(19) World Intellectual Property Organization International Bureau



PCT

(43) International Publication Date 14 October 2004 (14.10.2004)

- C08L 23/02, (51) International Patent Classification⁷: 23/14, 23/04, C08K 3/00, 5/14, H01B 7/00
- (21) International Application Number: PCT/US2004/009501
- (22) International Filing Date: 26 March 2004 (26.03.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/458,517 28 March 2003 (28.03.2003) US
- (71) Applicant (for all designated States except US): DOW GLOBAL TECHNOLOGIES INC. [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): WALTHER, Brian, W. [US/US]; 630 Highway 332, Lake Jackson, TX 77566 (US). BAKER, Carl, F. [US/US]; 217 Dewberry Drive, Lake Jackson, TX 77566 (US). BAKER, Sharon, L. [US/US]; 217 Dewberry, Lake Jackson, TX 77566 (US). CASSIDAY, Michael, D. [US/US]; 133 Papaya Drive, Lake Jackson, TX 77566 (US). DIEHL, Charles, F. [US/US]; 119 Dewberry Drive, Lake Jackson, TX 77566 (US). LIANG, Wenbin [US/US]; 6319 Aspen Cove Court, Sugar Land, TX 77479 (US). WRIGHT, David, P. [US/US]; 46 Whitby Circle, Somerset, NJ 08873 (US).

(10) International Publication Number WO 2004/087804 A1

- (74) Agent: HOPPE, James, T.; The Dow Chemical Company, Intellectual Property Section, P.O. Box 1967, Midland, MI 48674-1967 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LOW GLOSS THERMOFORMABLE FLOORING STRUCTURE

Thermoform sheet Thermoform Ή template L

(57) Abstract: A novel flooring composition was developed based on a blend comprising: a) an elastomer; b) a random propylene/alpha-olefin copolymer; c) a cross linking agent; and optionally d) a melt strength enhancing polymer. This composition achieves a unique balance of properties, exhibiting often-conflicting performance requirements. These include low gloss and excellent pattern duplication in embossing, low modulus, minimal odor, excellent grain acceptance and abrasion resistance, while remaining thermoformable and maintaining minimal shift in viscosity during recycle.

Find authenticated court documents without watermarks at docketalarm.com.

Schematic of Thermoform Embossability Index (EI) Measurement.

LOW GLOSS THERMOFORMABLE FLOORING STRUCTURE

Many polymer-processing methods involve the application of temperature and pressure to a resin formulation to fabricate a specific part. Examples of such processes include thermoforming, blow molding, injection molding and overmolding, calendaring, fiber forming, wire and cable, and extrusion coating. The parts resulting from these processes are often required to exhibit a variety of often-conflicting properties and thus industry is always looking for new formulations able to exhibit a desired combination of properties for a given processing method.

A variety of blend compositions have been formulated in an attempt to meet the requirements of the various molding processes. For instance, US Patent No. 5,639,818 describes a peroxide modified propylene homopolymer/polyethylene blend that exhibit superior extrusion coating properties, especially increased melt strength and reduced draw resonance behavior rendering them suitable for a wide variety of applications including thermoforming, blow molding as well as extrusion coating.

US Patent No. 6,433,062 B1 describes a process for the preparation of a thermoplastic elastomeric composition by melt kneading an organic peroxide with a mixture of a block copolymer (or hydrogenated block copolymer), a non-aromatic softening agent for rubber, an ethylene homopolymer or copolymer, and a propylene homopolymer or copolymer. The resulting composition exhibits improved heat deformation resistance, mechanical strength, moldability and processability.

US Patent No. 6,407,172 B1 describes a composition suitable for thermoforming, which demonstrates good grain retention and low cost. The composition comprises a mixture of a propylene homopolymer or copolymer, an ethylene-containing ionomer, a copolymer of ethylene and a glycidyl acrylate, polyethylene, optionally an uncrosslinked ethylene/propylene copolymer rubber, and optionally an ethylene alpha-olefin copolymer elastomer.

US Patent Application Publication No. 2001/0016620 A1 describes a crosslinked olefin thermoplastic composition comprising a crystalline polyolefin, an olefin-based copolymer rubber, and a paraffinic mineral oil softening agent which after molding results in articles with improved antifogging properties and high gloss.

...............

PC1/US2004/009501

US Patent No. 6,407,172 B1 describes thermoplastic polymer alloy composition comprising a blend of polypropylene, uncrosslinked ethylene copolymer, an ionomeric copolymer of ethylene and an α , β -unsaturated carboxylic acid, a crosslinking agent and a silicone elastomer. The compositions are said to be useful for forming interior skin sheets for applications where low gloss and high scuff resistance are desired.

US Patent No. 6,451,894 B1 describes molded articles made from thermoplastic blends of a crystalline or semi crystalline polyolefin and a multimodal elastomer of sequentially polymerized ethylene/alpha olefin monomers. Molded articles made from such blends exhibit increased paint adherence and improved resistance to fluid as well as higher weld line strength and low temperature ductility.

