			
Ingredient (Wt. Percent)	Acceptable	Desirable	Preferable
Functionalized polyolefin	1% - 99.9%	5% - 50%	9% - 45%
Optional additives	0% - 10%	0% -10%	0% - 10%

[00037] The masterbatch of the present invention may be added to the polypropylene compound in an amount ranging from about 0.5% to about 50%, and preferably from about 2% to about 25% weight percent of the polypropylene compound. The polypropylene compound may include one or more masterbatches containing different additives beneficial for the application of the final plastic article. If a high concentration of slip additive is required, the polypropylene compound may also be comprised of 50% or greater of the masterbatch by weight percent of the compound. To minimize migration of excess silicone additive, the stoichiometry between the polysiloxane and functionalized polyolefin is preferably a ratio in which there is sufficient functionalized polyolefin to react with all of the polysiloxane in the masterbatch.

[00038] Processing

[00039] *Masterbatch Production*

[00040] The preparation of the masterbatches of the present invention is uncomplicated. The masterbatches of the present invention can be made in continuous or batch operations.

[00041] Mixing in a continuous process typically occurs in an extruder that is elevated to a temperature that is sufficient to melt the polymer matrix with addition either at the head of the extruder or downstream in the extruder of the solid or liquid ingredient additives. Specific melt mixing equipments suitable for the manufacture of the said masterbatch include single screw extruder, co-rotating or counter-rotating twin screw extruder, multiple screw

extruder or co-kneader. Preferably the melt mixing equipment used is a twin screw co-rotating extruder equipped with screws having a length to diameter (L/D) ratio of at least 40. Extruder speeds can range from about 50 to about 500 revolutions per minute (rpm).

[00042] Processing conditions to be applied during mixing in a continuous process are dependent of the polymer carrier used. In the present case where the polymeric carrier is polypropylene, the processing temperatures are in the range of 140°C to 240°C.

[00043] Typically, the output from the extruder is pelletized into standard size pellets, or may also be cut by an underwater pelletizer to create beads. The pellets or beads are used for later extrusion or molding into polymeric articles.

[00044] To ensure constant and homogeneous quality of the masterbatch, the ingredients are preferably dosed in a twin screw extruder with gravimetric dosing units. The polymer carrier is added in the extruder via the main hopper and additives are either added via the main hopper or are incorporated into the polymer via a side feeder.

[00045] Mixing in a batch process typically occurs in a Banbury mixer that is capable of operating at a temperature that is sufficient to melt the polymer matrix to permit addition of the solid or liquid ingredient additives. The mixing speeds range from 60 to 1000 rpm. The output from the mixer is chopped into smaller sizes for later extrusion or molding into polymeric articles.

[00046] Masterbatch concentrates can be later let down into a polymer resin composition to produce the polypropylene compound, which can be molded, extruded, or calendered into plastic articles.

[00047] *Film Extrusion*

[00048] Subsequent extrusion or molding techniques of the final compound of the present invention to form polymer films or other articles are well known to those skilled in the art of thermoplastics polymer engineering. Without undue experimentation but with such references as “Extrusion, The Definitive Processing Guide and Handbook” published by Plastics Design

Library (www.elsevier.com), one can use different techniques for making articles using the compound of the present invention.

[00049] Polypropylene films may be formed, for example, from an extruded melt that is blown or cast or even cast and quenched, either onto a drum, a belt, in water, or the like. Cast films may be subsequently oriented, either uniaxially or biaxially, using conventional equipment such as drawing on heated rollers or using a tenter-frame, or combination thereof.

USEFULNESS OF THE INVENTION

[00050] The present invention may be used in numerous applications that would benefit from materials having stable slip properties. For example, the present invention may be desirable inside containers to promote the flow of the container's contents when pouring or mixing, but avoid possible contamination of the slip additive into the contents, such as food or medicine.

[00051] The present invention may also provide slip properties for higher temperature processing of films and other articles, including cast and biaxially-oriented films.

