Title: PROCESS FOR ADDITION OF ADDITIVES TO POLYMER PARTICLES

Abstract: A polyolefin polymer powder for use in rotational moulding requires the presence of stabilizers, including UV-stabilizers, to prevent degradation during processing and use. Described is a new process for preparing rotomoulding polymer particles comprising (i) obtaining a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 μm; (ii) heating a mixture of: A) at least one phenolic antioxidant; B) at least one organic phosphite or phosphonite antioxidant; C) at least one UV-stabiliser selected from Chimassorb 2020, Cyasorb UV 3346, Chimassorb 944, Cyasorb 4042 or Cyasorb 4611; D) a diluent; and optionally E) a metal stearate; to a temperature of between 20 and 200 °C; (iii) depositing the mixture onto said polyolefin polymer particles; and optionally (iv) blending a metal stearate to the resulting polyolefin polymer particles if component E was not present in said mixture.
PROCESS FOR ADDITION OF ADDITIVES TO POLYMER PARTICLES

This invention relates to a process for the preparation of moulded polyolefin polymer products, in particular to the moulding of a particulate polymer material by rotational moulding techniques and to the particulate polymer material and the moulded polymer products. These products may be used in the food industry.

Rotational moulding is a polymer moulding technique which is particularly suitable for the production of large polymer products, especially containers. It is quite different from other conventional moulding techniques such as injection moulding or blow moulding. A mould is charged with polymer powder, closed and placed in an oven where it is rotated so as to distribute the polymer powder over the mould surface. Once the polymer has melted and formed a coating on the mould surface the mould is cooled. Rotational moulding is described for example by Oliveira et al. in J. Materials Sci. 31: 2227-2240 (1996), Bawiskar et al in Polymer Engineering and Science 34: 815-820 (1994) and Bruins, "Basic Principles of Rotational Moulding", Gordon and Breach, NY, 1971.

The polyolefin polymer powder used in rotational moulding, e.g. a polypropylene or more generally a polyethylene, requires the presence of stabilizers, including UV-stabilizers, to prevent degradation between the time the polymer is produced and when it is moulded. Stabilisers are also vital in preventing degradation during the rotomoulding process and in the eventual rotomoulded article. Addition of stabiliser to the polymer particles is normally achieved by mixing polymer and stabilizers in an extruder mixer which applies shear force to mix the components and melt the polymer. The extrudate is then ground to produce a moulding powder of
appropriate particle size. Such a procedure however is highly energy-consuming and cross contamination may occur.

An alternative way of producing the stabilized moulding powder might thus have seemed to be to simply blend the stabilizers with an olefin polymer particulate which already has the appropriate particle size for rotational moulding, e.g. by spraying of liquid stabilizers or stabilizer solutions onto the polymer particulate and/or by simply mixing particulate stabilizers into the polymer particulate. This however has until now resulted in unacceptable deposits of the UV-stabilizer on the surface of the mould used in rotational moulding.

It has now been surprisingly found that a particular blend of additives may be employed in melt additivation without unacceptable deposits of the UV-stabilizer on the surface of the mould used in rotational moulding being formed. These blends must be very homogeneous and without wishing to be limited by theory, it is envisaged that the blends described below have greater solubility and compatibility with polymers such as polyethylene thus surprisingly allowing direct rotomoulding of the polymer powder without deposit formation.

Thus, viewed from one aspect the invention provides a process for the preparation of a polymer moulding powder for rotational moulding, said process comprising: (i) obtaining a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 \( \mu \)m; (ii) heating a mixture of:

A) at least one phenolic antioxidant preferably selected from [Octadecyl 3-(3',5'-di-tert. butyl-4-hydroxyphenyl)propionate] (e.g. Irganox 1076) or [Pentaerythrityl-tetrakis(3-(3',5'-di-tert. butyl-4-hydroxyphenyl)-propionate] (e.g. Irganox 1010);
B) at least one organic phosphite or phosphonite antioxidant preferably selected from [Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous acid ethylester] (e.g. Irgafos 38), [Tris(2,4-di-t-butylphenyl)phosphite] (e.g. Irgafos 168), tris-nonylphenyl phosphate, [Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite] (e.g. Irgafos P-EPQ) or [Phosphorous acid- cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester] (e.g. Ultranox 641);

