

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 August 2010 (05.08.2010)

(10) International Publication Number
WO 2010/085871 A1

PCT

(51) International Patent Classification:

B29C 41/06 (2006.01) **C08K 5/17** (2006.01)
C08J 3/20 (2006.01) **C08K 5/52** (2006.01)
C08K 3/22 (2006.01) **C08L 23/06** (2006.01)
C08K 5/13 (2006.01)

(21) International Application Number:

PCT/CA2010/000021

(22) International Filing Date:

12 January 2010 (12.01.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2,651,514 29 January 2009 (29.01.2009) CA

(71) Applicant (for all designated States except US): **NOVA CHEMICALS (INTERNATIONAL) S.A.** [CH/CH];
Avenue de la Gare 14, CH-1700 Fribourg (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **GIBBONS, Ian Robert** [CA/CA]; 94 Tuscarora Circle N.W., Calgary, Alberta T3L 2B9 (CA). **TIKUISIS, Tony** [CA/CA];
2205-1st Street, N.W., Calgary, Alberta T2M 2T7 (CA).

(74) Agents: **CHISHOLM, P., Scott et al.**; 2928-16 Street NE, Calgary, Alberta T2E 7K7 (CA).

(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, 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, KM, 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, PE, PG, PH, PL, PT, RO, RS, RU, 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, LS, MW, MZ, NA, 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, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: STABILIZED ROTOMOLDED PARTS

(57) Abstract: Easy processing rotomolding resins which have a high melt index, I₂, (as measured by ASTM D 1238) of from 2 to 10 (especially 3 to 8) grams/10 minutes and a narrow molecular weight distribution, Mw/Mn, of from 2.0 to 3.0 are difficult to stabilize with correctional additive packages. The present invention resolves this problem by the use of from 500 to 5000 parts per million by weight (ppm) of zinc oxide, in addition to a standard stabilizer additive package.



WO 2010/085871 A1

STABILIZED ROTOMOLDED PARTS**TECHNICAL FIELD**

This invention relates to a rotomolding process which employs an easily
5 processable polyethylene resin and a specific additive package.

BACKGROUND ART

Rotational molding, also known as rotomolding, is a well known process which is
widely used to produce hollow plastic parts such as gasoline containers, garbage cans,
agricultural storage vessels, septic tanks and sporting goods such as kayaks. The
10 process is undertaken by loading a charge of finely divided plastic resin into the mold
"shell", then rotating the mold (usually, on two axes) while heating it to a temperature
above the melting point of the plastic resin. The melted plastic flows through the mold
cavity under the forces caused by the rotation of the apparatus. The rotation continues
for sufficient time to allow the molten plastic to cover the surface of the mold. The mold
15 is then cooled to permit the plastic to freeze into a solid. The final stage of the molding
cycle is the removal of the part from the rotomolding machine.

The time required to complete the molding cycle is a function of the bulk
properties of the plastic which is being molded. For example, it is recognized by those
skilled in the art that the plastic resin which is charged into the mold is preferably finely
20 divided (i.e. ground into powder) and has a high bulk density and a narrow particle size
distribution to facilitate the "free flow" of the resin.

It will also be appreciated that the physical properties of the rotomolded part are
influenced by the use of a proper molding cycle time
with "undercooked" parts having poor strength properties and "overcooked" parts
25 suffering from poor appearance (a "burnt" color) and/or a deterioration of strength
properties. It is desirable to have a short molding cycle (so as to improve the
productivity of the expensive rotomolding machinery) and a broad "processing window"
(i.e. the rotomolding composition ideally provides "properly cooked" parts in a short
period of time but does not become "overcooked" for an extended period of time).

30 In addition, the properties of the rotomolded part are affected by the molecular
structure of the polymer used to prepare the part. Physical properties of importance
include stiffness (as indicated by the modulus of the part), environmental stress crack
resistance (or "ESCR"), impact resistance and resistance to warpage.

Thermoplastic polyethylene copolymer is a commonly used plastic resin for the manufacture of rotomolded parts. Conventional polyethylene copolymer resin (which is generally prepared by the copolymerization of ethylene with a C_{4to10} alpha olefin in the presence of a chromium catalyst or a Ziegler Natta catalyst) is typically used. The alpha olefin comonomer produces "short chain branches" (SCB) in the copolymer. These SCB reduce the crystallinity of the copolymer (in comparison to a linear ethylene homopolymer) and the copolymers typically have improved impact resistance in comparison to homopolymers. These conventional polyethylenes may be referred to as "heterogeneous" in the sense that the polyethylene is actually a mixture of different polyethylene chains having significantly different molecular weights and comonomer distributions. Most notably, a conventional heterogeneous polyethylene copolymer resin generally contains three fractions:

- i) a low molecular weight fraction having a high comonomer content (or high level of SCB) - this fraction is often referred to as "wax" or "extractables";
- ii) a very high molecular weight fraction having essentially no comonomer - this fraction is often referred to as "homopolymer"; and
- iii) a fraction of intermediate molecular weight and SCB content.