[00052] In addition, prolonged slip performance may be desirable in certain packaging applications, including packaging rolls, packaging bags, pouches, sheets, trays, carton liners, wrappers, screen printing films, lamination film, labels, adhesives, stretch and shrink wraps, and photographic materials.

[00053] The present invention may also be useful in release film applications as an alternative to silicone coated polyolefin films, which require the costly step of curing the silicone coating on the polyolefin skin.

EXAMPLES

[00054] Table 2 shows a list of ingredient for the Comparative Examples A-D and Examples 1-3, including a description, brand name, manufacturer and function of each ingredient. Table 3 shows the recipes for Masterbatches (MBs) I-VI.

Table 2 Description of Ingredients				
Name	Description	Brand	Manufacturer	Function
Polypropylene	Polypropylene copolymer	PKS359	Ineos	Carrier and film matrix resin
Non-reactive silicone MB	High molecular weight silicone gum (50%), Polypropylene (50%)	Pearlene SIPP MB-01	Momentive	Slip additive
Alkoxysilane functionalized polysiloxane (reactive silicone)	Ethoxy silyl terminated polydimethylsiloxane	3-0247 ETE POLYMER	Dow Corning	Slip additive
Epoxy functionalized polysiloxane (reactive silicone)	Epoxy functional polysiloxane	TEGOMER E-Si 2330	Evonik	Slip additive
Functionalized Polypropylene (0.2% MAH)	Maleic anhydride (MAH) grafted polypropylene (0.2% MAH; Melt flow index = 93 @ 230°C)	PRIEX25093	Solvay	Grafting agent for the reactive silicone
Functionalized Polypropylene (0.45% MAH)	Maleic anhydride (MAH) grafted polypropylene (0.45% MAH; Melt flow index = 97 230°C)	PRIEX25097	Solvay	Grafting agent for the reactive silicone

Table 2 Description of Ingredients				
Name	Description	Brand	Manufacturer	Function
Functionalized terpolymer of ethylene (2.8% MAH)	Ethylene ethyl acrylate maleic anhydride terpolymer (2.8% MAH)	LOTADER 8200	Arkema	Grafting agent for the reactive silicone
Functionalized polypropylene copolymer (containing MAH)	Maleic anhydride propylene copolymer	BHX-10016	Baker Petrolite	Grafting agent for reactive silicone
Amino-functionalized silane	3-Aminopropyl trimethoxysilane	DYNASILAN AMEO	Evonik	Co-agent with the reactive silicone
Catalyst	Tetra n-butyl titanate	TYZOR T-nBT	Dorf Ketal Chemicals	Silanol catalyst
Antiblock MB	Polypropylene masterbatch of crosslinked poly(methyl methacrylate) beads	On Cap AB PP MB	PolyOne	Anti-block additive

Table 3 Masterbatch Recipes						
	MB I	MB II	MB III	MB IV	MB V	MB VI
<i>Ingredient Name (by Wt. Percent)</i>						
Polypropylene carrier	90%	89%	88%	45%	67.5%	81%
Alkoxysilane functionalized polysiloxane (reactive silicone)	5%	5%	5%			
Epoxy functionalized polysiloxane (reactive silicone)				10%	10%	10%
Functionalized polypropylene (0.2% MAH)	5%	5%	5%			4.5%
Functionalized polypropylene (0.45% MAH)				45%		
Functionalized terpolymer of ethylene (2.8% MAH)					22.5%	
Functionalized polypropylene co-polymer (containing MAH)						4.5%
Amino-functionalized silane			1%			
Catalyst		1%	1%			
	100%	100%	100%	100%	100%	100%

[00055] Masterbatches I-VI were prepared by a continuous process using a BERSTORFF ZE25A co-rotating twin screw extruder having a screw length to diameter ratio of 60. Table 4 shows the mixing conditions of the twin screw extruder.