C) at least one UV-stabiliser selected from [1,6-Hexanediolamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with, N-butyl-1-butanimine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine] (e.g. Chimassorb 2020), [Poly((6-morpholino-s-triazine-2,4-diy1)(2,2,6,6-tetramethyl-4 piperidyl)imino)hexamethylene (2,2,6,6-tetramethyl-4-piperidyl)imino)] (e.g. Cyasorb UV 3346); [Poly((6-{(1,1,3,3-tetramethylbutyl)amino}-1,3,5-triazine-2,4-diy1)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-hexanediyl((2,2,6,6-tetramethyl-4-piperidyl)imino))] (e.g. Chimassorb 944); Cyasorb 4042 or Cyasorb 4611;

D) a diluent; and optionally

E) a metal stearate;

preferably under an inert atmosphere, to a temperature of between 20 and 200°C;

(iii) depositing the mixture onto said polyolefin polymer particles; and optionally

(iv) blending a metal stearate to the resulting polyolefin polymer particles if component E was not present in said mixture.

Viewed from another aspect the invention provides a polymer moulding powder for rotational moulding
obtainable by a process as hereinbefore described.

Viewed from yet another aspect the invention provides a process for the preparation of a moulded polymer item, said process comprising:

(i) obtaining a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 μm;
(ii) heating a mixture of:
   A) at least one phenolic antioxidant;
   B) at least one organic phosphite or phosphonite antioxidant;
   C) at least one UV-stabiliser;
   D) a diluent; and optionally
   E) a metal stearate;

to a temperature of between 20 and 200°C;
(iii) depositing the mixture onto said polyolefin polymer particles; optionally
(iv) blending a metal stearate to the resulting polyolefin polymer particles if component E was not present in said mixture;
(v) rotomoulding said particles.

Viewed from a still further aspect the invention provides moulded polymer items obtainable by a process in which a polymer moulding powder of the invention is rotomoulded.

Viewed from another aspect the invention provides use of a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 μm coated with a mixture of:
A) at least one phenolic antioxidant;
B) at least one organic phosphite or phosphonite antioxidant;
C) at least one UV-stabiliser;
D) a diluent; and optionally
E) a metal stearate;
in rotomoulding.
The components A to D and optionally E may be mixed in any convenient vessel but are preferably mixed in a batch or continuous mixer to ensure excellent mixing occurs. Suitable mixing apparatuses include Forberg, Idecon, and Lodge mixers. The mixture of components is preferably in the liquid state at 100°C, e.g. molten or in solution, and is preferably sprayed onto the polymer powder at between 100°C and 200°C. In this process it is preferred that the liquid stabilizer composition comprising components A to D and optionally E be heated to a temperature in the range 90 to 140°C, more preferably 100 to 130°C.

The polymer powder onto which the mixture is deposited, e.g. sprayed should preferably be at a temperature of between 20 to 80°C, e.g. 60°C or 75°C and should preferably be circulating in a mixer as spraying occurs. This ensures even distribution of the liquid stabilising solution over the polymer particles. The spraying may be direct, e.g. through a preheated spray die, or indirect, e.g. by directing a flow of liquid onto a diffuser. The mixture of components A to D and optionally E must be a liquid when spraying occurs.

The inert atmosphere may be provided by an conventional inert gas such as a noble gas or preferably nitrogen.

The moulding powder used according to the invention may be obtained by any convenient method but must have a mean particle size of 1 to 2000 μm. Preferably, the polymer particles has a mean polymer particle size (e.g. as determined using a particle size analyser such as a Malvern analyser) of 50 to 1000 μm, especially 100 to 500 μm. The particle size distribution is preferably such that:

\[ D(v, 0.5) \text{ is between } 100 \text{ and } 500 \mu m \]
\[ D(v, 0.1) \text{ is between } 50 \text{ and } 300 \mu m \]
\[ D(v, 0.9) \text{ is between } 300 \text{ and } 1000 \mu m \]
most preferably \[ D(v, 0.5) \text{ being between } \]
200 and 400 μm, \( D(v, 0.1) \) being between
100 and 200 μm, and \( D(v, 0.9) \) being between
400 and 600 μm.