These conventional polyethylenes are well suited for rotomolding. For example, whilst not wishing to be bound by theory, it has been postulated that the high molecular weight "homopolymer" fraction may enhance the stiffness or modulus of the rotomolded parts. However, as may be expected, the physical properties of a finished part (which has been molded with a proper cycle time) are largely "set" by the molecular structure of the polyethylene copolymer used to prepare the part. This, in turn, often results in finished parts with a suboptimal balance of properties.

More recently, homogeneous ethylene copolymers have become commercially available. These homogenous polymers have a uniform (or narrow) molecular weight distribution and a uniform comonomer distribution. This, in turn, causes the homogeneous copolymers to have a well defined melting point (in comparison to the heterogeneous polymers which have a melting point "range" or even multiple melting points).

The sharp melting point might have been expected to be advantageous for a rotomolding process. However, in practice, it has been found that parts prepared from a single homogeneous resin are prone to warpage and also

generally have poor modulus or stiffness. Blends of homogeneous resins have been shown to mitigate this warpage problem, as disclosed in U.S. patent no. 7,201,864 (the disclosure of which is incorporated herein by reference).

5 A desire for rotomolding processes with even faster cycle times has led to the use of polymers having comparatively melt index, I_2 , (as determined by ASTM D 1238 using a 2.16 kg weight). Melt index, I_2 , is inversely related to molecular weight – so, in other words, the use of lower molecular weight polyethylene has been observed to provide fast cycle times. In particular, a polyethylene resin with a melt index of from 2 to 10 (especially 3-8) and a narrow molecular weight distribution, M_w/M_n , of less than 3
10 has been found to provide a fast cycle time.

Unfortunately, conventional stabilization systems for rotomolding resins do not perform well for these easy processing/high MI resins. In particular, a conventional stabilization system which contains a primary antioxidant, a secondary antioxidant and a hindered amine light stabilizer in conventional amounts does not always provide a
15 level of stability in these easy processing resins that is generally observed in either conventional rotomolding resins (prepared with a Ziegler catalyst) or even lower melt index rotomolding resins that are prepared with a single site catalyst.

DISCLOSURE OF INVENTION

20 In one embodiment of this invention, there is provided a rotomolding process comprising

I) preparing a blend of:

A) a polyethylene resin having:

- a) a melt index, I_2 , as measured by ASTM D 1238 of from 2 to 10;
- b) a molecular weight distribution, M_w/M_n , of from 2.0 to 3.0;
- 25 c) a density of from 0.930 to 0.950 g/cc;

B) an additive package comprising:

- a) a primary antioxidant;
- b) a secondary antioxidant;
- c) at least one hindered amine light stabilizer; and
- 30 d) from 250 to 5000 ppm of Zinc Oxide (ZnO); and

II) subjecting said blend to rototational molding.

BEST MODE FOR CARRYING OUT THE INVENTION

Rotational molding technology is well known and is described in the literature. Reference may be made to United States Patent (USP) 5,530,055 (Needham, the

disclosure of which is incorporated herein by reference) for further details concerning the operation of a rotomolding process.

The rotomolding process of this invention uses a polyethylene resin that has a density of from 0.930 to 0.950 which is preferably a copolymer or inter polymer of ethylene with an alpha olefin.

In general, the term ethylene copolymer (or "interpolymer"), as used herein, is meant to refer to a copolymer of ethylene with at least one alpha olefin monomer containing from 3 to 10 carbon atoms. Thus, ethylene homopolymers are excluded but terpolymers are included. The physical properties of such ethylene copolymers are influenced by their molecular weight, molecular weight distribution, comonomer content and comonomer distribution. It is well known that the use of such comonomers produces copolymers that generally have decreased density and crystallinity as the amount of incorporated comonomer increases.

Conventional (heterogeneous) ethylene copolymers which are prepared with a conventional Ziegler-Natta catalyst generally have a comparatively broad molecular weight distribution (as defined by dividing weight average molecular weight, M_w , by number average molecular weight, M_n - i.e. molecular weight distribution equals M_w/M_n) and a broad comonomer distribution. These resins typically contain at least three distinct polymer fractions, namely a small amount (generally less than 5 weight %) of a low molecular weight, high comonomer content material (also known as "wax"); a significant fraction (15 to 25 weight %) of material having a very high molecular weight and a low comonomer content (also known as "homopolymer"); with the remainder of the copolymer being of intermediate density and molecular weight.

This lack of uniformity with respect to molecular weight and comonomer distribution has several disadvantages for example, the "wax" fraction may limit the use of these interpolymers in applications which come into contact with food and the "homopolymer" fraction is often associated with the poor impact resistance of goods made with these interpolymers. In addition, these heterogeneous polymers have a molecular weight distribution, M_w/M_n , of greater than 3.0.