Table 4 Extruder Mixing Conditions for Masterbatches I-VI	
Extruder Type	ZE25A twin screw extruder, with a screw size of 25 mm L/D=60
Zone 1	20 °C
Zone 2	140 °C
Zone 3	200 °C
Zone 4	210 °C
Zone 5	220 °C – silicone injection
Zone 6	220 °C
Zone 7	220 °C
Zone 8	220 °C
Zone 9	230 °C
Zone 10	240 °C
Die Temperature	240 °C
RPM	500
Pelletizer	Strand pelletizer
Pellet size	3mm

[00056] All of the ingredients for the masterbatches were fed into the throat of the extruder, except the silicone slip additives. The silicone slip additives were injected into the melt in zone 5 via injection ports.

[00057] Pellets produced from the above described process were then blended into the polymer resin matrix to produce the polypropylene compound. Table 5 shows the recipes and Table 6 shows the film extrusion conditions for all the Comparative Examples and Examples.

Table 5 Recipes (Wt. %) of Comparative Examples and Examples							
Example	A	B	C	D	1	2	3
Polypropylene matrix	94%	76%	76%	76%	86%	86%	86%
Non-reactive silicone MB	2%						
MB I		20%					
MB II			20%				
MB III				20%			
MB IV					10%		
MB V						10%	
MB VI							10%
Antiblock MB	4%	4%	4%	4%	4%	4%	4%
Total	100%	100%	100%	100%	100%	100%	100%
% Silicone	1%	1%	1%	1%	1%	1%	1%
% Total functionalized polyolefin	0%	1%	1%	1%	4.5%	2.25%	0.9%

[00058] The polypropylene compounds were extruded into a 2-layer laminate film, each layer having a thickness of 25 μ m, using a Labtech multilayer cast film line according to the conditions in Table 6, below.

Table 6 Film Extrusion Conditions of All Comparative Examples and Examples	
Extruder Type	Single screw extruder
Zone 1	200°C
Zone 2	240°C
Zone 3	240°C
Zone 4	240°C
Distributor	240°C
Head	245°C/240°C/245°C
Die	Slot die
RPM	Screw speed between 35 and 75 rpm to obtain thickness for film extrusion
Chill Roll	Chill roll at 20°C and 6 m/min

[00059] Evaluation of Polypropylene Films

[00060] Non-reactive silicone was compared to two types of reactive silicones for effectiveness as slip additives in polypropylene-based films. The reactive silicones evaluated were alkoxysilane functionalized polysiloxane and epoxy functionalized polysiloxane. The Example formulations satisfied the required criteria described in Table 7. The results of the Comparative Examples and Examples are shown in Table 8.

Table 7 Criteria and Testing Methods for Films		
<i>Criteria</i>	<i>Type</i>	<i>Test Method</i>
(1) No observed migration of silicone additive	Required	Films were tested for 12 weeks, after which migration would be unlikely to occur. Additive migration of the slip additive was observed by measuring the COF values on the layer of the film that had no slip additive. If there was no migration, static and dynamic COF values were 1 or greater for the layer with no slip additive. If migration occurred, static and dynamic COF values decreased below 1.
(2) COF values lower than the Control containing nonreactive silicone	Required	Threshold dynamic COF value of 0.4 or less and a static COF value of 0.6 or less.
(3) Stability of the slip additive	Required	Less than 15% change in the static and dynamic COF values, individually, from the 1st day after manufacturing and 20 days after manufacturing.

[00061] The COF values were measured using the ASTM D1894 Standard Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting. Haze and clarity were measured according to ASTM D1003: Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics using the BYK-GARDNER Haze Guard Plus.