\( D(v, 0.5) \) means the particle diameter below which
50% by volume of the particles fall; similarly \( D(v, 0.1) \)
is the particle diameter below which 10% by volume of
the particles fall). This choice of particle size and
uniformity ensures uniformity in the resulting
rotationally moulded product.

Polymer particles of a suitable size may be
obtained by methods such as grinding, extruding and
pelletising or simply synthesising polymer particles
having a suitable particle size directly.

For different polyolefin polymers, the optimum
10

particle sizes will differ slightly. However, by way of
example for polyethylenes with MFR, 1 to 40 and densities
920 to 950 kg/m³, the optimum particle size will
generally be 100 to 600 μm. Where the particle size is
20
too large, the melting characteristics in rotational
moulding will be poor leading to mechanically sub-
standard moulded products. On the other hand, where the
particle size is too small the powder will have poor
flow characteristics and will not distribute evenly in
the mould.

The polymers used will preferably have a narrow
molecular weight distribution \( M_w/M_n \) to ensure a
relatively sharp melting point and hence even
distribution in the mould. \( M_w/M_n \) values preferably lie
in the range 2 to 10, more especially 2 to 5.

Preferably the polymers should have a melting point of
100 to 180°C, more preferably 120 to 130°C, with a
melting range of less than 20°C.

The polyolefin polymer particulate preferably has a
very homogeneous molecular structure, seen as a narrow
melting range in the curve obtained by differential
scanning calorimetry and as a very even crystal
structure in micrographic studies. This ensures that
the powder melts evenly and that the homogeneity of the moulded product is high.

To ensure that the moulds used in rotational moulding may be loaded with sufficient polymer to produce moulded items with adequate wall thicknesses, it is also desirable that the moulding powder should have a bulk density of at least 300 kg/m³ more preferably at least 330 kg/m³, e.g. 330 to 500 kg/m³, more particularly 450 to 490 kg/m³.

The polymer density is conveniently in the range 800 to 1000 kg/m³, particularly 850 to 950 kg/m³. For polyethylene, the density is preferably 920 to 950 kg/m³, more preferably 930 to 940 kg/m³. For polypropylenes, the density is preferably 880 to 950 kg/m³, more preferably 890 to 910 kg/m³.

The polymer preferably has a melt flow rate MFR₂ of 1 to 30 g/10 min., more preferably 2 to 20 g/10 min. For polyethylenes, the MFR₂ is preferably 2 to 10 g/10 min., more preferably 5 to 7.5 g/10 min. For polypropylenes, the MFR₂ is preferably 10 to 20 g/10 min., more preferably 12 to 18 g/10 min.

The polymer moulding powder preferably has a dry flow of 10 to 40 s/100g, more preferably 15 to 30 s/100g.

The polymers used according to the invention are preferably homopolymers or copolymers of α-olefins, in particular polymers deriving from a C₂₋₄ α-olefin, particularly propylene and more particular ethylene, optionally together with one or more comonomers, e.g. selected from mono or dienes such as C₂₋₁₄ mono or dienes, particularly C₂₋₈ α-olefins. Preferably at least 50% by weight of the polymer structure derives from a C₂₋₄ α-olefin.

Such polymers may be prepared by conventional olefin polymerization techniques, e.g. using Ziegler Natta or metalloocene catalysts or chromium catalysts and polymerization processes such as gas phase, slurry, and
solution process, especially slurry processes. Typically gas phase, loop and tank reactors may be used. However it has been found that polyolefin polymer particles of appropriate size for preparation of the moulding powder may readily be prepared using supported catalysts, in particular catalysts comprising porous particulates loaded with the catalyst, e.g. the reaction product of a metallocene and an aluminoxane.

Such supported catalysts may be prepared for example by forming a slurry of particulate support, metallocene, aluminoxane and solvent, draining off excess solvent, rinsing of excess metallocene/aluminoxane and drying. Such catalyst support preparation techniques are known in the art.