US Patent No. 6,506,842 B1 describes a rheology-modified thermoplastic elastomer composition. The composition is prepared by peroxide-modification of a melt blend of an ethylene/alpha-olefin copolymer or a diene-modified ethylene/alpha-olefin copolymer and a high melting point polymer such as a polypropylene or a propylene/alpha olefin. The composition is peroxide modified sufficient to result in an increase in solidification temperature (that is, the temperature of the highest temperature peak endotherm measured during cooling by differential scanning calorimeter (DSC)) that is at least 10°C greater than that of the unmodified composition. These compositions have improved heat resistance and thus must be processed at higher temperatures.

Finally, US Patent Application Publication No. 2002/0115796 A1 describes thermoplastic elastomer compositions comprising a melt blend of an ethylene/alpha-olefin copolymer and a high melting point polymer such as a polypropylene or a propylene/alpha which is rheology modified using a combination of a peroxide and free radical coagents. The use of the coagent is said to increase the melt toughness and high temperature tensile properties as compared to the same compositions, which are rheology modified by peroxides alone.

Thermoforming is another of the family of processes that deal with the pressing or squeezing of pliable plastic into a final shape, and is the general term used for the process of making plastic parts from a flat sheet of plastic, through the application of pressure and temperature. However, thermoforming is differentiated from extrusion or blow molding, as in the former, the initial resin state is fluid rather than solid, whereas thermoforming always begins with a contiguous sheet of rubbery plastic. This sheet has been processed from resin

WO 2004/08/804

OCKE.

pellets or powder by casting, calendaring, rolling, extruding, compression molding or other techniques. The thermoforming process is a result of four subsequent steps, namely; 1) heating the sheet, 2) stretching it; 3) cooling it on the mold surface; and 4) trimming the resulting part from its surroundings

These deformation processes must occur while the polymer is in a rubbery solid state that is, above its glass transition temperature (Tg) but below its crystalline melting temperature (Tm) allowing easy uptake of the mold configuration. Thus the glass transition temperature, Tg, is the absolute lowest temperature at which the polymer can be formed. As processing temperatures increase above Tg, amorphous polymers become increasingly easier to process, but in crystalline polymers, the crystallite order restricts amorphous phase chain morphology, until the melting point is reached. Thus the normal thermoforming or "forming" temperature for an amorphous polymer is closely related to Tg, but for crystalline polymers the forming temperature is more dependent on the Tm. Typically, for single component amorphous materials, the lower forming temperature is about 20-30°C above Tg, and the normal forming temperature is 70-100°C above Tg. In contrast, the forming temperature is often within a few degrees of the polymer Tm.

Once the plastic sheet is at the proper thermoforming temperature it can be stretched. The various thermoplastic sheet-forming techniques include, vacuum forming, pressure forming, matched mold forming, all of which require clamping, heating and shaping the sheet into or over a mold. Before forming, the heated sheet is virtually stress free. When properly formed, the sheet is almost completely stretched at the forming temperature before it is cooled against the mold. This results in a minimum of internal stress in the finished part.

In order to be readily formable, the heated sheet, when at forming temperature, must have certain physical properties including high melt strength, over a broad temperature range. The physical properties and melt strength of some thermoplastic polymers can be improved by the use of crosslinking agents, including peroxide and irradiation. A small amount of crosslinking serves to partially immobilize the polymer while above its traditional melting point by the introduction of a small amount of ultra high molecular weight material within the bulk polymer matrix resulting in an increase in the low shear viscosity and storage modulus. Thus, instead of becoming fluids above their melting points, lightly crosslinked thermoplastics remain soft thermoformable solids extending the range of the thermoforming

WO 2004/08/804

temperature for such materials. However, too high a degree of crosslinking restricts the type of gross deformation required for successful thermoforming.

In addition to having the necessary strength requirements for molding the heated sheet, many applications require the resulting article to be embossed and also exhibit a specific gloss level. The degree of gloss can be regulated to some degree by the processing conditions such as extrudate or sheet temperature. Low gloss usually results from low extrudate or sheet temperature. In addition, while remaining relatively constant up to a certain thermoforming temperature, above this temperature, gloss begins to increase exponentially with further temperature increase. However, embossability increases much more linearly across the same temperature range.

The introduction of crosslinking in a polymer causes a decrease in the level of gloss of a finished part as a small amount of ultra high molecular weight material within the bulk polymer matrix causes distortions in the surface on cooling which in turn leads to a lower surface gloss. These distortions are due to the increased relaxation time of the ultra high molecular weight fraction relative to the bulk polymer matrix.

Flooring applications such as automotive flooring mats and liners have historically required the use of polymer compositions that exhibit both good thermoformability and excellent embossing pattern retention. Furthermore, such applications also generally require low surface gloss of the flooring for aesthetics and non-marking performance attributes. Recently, industry has developed the additional needs that such compositions also exhibit improved softer hand feel.

To date, typical polymer formulations used for such applications are made primarily of thermoplastic polyolefin (TPO) with polypropylene as the major component of the polymeric blend. Polypropylene is used as it has good abrasion resistance and thermal dimensional stability (that is, very important in automotive applications, which often require a high temperature dimensional stability and abrasion resistance). Flooring that is thermoformed from such compositions typically exhibit good thermoformability with excellent embossability. However, the flooring has relatively high stiffness.

Therefore it would be highly advantageous if new polymer compositions could be discovered which typically exhibit good thermoformability and excellent embossability and also exhibit low surface gloss for aesthetics and non-marking performance attributes.

DOCKET



Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time** alerts and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.