Table 8

Example	A	B	C	D	1	2	3
<u>COF within 1 Day after Film Manufacturing</u> (ASTM D1894)							
Static COF	0.87	0.63	0.85	1.41	0.46	0.6	0.59
Dynamic COF	0.72	0.56	0.66	1.3	0.37	0.36	0.37
<u>COF 4 Days after Film Manufacturing</u> (ASTM D1894)							
Static COF	-	0.58	-	-	0.61	0.57	0.53
Dynamic COF	-	0.37	-	-	0.35	0.34	0.32
<u>COF 20 Days after Film Manufacturing</u> (ASTM D1894)							
Static COF	0.89	0.6	0.48	-	0.52	0.54	0.7
Dynamic COF	0.8	0.39	0.39	-	0.33	0.33	0.37
Δ Static COF (COF Day 1/COF Day 20)	-0.02	0.03	0.37	N/A	-0.06	0.06	-0.11
Δ Dynamic COF (COF Day 1/COF Day 20)	-0.08	0.17	0.27	N/A	0.04	0.03	0
Haze (ASTM D1003)	2.5	3	7	9.5	1.5	3.5	2
Clarity (ASTM D1003)	98.6	98.4	94.8	74.4	96.9	94.3	98.7

Table 8							
Example	A	B	C	D	1	2	3
Additive migration to other film layer after 12 weeks (Yes/No)	No	No	No	No	No	No	No
Observations by microscope	No Gel	No Gel	No Gel	Gels Form	No Gel	No Gel	No Gel

[00062] The control film, Comparative Example A, contained the non-reactive silicone MB, which had a high molecular weight silicone gum as the slip additive. The polypropylene compound of Comparative Example A contained 1% silicone by weight. Comparative Example A exhibited moderate slip performance with static and dynamic COF values of 0.87 and 0.72 respectively, measured within the first day of manufacturing. No migration of the silicone additive was observed 12 weeks after manufacturing.

[00063] The Comparative Examples B-D and Examples 1-3 each tested a reactive silicone as the slip additive, replacing the non-reactive silicone of Comparative Example A. For comparison with the control film, Comparative Examples B-D and Examples 1-3 were also formulated to contain 1% silicone by weight of the compound.

[00064] Replacing the silicone gum as slip additive, Masterbatches I, II and III contained ethoxy silyl terminated polydimethylsiloxane, also referred to as an alkoxysilane functionalized polysiloxane, in addition to a functional polyolefin containing maleic anhydride (MAH). During production, the alkoxysilane functionalized polysiloxane hydrolyzed, producing silanol end groups on each chain. The silanol end groups then underwent a condensation reaction to create new Si-O bonds linking the polysiloxane to another polysiloxane, thereby forming a longer polysiloxane chain.

[00065] The anhydride of the grafted polypropylene (0.2% MAH) in Masterbatches I, II and III assisted to catalyze the silanol hydrolysis and condensation reactions.

[00066] Masterbatches II and III contained an additional silanol catalyst to catalyze the hydrolysis and condensation reactions. In addition, Masterbatch III contained an amino functionalized silane, which reacted with the maleic anhydride (MAH)-grafted polypropylene.

[00067] The resulting films of Masterbatches I, II and III, respectively Comparative Examples B, C and D showed no migration of the silicone slip additive after 12 weeks. Although Comparative Examples B and C showed

improved COF values at manufacturing, both formulations evidenced instability indicated by a change greater than 15% in the COF values 20 days after manufacturing.

[00068] For Comparative Example D, much higher COF values were measured after manufacturing compared to Comparative Example A, so no further testing was conducted. The higher COF values were due to the formation of gels from the grafting of the amino-functionalized silane to the MAH-grafted polyolefin, which created co-polymers that were incompatible to the overall polyethylene matrix. As a result of the gels, the film had a rough surface that negatively affected slip performance.

[00069] Masterbatches IV, V, and VI tested the second type of reactive silicone as a slip agent, epoxy functionalized polysiloxane. Each masterbatch also included one or more functionalized polyolefins containing MAH. The films of Examples 1-3, contained 10% of Masterbatches IV, V, and VI respectively. These films unexpectedly demonstrated improved static and dynamic COF values compared to the Control, Comparative Example A, and showed less than a 15% change in both COF values 20 days after manufacturing. No migration of the silicone additive was observed in Examples 1-3 after 12 weeks. Films of Examples 1-3 showed excellent optical properties within 5% of the haze and clarity measurements of the Control film according to ASTM D1003. Experiments conducted of films containing 5% by weight of Masterbatches IV, V, and VI also showed similar success.