In contrast, the rotomolding compositions used in this invention have a narrow molecular weight distribution. In particular the polyethylene resin of this invention must also have a molecular weight distribution M_w/M_n of from 2.0 to 3.0 (preferably from 2.2 to 2.8). Thus, preferred rotomolding compositions used in this invention are characterized by having less than 2.0 weight % of low molecular weight, high

comonomer content wax (i.e. for further clarity, less than 2.0 weight % of hexane extractables as determined by the test method established by the United States Food and Drug Administration and published under CFR 177.1520 (c)) and less than 10 weight % of high molecular weight homopolymer (i.e. for further clarity, less than 10 weight % of the rotomolding composition contains less than 1 short chain branch per 1000 carbon atoms as determined by Temperature Rising Elution Fractionation or TREF).

Rotomolding compositions for use in this invention are further characterized by density and melt flow characteristics. Specifically, the density range is from 0.930 to 0.950 grams per cubic centimeter (preferably 0.935 to 0.945) and the melt index ("I₂", as determined by ASTM D-1238, using a 2.16 kilogram load at a temperature of 190°C) is from 2 to 10 grams per 10 minutes (preferably 3 to 8). Melt index might be regarded as an indicator of molecular weight, though an inverse relationship between the two exists. That is, as the molecular weight of the polymer increases, the flow index (I₂) decreases.

The compositions used in this invention preferably contain at least two ethylene copolymer blend components. Each of these components may be prepared by the copolymerization of ethylene with a C_{4to20} alpha olefin in the presence of a catalyst system which produces homogenous polymers (i.e. as above, polymers with a narrow molecular weight distribution and narrow composition distribution). Exemplary catalyst systems include the vanadium catalyst system disclosed in USP 3,645,992 (Elston), "metallocene" catalysts (as disclosed, for example, in USP 5,324,800), "constrained geometry" catalysts (as disclosed, for example, in USP 5,064,802 Stevas et al.) and the phosphinimine catalyst systems described in the USP 6,372,864 (Brown et al.).

As previously noted, it is desirable to reduce the rotomolding cycle time so as to improve the productivity of the expensive machinery. It is further desirable to produce parts which have excellent environmental stress crack resistance; high ductility and good stiffness. This may be illustrated by considering a molded tank for liquids - the tank needs to be resistant to the elements; it should be resistant to impact (for example, it should not shatter when struck with a blunt object) and the tank needs to be stiff enough to maintain its shape when filled with liquid.

It is known to prepare rotomolded parts with a single "homogeneous" resin (i.e. a resin with a uniform comonomer distribution). Homogeneous resins do not contain the "high density" fraction which exists in conventional Ziegler Natta ("Z/N") resins and,

thus, a homogeneous resin will have a lower (and sharper) melting point than a Z/N resin of similar molecular weight and density. This, in turn may allow cycle times to be reduced using a single homogeneous resin (in comparison to the cycle time required for similar Z/N resin). However, the resulting parts are prone to warpage. In addition, the
5 rotomolded parts prepared from homogeneous resins have poor stiffness in comparison to parts prepared from Z/N resins. The well defined melting point of the homogeneous resins used to prepare the present rotomolded parts may also assist with the fabrication of custom parts (in which thin molds with irregular shapes must be filled within tight tolerances).

10 The preferred blend components may be prepared as distinct polymers in separate polymerization reactions and then blended together to provide the present compositions. The blend components may be blended using conventional mixing/blending equipment such as a single or twin screw extruder; and internal batch mixer such as a Bamberg mixer; or a continuous mixer such as a Farrel mixer. The
15 mixing time and temperatures may be readily optimized by those skilled in the art without undue experimentation. As a guideline, mixing temperatures of from 150 to 250°C are suitable and mixing times of 1-10 minutes may provide satisfactory results. Alternatively (and preferably), the blend components may be prepared in a multiple reactor polymerization system as disclosed in the Examples.

20 Typically, each blend component is a copolymer of ethylene with C_{4to8} alpha olefin such as butene-1, pentene-1, 4-methyl-1-pentene, hexene-1 or octene-1; with hexene-1 and octene-1 being most preferred.

As previously disclosed, the overall rotomolding composition of this invention has a narrow molecular weight distribution of less than 3.0. Preferred compositions are
25 prepared with two blend components, each of which represents from 20 to 80 weight % of the total composition. It follows from these preferences that each of the two blend components preferably has a similar molecular weight as well as a narrow molecular weight distribution (i.e. in the sense that the composition would have a molecular weight distribution of greater than 3.0 if the blend components had substantially different
30 molecular weights or if one or both of the blend components had a broad molecular weight distribution).

In addition, it is preferred that each of the blend components has essentially the same density (which, as used herein, means that the difference in density between each of the blend components is less than 0.015 grams per cubic centimeter).

The preferred rotomolding composition used in this invention preferably has a relatively sharp and low melting point in comparison to a heterogeneous resin of similar average molecular weight and density. In this sense, the present rotomolding compositions are similar to a single homogeneous resin (i.e. a single homogeneous resin will also have a relatively sharp and low melting point in comparison to a conventional heterogeneous resin of similar average molecular weight and density).

In the broadest sense, the polyethylene resin used in this invention must satisfy the following three conditions:

- 1) a melt index, I_2 , of from 2 to 10 (preferably from 3 to 8);
- 2) a molecular weight distribution, M_w/M_n , of from 2.0 to 3.0 (preferably from 2.2 to 2.8); and
- 3) a density of from .930 to .950 g/cc.