The catalyst support material used to carry an olefin polymerization catalyst is conveniently an inorganic or organic material, e.g. an inorganic oxide such as silica, alumina or zirconia or an inorganic halide such as magnesium chloride, or a polymer such as an acrylate or methacrylate. Preferably the support material, if inorganic, is subjected to a heat treatment (calcination) before catalyst impregnation, e.g. by a period of heat treatment in a dry, non-reducing (e.g. oxygen containing) atmosphere such as air at a temperature of at least 200°C, preferably at least 400°C and especially preferably at least 600°C, for a period of 0.5 to 50 hours, e.g. 2 to 30 hours, preferably 10 to 20 hours. The support material before calcination conveniently has a surface area of 20 to 500 m²/g (BET method), a porosity of 0.2 to 3.5 m³/g and a mean particle size of 10 to 200μm.

The catalyst with which the support material is impregnated may be any polymerization catalyst although preferably it will be a Ziegler Natta catalyst (i.e. the combination of a transition metal (e.g. Ti, V or Cr) compound and an aluminium compound), a pyrazolyl catalyst (e.g. as described in WO97/17379, US-A-4808680,

Examples of suitable catalysts are known from:


For metalloocene-based catalysts, the catalytically effective metal is preferably a transition metal or a lanthanide, especially a group 4, 5 or 6 metal, e.g. Ti, Zr or Hf. Such metalloccenes include a η-bonding ligand, e.g. an optionally substituted optionally fused homo or heterocyclic cyclopentadienyl ligand, preferably with 1, 2 or 3 η-bonding groups coordinating the metal (the term metalloocene is often used to denote complexes in which a metal is coordinated by η-bonding groups - here, however, it is used in its broader sense to cover complexes in which the metal is coordinated by one or more η-bonding groups, i.e. groups which use their π-orbitals to complex the metal). Examples of such η-bonding ligands include cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl and octahydrofluorenyl ligands and bridged dimers where such η-ligands are attached, e.g. via a 1, 2, 3 or 4 atom chain (e.g. containing C, N, O, S, Si or P chain atoms - for example an ethylene or Si(CH₃)₂ group), to a further such η-ligand.

Thus by way of example the metalloocene catalyst may be of formula I

\[(\text{CpR'}_k)_m \text{MR}_n \text{X}_q\] (I)

where Cp is a fused or non fused homo or heterocyclic cyclopentadienyl η-ligand;
R' is a hydrocarbyl, hydrocarbyloxy,
hydrocarbylsilyloxy or hydrocarbylgermyloxy group containing 1 to 20 carbon atoms or one R' is a bridging group to a further fused or non fused homo or heterocyclic cyclopentadienyl η-ligand, the bridging group preferably providing a 1, 2, 3 or 4 atom chain between the cyclic groups, for example with C, N, O, S, P or Si chain atoms, especially C and/or Si, e.g. an ethylene group;

k is zero or an integer having a value of 1, 2, 3, 4 or 5;

M is a group 4, 5 or 6 metal;
X is a halogen atom;
R is hydrogen or a hydrocarbyl or hydrocarbyloxy group containing 1 to 20 carbon atoms;

m is the integer 1, 2 or 3;

n and q are zero or integers 1, 2 or 3; and the sum of m, n and q corresponds to the degree of coordination possible for M in the oxidation state in which it exists.

Preferably the metallocene contains at least one Cp group other than unsubstituted cyclopentadienyl, i.e. preferably the metallocene is a "substituted metallocene".

Particularly preferably the metallocene is a bridged bis-indenyl metallocene.

Many metallocene catalysts are known, e.g. as described in the patent publications mentioned above and the patent publications of Exxon, Mobil, BASF, DOW, Fina, Hoechst and Borealis, e.g. EP-A-206749, etc.