[00070] Selection of the appropriate reactive silicone for different polyolefin-based compounds is difficult and unpredictable. Silicone's effectiveness as a non-migrating slip additive is affected by multiple variables, including the reactivity to, compatibility with, and surface energy of the reactive silicone relative to the polyolefin matrix.

[00071] Comparative Examples B and C demonstrated that although the hydrolysis and condensation reactions of the polysiloxane formed longer silica chains, which increased the density of the polysiloxane, these formulations were

not stable over longer periods of time. Comparative Example D showed that adding an amino functionalized silane to react with the MAH group, created gels rather than leading to increased stability.

[00072] Examples 1-3 did not undergo any hydrolysis or condensation reactions. Instead, Examples 1 and 2 relied only on the reactivity of the epoxy group of the polysiloxane with the functionalized polyolefin to create a linkage that, unexpectedly, immobilized the polysiloxane in the polypropylene matrix, while also achieving improved slip properties compared to the control film.

[00073] Therefore, whereas the alkoxysilane functionalized polysiloxanes did not represent an improvement from the non-reactive silicone used in the control film, epoxy functionalized polysiloxanes unexpectedly satisfied all of the required criteria in Table 7 compared to the Control.

[00074] The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A masterbatch for polypropylene, comprising:

- (a) polypropylene carrier,
- (b) epoxy functionalized polysiloxane,
- (c) functionalized polyolefin, and
- (d) optionally, other additives;

wherein the functionalized polyolefin contains a maleic anhydride group and is a grafting agent for the epoxy functionalized polysiloxane.

2. The masterbatch of Claim 1, wherein the ingredients by weight percent of the masterbatch are listed in the chart below.

Polypropylene carrier	45% - 81%
Epoxy functionalized polysiloxane	5% - 10%
Functionalized polyolefin	9% - 45%
Optional additives	0% - 10%

3. The masterbatch of Claim 1 or Claim 2, wherein the functionalized polyolefin is selected from the group consisting of maleic anhydride grafted polypropylene, maleic anhydride polypropylene copolymer, ethylene ethyl acrylate maleic anhydride terpolymer, and combinations of them.

4. A polypropylene compound comprising the masterbatch of any one of Claims 1-3 and polypropylene resin.

5. A polypropylene compound comprising:
 - (a) polypropylene matrix and
 - (b) a slip additive comprising
 - (i) polypropylene carrier,
 - (ii) epoxy functionalized polysiloxane,
 - (ii) functionalized polyolefin, and
 - (iv) optionally, other additives;wherein the functionalized polyolefin contains a maleic anhydride group and is a grafting agent for the epoxy functionalized polysiloxane,
6. The polypropylene compound of Claim 5, wherein the functionalized polyolefin is miscible with the polypropylene matrix.
7. The polypropylene compound of Claim 5 or 6, wherein the epoxy functionalized polysiloxane is between about 0.1 % to about 10% of the weight percent of the polypropylene compound.
8. The polypropylene compound of any one of Claims 5-7, wherein the epoxy functionalized polysiloxane is 1% or less of the weight percent of the polypropylene compound.
9. The polypropylene compound of any one of Claims 5-8, wherein the additive is selected from the group consisting of anti-blocking agents; adhesion promoters; biocides (antibacterials, fungicides, and mildewcides), anti-fogging agents; anti-static agents; bonding, blowing and foaming agents; dispersants; fillers and extenders; fire and flame retardants and smoke suppressants; impact modifiers; initiators; lubricants; micas; pigments, colorants and dyes; plasticizers; processing aids; other slip or release agents; silanes, titanates and zirconates; stabilizers; stearates; ultraviolet light absorbers; viscosity regulators; waxes; and combinations of them.