A polyethylene resin which meets these conditions is easily processed in a rotomolding operation. However, as will be shown in the Examples, this type of resin is difficult to stabilize with a conventional additive package. In particular, this type of resin is prone to deterioration in "Weather-o-Meter" (WOM) testing.

The Weather-o-Meter™ machines are well known to those skilled in the art and are used to simulate weathering conditions. The machines are available from Atlas Electric Devices Company and may be used in accordance with various ASTM test methods.

Additives

Rotomolding compositions conventionally contain an additive package to protect the polymer from decomposing during the processing and/or exposure to the elements and to improve processing cycle times and windows. Reference is made to "Influence of Stabilizers in Rotational Molding" (Gupta and Stadler; paper presented at 22nd Annual Fall Meeting of the Association of Rotational Molders; 5-8 October 1997) for details.

The additive system of this invention includes a hindered Amine Light Stabilizers (or HALS); a secondary antioxidant that is preferably a phosphite or phosphonite (especially a diphosphite as illustrated in the examples); a "primary" antioxidant that is preferably selected from the group consisting of hindered phenols, hydroxyl amines, amine oxides and lactones and zinc oxide.

The easy processing resins used in this invention deteriorate comparatively quickly in a WOM when stabilized with a conventional additive package which contains

a primary antioxidant, a secondary antioxidant and a HALS. The addition of ZnO provides a surprising improvement in WOM ageing.

The additives may be incorporated into the compositions using mixing equipment such as an extruder, or internal batch mixer (also known as a banbury mixer). The additive may be added "neat" (i.e. directly to the resin); as a "masterbatch" (i.e. by premixing the additives with a small amount of polyethylene which is subsequently mixed with the bulk of the composition); or as "preblends" (i.e. mixtures of the additives). Exemplary additives are set out below.

In summary, the additive package used in the present invention must contain at least four components, namely 1) a primary antioxidant; 2) a secondary antioxidant; 3) a hindered amine light stabilizer and 4) zinc oxide.

1. Primary Antioxidants

As used herein, the term primary antioxidant refers to a molecule which is capable of providing free radicals with a polyethylene matrix. Preferred primary antioxidants include hindered phenols, hydroxylamines, amine oxides and lactones. A combination of more than one primary antioxidant may be used. The use of a hindered phenol or a hydroxylamine is preferred. The preferred amount of primary antioxidant is from 100 to 1000 ppm.

Exemplary primary antioxidants are described in more detail in section 1 below.

1.1 Alkylated Mono-Phenols

For example, 2,6-di-tert-butyl-4-methylphenol; 2-tert-butyl-4,6-dimethylphenol; 2,6-di-tert-butyl-4-ethylphenol; 2,6-di-tert-butyl-4-n-butylphenol; 2,6-di-tert-butyl-4-isobutylphenol; 2,6-dicyclopentyl-4-methylphenol; 2-(.alpha.-methylcyclohexyl)-4,6-dimethylphenol; 2,6-di-octadecyl-4-methylphenol; 2,4,6,-tricyclohexyphenol; and 2,6-di-tert-butyl-4-methoxymethylphenol.

1.2 Alkylated Hydroquinones

For example, 2,6di-tert-butyl-4-methoxyphenol; 2,5-di-tert-butylhydroquinone; 2,5-di-tert-amyl-hydroquinone; and 2,6diphenyl-4-octadecyloxyphenol.

1.3 Hydroxylated Thiodiphenyl Ethers

For example, 2,2'-thio-bis-(6-tert-butyl-4-methylphenol); 2,2'-thio-bis-(4-octylphenol); 4,4'thio-bis-(6-tertbutyl-3-methylphenol); and 4,4'-thio-bis-(6-tert-butyl-2-methylphenol).

1.4 Alkylidene-Bisphenols

For example, 2,2'-methylene-bis-(6-tert-butyl-4-methylphenol); 2,2'-methylene-bis-(6-tert-butyl-4-ethylphenol); 2,2'-methylene-bis-(4-methyl-6-(alpha-methylcyclohexyl)phenol); 2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol); 2,2'-methylene-bis-(6-nonyl-4-methylphenol); 2,2'-methylene-bis-(6-nonyl-4-methylphenol); 2,2'-methylene-bis-(6-(alpha-methylbenzyl)-4-nonylphenol); 2,2'-methylene-bis-(6-(alpha, alpha-dimethylbenzyl)-4-nonyl-phenol); 2,2'-methylene-bis-(4,6-di-tert-butylphenol); 2,2'-ethylidene-bis-(6-tert-butyl-4-isobutylphenol); 4,4'-methylene-bis-(2,6-di-tert-butylphenol); 4,4'-methylene-bis-(6-tert-butyl-2-methylphenol); 1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenol)butane 2,6-di-(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol; 1,1,3-tris-(5-tert-butyl-4-hydroxy-2-methylphenyl)butane; 1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-dodecyl-mercaptopbutane; ethyleneglycol-bis-(3,3-bis-(3'-tert-butyl-4'-hydroxyphenyl)-butyrate)-di-(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene; di-(2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl)terephthalate; and other phenolics such as monoacrylate esters of bisphenols such as ethylidene bis-2,4-di-t-butylphenol monoacrylate ester.