Typical examples of suitable metallocenes include the following:

cyclopentadienyl, indenyl, fluorenyl, pentamethyl-cyclobutadienyl, methyl-cyclopentadienyl, 1,3-di-methyl-cyclopentadienyl, i-propyl-cyclopentadienyl, 1,3-di-i-propyl-cyclopentadienyl, n-butyl-cyclopentadienyl, 1,3-di-n-butyl-cyclopentadienyl, t-butyl-cyclopentadienyl, 1,3-di-t-butyl-cyclopentadienyl, trimethylsilyl-
cyclopentadienyl, 1,3-di-trimethylsilylcyclopentadienyl, benzyl-cyclopentadienyl, 1,3-di-benzyl-cyclopentadienyl, phenyl-cyclopentadienyl, 1,3-di-phenyl-cyclopentadienyl, naphthyl-cyclopentadienyl, 1,3-di-naphthyl-cyclopentadienyl, 1-methyl-indenyl, 1,3,4-tri-methyl-cyclopentadienyl, 1-i-propyl-indenyl, 1,3,4-tri-i-propyl-cyclopentadienyl, 1-n-butyl-indenyl, 1,3,4-tri-n-butyl-cyclopentadienyl, 1-t-butyl-indenyl, 1,3,4-tri-t-butyl-cyclopentadienyl, 1-trimethylsilylindenyl, 1,3,4-tri-trimethylsilyl-cyclopentadienyl, 1-benzyl-indenyl, 1,3,4-tri-benzyl-cyclopentadienyl, 1-phenyl-indenyl, 1,3,4-tri-phenyl-cyclopentadienyl, 1-naphthyl-indenyl, 1,3,4-tri-naphthyl-cyclopentadienyl, 1,4-di-methyl-indenyl, 1,4-di-i-propyl-indenyl, 1,4-di-n-butyl-indenyl, 1,4-di-t-butyl-indenyl, 1,4-di-trimethylsilyl-indenyl, 1,4-di-benzyl-indenyl, 1,4-di-phenyl-indenyl, 1,4-di-naphthyl-indenyl, methylfluorenyl, i-propyl-fluorenyl, n-butyl-fluorenyl, t-butyl-fluorenyl, trimethylsilyl-fluorenyl, benzylfluorenyl, phenyl-fluorenyl, naphthyl-fluorenyl, 5,8-di-methyl-fluorenyl, 5,8-di-i-propyl-fluorenyl, 5,8-di-n-butyl-fluorenyl, 5,8-di-t-butyl-fluorenyl, 5,8-di-trimethylsilyl-fluorenyl, 5,8-di-benzyl-fluorenyl, 5,8-di-phenyl-fluorenyl and 5,8-di-naphthyl-fluorenyl.

The catalysts may require the use of a co-catalyst or catalyst activator. Preferred as co-catalysts are boron compounds and more preferably aluminoxanes, in particular the C_{10} alkyl aluminoxanes and most particularly methyl aluminoxane (MAO).

Such aluminoxanes may be used as the sole co-catalyst or alternatively may be used together with other co-catalysts. Thus besides or in addition to aluminoxanes, other cation complex forming catalyst activators may be used. In this regard mention may be made of the silver and boron compounds known in the art. What is required of such activators is that they should react with the metalloocene or pyrazolyl complex to yield
an organometallic cation and a non-coordinating anion (see for example the discussion on non-coordinating anions \( J^- \) in EP-A-617052 (Asahi)).

Aluminoxane co-catalysts are described by Hoechst in WO94/28034. These are linear or cyclic oligomers having up to 40, preferably 3 to 20, \(-[\text{Al}(\text{R}^n)\text{O}]^-\) repeat units (where \( \text{R}^n \) is hydrogen, \( C_{1-10} \) alkyl (preferably methyl) or \( C_{6-18} \) aryl or mixtures thereof).

Where a co-catalyst is used, it may be used separately but more preferably it is also loaded onto the porous support material. In this event it is preferred to allow the catalyst and the co-catalyst to react in a liquid phase and to load the reaction product onto the support.

Particularly preferred polymer particles can be prepared if the procedure described in WO00/22011 is followed. Thus, if a mechanically fluidised porous particulate support is impregnated with a suitable catalyst and a cocatalyst and the monomer(s) are polymerised, ideal polymer particles for rotomoulding are obtained.

The UV-stabilizer or mixture of stabilisers used in the present invention should be compatible with the polymer, should have a relatively low melting point and/or good compatibility with the additive blend. Thus UV stabilisers which are soluble or partially soluble in the polymer (e.g. polyethylene) are preferred. It is also preferred if the UV-stabilisers are approved for use in polyolefins in contact with food. Preferred UV stabilisers are high molecular weight hindered amine light stabilisers, e.g. those having a molecular weight of 1500 to 4000, preferably 2000 to 3000.