10. The polypropylene compound of any one of Claims 5-9, wherein one or more additives are added in the form of a masterbatch concentrate.
11. The polypropylene compound of any one of Claims 5-10, in the shape of a molded plastic article, an extruded plastic article, or a calendered plastic article.
12. A film having at least one layer comprised of the polypropylene compound of any one of Claims 5-10.
13. A laminate of the film of Claim 12, wherein there is more than one film layer, and wherein each layer comprises same or different ingredients.
14. The laminate of Claim 13, wherein there is a skin layer contacting one surface of a core layer also having an opposing surface; and wherein the skin layer has a thickness between about 0.5 microns and about 1 millimeter.
15. The laminate of Claim 14, further comprising a second skin layer contacting the opposing surface of the core layer, wherein the core layer comprises polyolefin resin.
16. The laminate of Claims 14 or 15, wherein the skin layer has dynamic coefficient of friction value of 0.4 or less and static coefficient of friction value of 0.6 or less, according to the ASTM D1894-01 method, within 1 day after manufacturing of the laminate.
17. The laminate of Claims 14 or 15, wherein the change between static coefficient of friction and dynamic coefficient of friction values of the skin layer within 1 day after manufacturing and 20 days after manufacturing, according to the ASTM D1894-01 method, is 15% or less.

18. The laminate of Claims 14 or 15, wherein there is essentially no migration of the slip additive from the skin layer into another film layer measured 12 weeks after manufacturing.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/050534

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.: 13-18
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:
The above claims directly or indirectly refer to claim(s) which is/are not drafted in accordance with the second and/or third sentence of Rule 6.4(a). Thus, no meaningful search could be carried out.

3. ☒ Claims Nos.: 4, 8-12
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 an additional fee, this Authority did not invite payment of any additional fee.

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.

A. CLASSIFICATION OF SUBJECT MATTER**C08L 23/10(2006.01)i, C08L 83/04(2006.01)i, C08L 23/26(2006.01)i, C08J 3/22(2006.01)i, C08J 5/18(2006.01)i**

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)

C08L 23/10; C08K 3/00; C08L 33/08; B32B 27/32; C04B 24/16; C08L 23/00; C08K 5/54; C08L 23/02; B32B 7/06; C08L 83/00; C08K 3/22; C08L 83/04; C08L 23/26; C08J 3/22; C08J 5/18

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: masterbatch, polypropylene carrier, polypropylene matrix, epoxy, polysiloxane, maleic anhydride, polyolefin, slip additive, grafting agent.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007-0276063 A1 (SCHAUDER, J.-R. et al.) 29 November 2007 See abstract, claims 1, 2, 8, 20, 21 and paragraphs [0001], [0008], [0010], [0021], [0032].	1-3,5-7
A	US 2006-0057412 A1 (JACOB, S. et al.) 16 March 2006 See abstract, claims 1, 5, 11 and paragraphs [0001], [0007], [0008], [0010]-[0012], [0055], [0056], [0092], [0093].	1-3,5-7
A	EP 0158140 B1 (UNION CARBIDE CORPORATION) 16 October 1985 See abstract, claims 1, 7 and page 2, lines 3-37, page 3, lines 13-43 & lines 51-57, page 4, lines 4-9, 18-42, & lines 49-51.	1-3,5-7
A	EP 0073027 A2 (UNION CARBIDE CORPORATION) 02 March 1983 See abstract, claims 1-3, 7 and page 3, line 22 - page 4, line 11, page 4, lines 18-28.	1-3,5-7
A	US 2012-0059105 A1 (KERSTETTER, III, R. H. et al.) 08 March 2012 See abstract, claims 1, 9, 17 and paragraphs [0003], [0009], [0030], [0055].	1-3,5-7
A	WO 2010-039376 A1 (EXXONMOBIL OIL CORPORATION) 08 April 2010 See abstract, claims 1, 7-9, 17, 21 and paragraphs [0002], [0087].	1-3,5-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* 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 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