1.5 Hydroxylamines and Amine Oxides

For example, N,N-dibenzylhydroxylamine; N,N-diethylhydroxylamine; N,N-dioctylhydroxylamine; N,N-dilaurylhydroxylamine; N,N-ditetradecylhydroxylamine; N,N-dihexadecylhydroxylamine; N,N-dioctadecylhydroxylamine; N-hexadecyl-N-octadecylhydroxylamine; N-heptadecyl-N-octadecylhydroxylamine; and N,N-dialkylhydroxylamine derived from hydrogenated tallow amine. The analogous amine oxides (as disclosed in USP 5,844,029, Prachu et al.) are also suitable.

2. Secondary Antioxidants

The term secondary antioxidant refers to an additive that is used to scavenge peroxides. Examples include triphenyl phosphite; diphenylalkyl phosphates; phenyldialkyl phosphates; tris(nonyl-phenyl)phosphite; trilauryl phosphite; trioctadecyl phosphite; distearyl pentaerythritol diphosphite; tris(2,4-di-tert-butylphenyl)phosphite; diisodecyl pentaerythritol diphosphite; 2,4,6-tri-tert-butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite; bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite tristearyl sorbitol triphosphite; and tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene diphosphonite, phosphorous compounds (especially phosphites and phosphonites) and sulfur compounds (especially esters of betatriodipropionic acid) and dialkylsulfides.

Phosphorus compounds are preferred, especially the phosphites and phosphonites. A combination of more than one secondary antioxidant may be used.

It is particularly preferred to include a diphosphite and diphosponite as these additives may extend the "processing window" (i.e. allowing the part to remain in the mold for an extended period of time without becoming "overcooked" to the point of discoloration and/or the loss of physical properties). The preferred amount of secondary antioxidant is from 100 to 3000 ppm.

3. Hindered Amine Light Stabilizers

In general, a hindered amine light stabilizer (HALS) has a hindered amine functional group (which is preferably a tetramethyl piperidine group) together with an organic "structure" or "backbone" that is used to deliver the functional group to the polymer that is being stabilized. The number average molecular weight (Mn) of these HALS structures typically range from about 600 to about 15,000. HALS are well known items of commerce and are readily available from such suppliers as Ciba Specialty Chemicals and Cytec Incorporated.

Examples of HALS include bis (2,2,6,6-tetramethylpiperidyl)-sebacate; bis-5 (1,2,2,6,6-pentamethylpiperidyl)-sebacate; n-butyl-3,5-di-tert-butyl-4-hydroxybenzyl malonic acid bis(1,2,2,6,6-pentamethylpiperidyl)ester; condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidine and succinic acid; condensation product of N,N'-(2,2,6,6-tetramethylpiperidyl)-hexamethyldiamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine; tris-(2,2,6,6-tetramethylpiperidyl)-nitrilotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4butane-tetra-arbonic acid; and 1,1'-(1,2-ethanediyl)-bis-(3,3,5,5-tetramethylpiperazinone). These amines typically called HALS (Hindered Amines Light Stabilizing) include butane tetracarboxylic acid 2,2,6,6-tetramethyl piperidinol esters. Such amines include hydroxylamines derived from hindered amines, such as di(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate; 1-hydroxy 2,2,6,6-tetramethyl-4-benzoxypiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-(3,5-di-tert-butyl-4-hydroxy hydrocinnamoyloxy)-piperidine; and N-(1-hydroxy-2,2,6,6-tetramethyl-piperidin-4-yl)-epsilon-caprolactam.

Additional details concerning suitable HALS for use in the present invention are disclosed in U.S.P. 5,037,870 and 5,134,181, the disclosures of which are incorporated herein by reference. The preferred amount of HALS is from 300 to 3000 ppm.

4. Zinc Oxide

The use of from 250 to 5000 ppm of zinc oxide (ZnO) is essential to the present invention. ZnO is widely used as a polyolefin additive. Any of the commercially available ZnO products which are presently used in polyolefins are potentially suitable for use in the present invention. Preferred zinc oxide is prepared by the so called "French Process" and has a mean particle size of less than 1 micron. ZnO sold under the trademark "KAYDOX 911" is suitable. Representative physical properties of KAYDOX 911 ZnO are reported by the manufacturer as: a) mean particle size: 0.12 microns and b) surface area: 9.0 m²/g.

10 Other Additives

Polyamide Stabilizers

For example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

Basic Co-stabilizers

For example, melamine; polyvinylpyrrolidone; dicyandiamide; triallyl cyanurate; urea derivatives; hydrazine derivatives; amines; polyamides; polyurethanes; alkali metal salts and alkaline earth metal salts of higher fatty acids, for example, Ca stearate, calcium stearoyl lactate, calcium lactate, Zn stearate, Mg stearate, Na ricinoleate and K palmitate; antimony pyrocatecholate or zinc pyrocatecholate, including neutralizers such as hydrotalcites and synthetic hydrotalcites; and Li, Na, Mg, Ca, Al hydroxy carbonates.