Particular suitable UV stabilisers therefore include \([1,6\text{-Hexanediarmine, } N, N'\text{-bis}(2,2,6,6\text{-tetramethyl}-1\text{-piperidinyl})^-\text{, polymer with } 2,4,6\text{-trichloro-1,3,5-triazine, reaction products with, } N\text{-butyl-1-butanaline and } N\text{-butyl-2,2,6,6-tetramethyl-4-}\]

piperidinamine] (e.g. Chimassorb 2020), Poly([6-
morpholino-s-triazine-2,4-diyl](2,2,6,6-tetramethyl-4-
piperidyl)imino)hexamethylene (2,2,6,6-tetramethyl-4-
piperidyl)imino)) (e.g. Cyasorb UV 3346) or Poly((6-
((1,1,3,3-tetramethylbutyl)amino)-1,3,5-triazine-2,4-
diyl)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-
hexanediyl((2,2,6,6-tetramethyl-4-piperidyl)imino))
(e.g. Chimassorb 944). Also of use as UV stabilisers
are Cyasorb 4042 or Cyasorb 4611 both available from

Cytec.

Especially preferably the UV stabiliser is [1,6-
Hexanediame, N, N'-bis(2,2,6,6-tetramethyl-4-
piperidinyl)-, polymer with 2,4,6-trichloro-1,3,5-
triazine, reaction products with, N-butyl-1-butamine
and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine]. The
structures of most of these stabilisers are illustrated
in the scheme below.
Name: 1,6-Hexanediame, \( \text{N, N'}-\text{bis}(2,2,6,6-\text{tetramethyl-4-piperidinyl}) \), polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with, \( \text{N-butyl-1-butamine} \) and \( \text{N-butyl-2,2,6,6-tetramethyl-4-piperidinamine} \)

CAS-no. 192268-64-7

Name: Poly(\((1,1,3,3-\text{tetramethylbutylamino})-1,3,5-\text{triazine}-2,4-diydly)(2,2,6,6-\text{tetramethyl-4-piperidyl}limino)-1,6-\text{hexanediyl} ((2,2,6,6-\text{tetramethyl-4-piperidyl}limino))\)

CAS-no. 71878-19-8

Name: Poly(\((6-\text{morpholino-3-triazine}-2,4-diydly})(2,2,6,6-\text{tetramethyl-4-piperidyl}limino)\)hexamethylene

CAS-no. 82451-48-7

Name: Poly(\((6-\text{morpholino-3-triazine}-2,4-diydly})(2,2,6,6-\text{tetramethyl-4-piperidyl}limino)\)hexamethylene

Name: Poly(\((6-\text{morpholino-3-triazine}-2,4-diydly})(2,2,6,6-\text{tetramethyl-4-piperidyl}limino)\)hexamethylene

Name: Poly(\((6-\text{morpholino-3-triazine}-2,4-diydly})(2,2,6,6-\text{tetramethyl-4-piperidyl}limino)\)hexamethylene
Chimassorb 2020 and Chimassorb 944 are available from Ciba Specialty Chemicals. Cyasorb 3346 is available from Cytec or from Everlight (Taiwan) where it is sold under the trade name Eversorb 92. Cyasorb 4042 and Cyasorb 4611 are available from Cytec.

Besides the UV-stabilizer, the polymer moulding powder used according to the invention has materials capable of inhibiting degradation of the polyolefin polymer, i.e. antioxidants and antacids.