27 August 2013 (27.08.2013)

Date of mailing of the international search report

27 August 2013 (27.08.2013)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City,
302-701, Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

KIM Dong Seok

Telephone No. +82-42-481-8647



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/050534

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007-0276063 A1	29/11/2007	US 7790795 B2 WO 2007-139622 A2 WO 2007-139622 A3	07/09/2010 06/12/2007 31/01/2008
US 2006-0057412 A1	16/03/2006	EP 1793998 A1 EP 1793998 B1 JP 04-482033 B2 JP 2008-513251 A US 7193018 B2 WO 2006-033819 A1	13/06/2007 16/04/2008 16/06/2010 01/05/2008 20/03/2007 30/03/2006
EP 0158140 B1	29/05/1991	AU 3975485 A AU 570777 B2 CA 1269781 A1 DE 3582948 D1 EP 0158140 A2 EP 0158140 A3 FI 850975 A0 FI 850975 D0 IN 164371 A1 JP 01-049420 B JP 60-238340 A KR 10-1990-0005625 B1 US 04535113 A	19/09/1985 24/03/1988 29/05/1990 04/07/1991 16/10/1985 09/09/1987 12/03/1985 12/03/1985 04/03/1989 24/10/1989 27/11/1985 01/08/1990 13/08/1985
EP 0073027 A2	02/03/1983	AU 551430 B2 AU 8742882 A BR 8204792 A CA 1185384 A1 DE 3276240 D1 EP 0004752 A2 EP 0004752 B1 EP 0049155 A2 EP 0049155 B1 EP 0073027 A3 EP 0073027 B1 EP 0107211 A3 EP 0120115 A1 EP 0120115 B1 ES 515124 D0 ES 8400129 A1 JP 01-003909 B JP 1304325 C JP 1321805 C JP 1379058 C JP 1488125 C JP 1523944 C JP 1530075 C JP 54-154491 A	01/05/1986 24/02/1983 02/08/1983 09/04/1985 11/06/1987 17/10/1979 25/01/1984 07/04/1982 12/02/1986 22/02/1984 06/05/1987 14/08/1985 03/10/1984 29/12/1999 16/10/1983 01/01/1984 24/01/1989 28/02/1986 11/06/1986 28/05/1987 23/03/1989 12/10/1989 15/11/1989 05/12/1979

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/050534

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		JP 57-126804 A	06/08/1982
		JP 58-065724 A	19/04/1983
		JP 59-159850 A	10/09/1984
		JP 60-030325 B	16/07/1985
		JP 60-035027 A	22/02/1985
		JP 60-050824 B	11/11/1985
		JP 60-069139 A	19/04/1985
		JP 61-048523 B	24/10/1986
		JP 62-014172 B	01/04/1987
		JP 63-036339 B	20/07/1988
		JP S643909 B1	24/01/1989
		JP S643909 B2	24/01/1989
		KR 10-1986-0001033 B1	28/07/1986
		US 04291136 A	22/09/1981
		US 04328323 A	04/05/1982
		US 04343917 A	10/08/1982
		US 04353997 A	12/10/1982
		US 04369289 A	18/01/1983
		US 04404349 A	13/09/1983
		US 04434272 A	28/02/1984
		US 04440907 A	03/04/1984
		US 04446279 A	01/05/1984
		US 04552941 A	12/11/1985
		US 04575535 A	11/03/1986
US 2012-0059105 A1	08/03/2012	CN 103080213 A	01/05/2013
		CN 103097454 A	08/05/2013
		EP 2611863 A1	10/07/2013
		EP 2611864 A1	10/07/2013
		US 2012-059104 A1	08/03/2012
		WO 2012-030577 A1	08/03/2012
		WO 2012-030577 A8	15/11/2012
		WO 2012-030578 A1	08/03/2012
WO 2010-039376 A1	08/04/2010	None	