Nucleating Agents

For example, 4-tert-butylbenzoic acid; adipic acid; diphenylacetic acid; sodium salt of methylene bis-2,4-dibutylphenyl; cyclic phosphate esters; sorbitol tris-benzaldehyde acetal; and sodium salt of bis(2,4-di-t-butylphenyl) phosphate or Na salt of ethylidene bis(2,4-di-t-butyl phenyl)phosphate. Nucleating agents may improve stiffness of the rotomolded part.

Fillers and Reinforcing Agents

For example, calcium carbonate; silicates; glass fibers; asbestos; talc; kaolin; mica; barium sulfate; metal oxides and hydroxides; carbon black and graphite.

Miscellaneous

For example, plasticizers; UV absorbers; epoxidized vegetable oils, such as epoxidized soybean oils; lubricants; emulsifiers; pigments; optical brighteners; flame

proofing agents; anti-static agents; blowing agents and thiosynergists, such as dilaurylthiodipropionate or distearylthiodipropionate.

Foamable rotomolded parts are also contemplated. As disclosed in USP 5,532,282 (Needham) foaming agents are useful to reduce part weight, provide a higher insulation value, increase stiffness and reduce resin cost. Generally, foaming agents may be classified as "physical" or "chemical" foaming agents. Typically, physical foaming agents are normally gaseous at the temperature at which the plastic mass is to be foamed. Chemical foaming agents are typically compositions which decompose or react to form a gas. Heat decomposable, foaming agents include organic compounds such as azodicarbonamide, 4,4'-oxybisbenzene-sulfonyl hydrazide, and p-toluenesulfonyl hydrazide; disadvantages include cost and unpleasant odor. Carbon dioxide-releasing, foaming agents include inorganic salts such as sodium, ammonium and potassium bicarbonate. A foaming coagent is advantageously used with a reactive type, chemical foaming agent, and for an acid-released foaming agent, a fatty acid such as stearic acid or a mild organic acid such as citric acid is often used as the coagent.

Useful co-additives, when foaming thermoplastics, include foam nucleating agents. A foam nucleating agent promotes uniform cell size and reduces the existence of surges and voids in the foam. Suitable foam nucleating agents include calcium carbonate; pigments such as carbon black; and silicates such as kaolins, talc, aluminum silicate, magnesium silicate and calcium silicate.

Similarly, crosslinkable rotomolded parts are contemplated. As disclosed in USP 5,367,025 (Needham) crosslinking agents may include a combination of organic peroxide initiator and a crosslinking co-agent. For rotomolding, dialkyl peroxides used include 2,5-dimethyl-2,5-di(t-butylperoxy)hexane or alpha,alpha'-bis(t-butylperoxy)diisopropylbenzene or those disclosed in USP 3,214,422. Co-agents used by those experienced in the art of crosslinking polyethylene, include triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, trimethololpropane trimethacrylate and related monomers.

EXAMPLES

Experimental procedures are described below:

Four different types of polyethylene resin were used. Two were prepared with a conventional Ziegler Natta (Z/N) catalyst and each had a molecular weight distribution, Mw/Mn, of between 3.2 and 3.5. Conventional resin "Z/N1" also had a melt index, I₂, of

5 g/10 minutes and a density of 0.935 g/cc. Conventional resin "Z/N2" had a melt index, I_2 , of 1.8 g/10 minutes and a density of 0.942 g/cc.

Two "single site catalyst" (SSC) resins were also used. Each of SSC1 and SSC2 resin had a molecular weight distribution, M_w/M_n , of between 2.2 and 2.8. SSC1
5 had a melt index, I_2 , of 5 g/10 minutes and a density of 0.939 g/cc. SSC2 had a melt index, I_2 , of 1.7 g/10 minutes and a density of 0.944 g/cc.

The resins were blended with the additive packages described in Table 1 and ground into fine powder for the preparation of rotomolded parts. For clarification: the compounded resin used in experiment 1 was conventional polyethylene ZN1 and
10 contained 300 ppm of primary antioxidant (Lowinox™ 1790); 1500 ppm of secondary antioxidant (Irgafos 168) and 2200 ppm of HALS (Cyasorb UV3346).

Also for clarity: the composition of experiment 3 contained 500 ppm of primary antioxidant 1; 250 ppm of primary antioxidant 2; 800 ppm of secondary antioxidant 1 and 500 ppm of secondary antioxidant 2.

15 Rotomolded parts were then prepared in a rotational molding machine sold under the tradename Rotospeed RS3-160 by Ferry Industries Inc. The machine has two arms which rotate about a central axis. Each arm is fitted with a plate which rotates on an axis that is roughly perpendicular to the axis of rotation of the arm. Each plate is fitted with three cast aluminum molds that produce plastic cubes having dimensions of
20 12.5 inches (31.8 cm) x 12.5 inches x 12.5 inches. These molds produce parts having a nominal thickness of about 0.25 inches (0.64 cm) when initially filled with a standard charge of about 3.7 kg of polyethylene resin.