The phenolic antioxidant should be approved for use in polyolefins in contact with food and is preferably [Octadecyl 3-(3',5'-di-tert. butyl-4-hydroxyphenyl)propionate] (e.g. Irganox 1076) or [Pentaerythrityl-tetrakis(3-(3',5'-di-tert. butyl-4-hydroxyphenyl)-propionate] (e.g. Irganox 1010). It is also possible to employ a mixture of these compounds. Irganox 1010 and Irganox 1076 are available from Ciba Specialty Chemicals. Great Lakes Chemicals also sells these compounds where they are sold under the trade names Alkanox 20 and Alkanox 240 respectively. The phenolic antioxidant is most preferably [Octadecyl 3-(3',5'-di-tert. butyl-4-hydroxyphenyl)propionate]. The structures of these compounds are illustrated below.

\[
\text{CAS-no. 2082-79-3}
\]

Name: Octadecyl 3-(3',5'-di-tert. butyl-4-hydroxyphenyl)propionate

\[
\text{CAS-no. 6683-19-8}
\]

Name: Pentaerythrityl-tetrakis(3-(3',5'-di-tert. butyl-4-hydroxyphenyl)-propionate
The organic phosphite or phosphonite antioxidant should be approved for use in polylefins in contact with food and may be [Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl) phosphorous acid ethylester] (e.g. Irgafos 38), tris-nonylphenyl phosphite, [Tris (2,4-di-t-butylphenyl) phosphite] (e.g. Irgafos 168), [Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite] (e.g. Irgafos P-EPQ) or [Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester] (e.g. Ultranox 641). The Irgafos range are available from Ciba Specialty Chemicals and Ultranox 641 is available from GE Specialty Chemicals. Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite is also sold under the trade names Alkanox 24-44 by Great Lakes Chemicals and Sandostab P-EPQ by Clariant. Irgafos 38, Irgafos P-EPQ and Ultranox 641 are preferred. Especially preferred is the organic phosphite antioxidant is Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous acid ethylester. Structures of these compounds are illustrated below.
Name: Bis(2-methyl-4,6-bis(1,1-dimethylethyl) phenyl) phosphorous acid ethylester

CAS-no. 14560-60-8

Name: Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester

CAS-no. 161717-32-4

Name: Tris (2,4-di-t-butyphenyl) phosphite

CAS-no. 31570-04-4

Name: Tetrakis-(2,4-di-t-butyphenyl)-4,4'-biphenylen-di-phosphonite

CAS-no. 38613-77-3 119345-01-6

Name: Tris-nonylphenyl phosphite

CAS-no. 26523-78-4
Examples of antacids include metal stearates, most preferably Zn-stearate or Ca-stearate. The stearate may be blended to the coated polymer particles as a fine powder or may be deposited onto the polymer powder as part of the additive mixture.

Suitable diluents are mineral oil, silicon oil, waxes e.g. polyethylene wax, epoxidised soybean oil, antistatic agents, glyceryl monocarboxylic ester, and N,N-bis(2-hydroxyethyl) dodecanamide. Especially preferably the diluent is mineral oil or N,N-bis(2-hydroxyethyl) dodecanamide. N,N-bis(2-hydroxyethyl) dodecanamide is believed to act not only as a diluent but also as an antistatic agent which may be beneficial for rotomoulding and in rotomoulded articles. The use of N,N-bis(2-hydroxyethyl) dodecanamide may also improve surface finish.

The polymer moulding powder should preferably comprise 0.01 to 0.5 wt%, e.g. 0.1 to 0.2 wt% organic phosphite or phosphonite antioxidant, 0.01 to 0.5 wt%, e.g. 0.1 to 0.3 wt% phenolic antioxidant, 0.01 to 2 wt%, e.g. 0.1 to 1 wt% UV stabiliser, 0.01 to 0.05 wt%, e.g. 0.1 to 0.3 wt% metal stearate and 0.02 to 3 wt%, e.g. 0.1 to 1 wt% diluent.

Besides the stabilizer(s), the moulding powder may contain with other additives, e.g. lubricants, anti-fogging agents, antistatic agents, clarifiers, nucleating agents, blowing agents, plasticizers, flame retardants, etc. Where the rotomoulded items made using the moulded polymer powder are for use in the food industry preferably all the ingredients in the rotomoulding powder will be of a grade approved for food contact purposes.

Rotational moulding using the moulding powder of the invention may be effected conventionally, e.g. using commercially available rotomoulding apparatus. The oven temperature and oven curing time may be selected according to the melting characteristics of the polymer.
and the thickness of the item being produced.

The polymer moulding powder of the invention may be employed as the sole polymer rotomoulding component or may be combined with other polymers.