A gas fired furnace which is capable of providing 2 million British thermal units (Btu) per hour is used to provide hot air that is circulated about the molds by a fan. The
25 temperature within the enclosed oven is maintained at a temperature of between 520°F (271°C) and 600°F (316°C) for specified periods of time while the machine rotates the arms (typically, at about 8 revolutions per minute (rpm) and the plate (typically, at about 2 rpm).

The "cooked parts" are then cooled by opening the oven. Water spray may also
30 be used to facilitate cooling. "Cook times", rotation speed, temperatures and cooling cycles are computer controlled with appropriate software which also includes a data acquisition system.

Physical properties of the polyethylene resins and /or specimens cut from the molded cubes were measured using the following standard test methods:

Melt Index (I_2) was measured according to ASTM D 1238 at 230°C using a 2.16 kg load.

Tensile strength was measured using an Instron machine.

Samples from the molded parts were placed in the Weather-o-Meter (WOM) and subjected to heat and light to simulate weathering conditions. The tensile strength of the samples was measured prior to being placed in the WOM. Samples were withdrawn from the WOM at regular intervals and tensile strength was again determined. The testing was stopped when the measured tensile value was less than 50% of the original value. For example, experiment ZN1 retained more than 50% elongation at 11,000 hours in the WOM. The next test was conducted at 15,000, at which time the tensile value had fallen to below 50% of the original value – so this test result is shown as >11,000 hrs., <15,000 hrs. The results in Table 1 show that both conventional Z/N resins were well stabilized by a “conventional” additive package (experiments 1 and 2).

In addition, the SSC resin with a 1.7 MI was also well stabilized by a conventional additive package (experiment 4). However, the SSC resin with <5 MI failed at between 2000 and 4000 WOM hours (experiment 3). In contrast, the inventive compositions (with ZnO) perform much better in WOM testing (experiments 6-8).

INDUSTRIAL APPLICABILITY

This invention relates to the rotomolding of polyethylene resin compositions which allow for very fast/efficient rotomolding cycle times. The polyethylene resin has a comparatively high melt index (I_2) and a narrow molecular weight distribution, which permits fast molding cycle times. However the resin was found to be difficult to stabilize. The addition of from 250 to 3000 ppm of zinc oxide was found to improve the stability of the resin while still allowing for the fast cycle time. Rotomolded parts having low levels of warpage/part deflection may also be produced according to this invention. For example, small deflections were sometimes observed in the surface of molded cubes prepared in accordance with the Examples particularly when 500 ppm of hydroxyl amine was contained in the additive package. The level/occurrence of deflection was reduced when the level of hydroxyl amine was lowered to 250 ppm and the amount of ZnO was 750 ppm (with about 1100 ppm of mixed phosphites and 1500 ppm of hindered amine light stabilizer also being included). The process of this invention may be used to prepare a large variety of rotomolded parts such as storage containers for liquids, children's toys and sporting goods such as Kayaks.

TABLE 1

|--|

Resin MI Values: ZN1=5; ZN2=1.8; SSC1=5; SSC2=1.7 (all g/10 minutes)

P1 = hindered phenol sold as Lowinox™ 1790 by Chemtura Corporation

P2 = hydroxyl amine sold as IRGASTAB™ FS042 by Ciba

P3 = hindered phenol sold as IRGANOX™ 1076 by Ciba

S1 = phosphite sold as IRGAFOS™ 168 by Ciba

S2 = diphosphite sold as DOVERPHOS™ 9228-S by Dover Chemicals

H1 = HALS sold as CYASORB™ UV3346 by Cytec

H2 = HALS sold as CHIMASSORB™ 944 by Ciba

H3 = HALS sold as TINUVIN™ 622 by Ciba

CLAIMS

1. A rotomolding process comprising
 - I) preparing a blend of:
 - A) a polyethylene resin having:
 - 5 i) a melt index, I_2 , as measured by ASTM D 1238 of from 2 to 10;
 - ii) a molecular weight distribution, M_w/M_n , of from 2.0 to 3.0;
 - iii) a density of from 0.930 to 0.950 g/cc;
 - B) an additive package comprising:
 - 10 a) a primary antioxidant;
 - b) a secondary antioxidant;
 - c) at least one hindered amine light stabilizer; and
 - d) from 250 to 3000 ppm of ZnO; and
 - II) Subjecting said blend to rototational molding.
2. The process of claim 1 wherein said polyethylene resin is a blend of more than
 - 15 one polyethylene blend component.
3. The process of claim 2 wherein said polyethylene resin has a M_w/M_n of from 2.2 to 2.8.
4. The process of claim 1 wherein
 - a) said primary antioxidant is selected from the group consisting of
 - 20 hindered phenols and hydroxylamines; and
 - b) said secondary antioxidant is selected from the group consisting of phosphites phosphonites.
5. The process of claim 4 wherein said phosphite is a combination of a monophosphite and a diphosphite.

25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2010/000021

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **B29C 41/06** (2006.01) , **C08J 3/20** (2006.01) , **C08K 3/22** (2006.01) , **C08K 5/13** (2006.01) ,
C08K 5/17 (2006.01) , **C08K 5/52** (2006.01) **C08L 23/06** (2006.01)

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 (2006.1): B29C 41/06, C8J 3/20, C08K 3/22, C08K 5/13, C08K 5/17, C08K 5/52, C08L 23/06, C08K, C08J, B29C

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
EPOQUE (Epodoc, WPI): polyethylene, PE, compound, blend, roto-moulding, rotational, ZnO, zinc oxide.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/62832 A1 (FATNES, A. M. et al.) 30 August 2001 (30-08-2001) *Abstract; Pages 2-42; Claims*	1 to 5
X	WO 01/62833 A1 (FATNES, A. M. et al.) 30 August 2001 (30-08-2001) *Abstract; Pages 2-42; Claims*	1 to 5
X	GB 2347426 A (STADLER, U. L.) 6 September 2000 (06-09-2000) *Abstract; Pages 3-38; Claims*	1 to 5
Y	US 5530055 A (NEEDHAM, D. G.) 25 June 1996 (25-06-1996) *Abstract; Col. 2, line 21 to Col. 7, line 55; Claims*	1 to 5

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

30 March 2010 (30-03-2010)

Date of mailing of the international search report

14 April 2010 (14-04-2010)

Name and mailing address of the ISA/CA

Canadian Intellectual Property Office

Place du Portage I, C114 - 1st Floor, Box PCT

50 Victoria Street

Gatineau, Quebec K1A 0C9

Facsimile No.: 001-819-953-2476

Authorized officer

Colin Watts (819) 934-9085

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2010/000021

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6444733 B1 (STADLER, U. L.) 3 September 2002 (03-09-2002) *Abstract; Col. 9, line 16 to Col. 28, line 56; Claims*	1 to 5

INTERNATIONAL SEARCH REPORT

International application No.

Information on patent family members**PCT/CA2010/000021**

Patent Document	Publication	Patent Family	Publication
Cited in Search Report	Date	Member(s)	Date
WO 0162832A1	30-08-2001	AU771119B2	11-03-2004
		AU3390901A	03-09-2001
		EP1263847A1	11-12-2002
		GB0004044D0	12-04-2000
		US2003078340A1	24-04-2003
WO 0162833A1	30-08-2001	AT285434T	15-01-2005
		AU3575901A	03-09-2001
		AU2001235759B2	04-03-2004
		BR0108532A	22-04-2003
		CN1404498A	19-03-2003
		CN1252150C	19-04-2006
		DE60107928D1	27-01-2005
		DE60107928T2	19-05-2005
		EP1261660A1	04-12-2002
		EP1261660B1	22-12-2004
		ES2230275T3	01-05-2005
		GB0004043D0	12-04-2000
		JP2003524046T	12-08-2003
		US2003146542A1	07-08-2003
GB 2347426 A	06-09-2000	US20040152807A1	05-08-2004
		US20020156162A1	24-10-2002
		US6902695A	2005-06-07
		US6444733A	03-09-2002
		TW0500751B	01-09-2002
		RU2242364C2	20-12-2004

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2010/000021

NL1014465C	29-01-2002
NL1014465A	24-09-2000
JP2000248075A2	12-09-2000
IT1317865B1	15-07-2003
GB2347426B	10-10-2001
GB0004230A	12-04-2000
FR2791063B1	28-03-2003
ES2170639BA	16-11-2003
ES2170639AA	01-08-2002
DE10009416A1	09-09-2000
CN1269378A	11-10-2000
CN1196740C	13-04-2005
BR0000971B1	05-05-2009
BR0000971A	03-10-2000
BE1013624AF	07-05-2002
BE1013624AF	07-05-2002
AU0773607B2	27-05-2004
AU0019522A5	07-09-2000

US 5530055 A	25-06-1996	CA2163138A1	10-06-1996
--------------	------------	-------------	------------

US 6444733 B1	03-09-2002	AU773507B2	27-05-2004
		AU1952200A	07-09-2000
		BE1013624A5	07-05-2002
		BR0000971A	03-10-2000
		BR0000971B1	05-05-2009
		CA2299712A1	01-09-2000
		CA2299712C	29-07-2008
		CN1269378A	11-10-2000
		CN1196740C	13-04-2005
		DE10009416A1	07-09-2000
		ES2170639A1	01-08-2002

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2010/000021

ES2170639B1	16-11-2003
FR2791063A1	22-09-2000
FR2791063B1	28-03-2003
GB0004230D0	12-04-2000
GB2347426A	06-09-2000
GB2347426B	10-10-2001
ITMI20000398D0	01-03-2000
ITMI20000398A1	03-09-2001
IT1317865B1	15-07-2003
JP2000248075A	12-09-2000
NL1014465A1	04-09-2000
NL1014465C2	29-01-2002
RU2242364C2	20-12-2004
TW500751B	01-09-2002
US2004152807A1	05-08-2004
US6902695B2	07-06-2005
US2002156162A1	24-10-2002