The invention is illustrated further by the following non-limiting Examples.

**EXAMPLE 1**

Polyethylene powder (bulk density 460 to 480 kg/m³, MFR₂ 5.9 to 6.8 g/10 min., and particle size distribution: 600 μm max. 0%, 500 μm max 5%, 425 μm max 5-30%, 300 μm max 20-40%, 212 μm max 15-35%, 150 μm max 8-20%, < 150 μm max 10%) is obtained by metalloocene catalysed polymerization of ethylene with hex-1-ene as comonomer.

**EXAMPLE 2**

PE powder from Example 1 = 10kg (to 100 wt%)

Irganox 1076 6g
Irgafos 38 12g
Chimassorb 2020 17g
Ondina 941 white mineral oil 38g
Zinc Stearate 18g

Irganox 1076 (6 g), Irgafos 38 (12 g), Chimassorb 2020 (17 g) together with Ondina 941 mineral oil (38 g available from the Shell Oil Company) were heated to 100-130°C under a nitrogen atmosphere. In a mechanically fluidised bed mixer, e.g. a Forberg mixer, the hot additives were sprayed onto a circulating polyethylene powder prepared as described in Example 1, the powder having a temperature of 60°C. Zinc Stearate powder was added and the mixture blended for another five minutes.
EXAMPLE 3

Rotational moulding

The moulding powder of Example 2 was moulded using a Rotospeed E-60 Express rotomoulding machine. There was no deposit of UV-stabilizer on the mould (visual inspection of the mould and FT-IR analysis) and the moulded products had satisfactory impact strength and UV stability.

The rotomoulding machine was a shuttle machine with one cranked arm provided with a 44 kW propane gas burner, a 10000 CFM (283 m³/min) circulating fan, a 750 CFM (21 m³/min) exhaust fan, and two 3350 CFM (95 m³/min) forced air cooling fans. The oven temperature used was 280°C with an oven time of 14 minutes and a cooling time of 16 minutes.

The mould used was an aluminium box mould of approximately 7.4 litre volume. The rotation ratio was 9:1.4 and the rotational rates were 9/mm and 1.4/min. The moulding powder load was 700 g giving a wall thickness of approximately 4 mm.

No deposits could be discovered in the mould even after 10 successive mouldings.

Rotomoulded items prepared as in Example 3 were compared to a conventional rotomoulding powder (RM8343 from Borealis). Melt flow rate and impact properties were comparable.

Additivated polymer powder was stored at 23°C and 50% humidity and 50°C and 95% humidity respectively for 150 days. Additive analysis showed that the hydrolytic stability was good (no reaction, no hydrolysis of
additives). Melt flow rate of the powder did not change.

**Example 4**

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE powder from Example 1</td>
<td>10kg (to 100 wt%)</td>
</tr>
<tr>
<td>Irganox 1076</td>
<td>6g</td>
</tr>
<tr>
<td>Irgafos 38</td>
<td>12g</td>
</tr>
<tr>
<td>Chimassorb 2020</td>
<td>17g</td>
</tr>
<tr>
<td>Ondina 941 white mineral oil</td>
<td>38g</td>
</tr>
<tr>
<td>Zinc Stearate</td>
<td>18g</td>
</tr>
</tbody>
</table>

Irganox 1076 (6 g), Irgafos 38 (12 g), Chimassorb 2020 (17 g), Zn-stearate (18 g) together with Ondina 941 mineral oil (38 g available from the Shell Oil Company) were heated to 120-140°C under a nitrogen atmosphere. In a mechanically fluidised bed mixer, e.g. a Forberg mixer, the hot additives were sprayed onto a circulating polyethylene powder prepared as described in Example 1, the powder having a temperature of 60°C. The mixture was blended for another five minutes.

**Example 5**

Influence of UV stabiliser on properties of rotomoulded article.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE powder from Example 1</td>
<td>10 kg (to 100 wt%)</td>
</tr>
<tr>
<td>Irganox 1076</td>
<td>6 g - (600 ppm)</td>
</tr>
<tr>
<td>Irgafos 38</td>
<td>12 g - (1200 ppm)</td>
</tr>
<tr>
<td>UV stabiliser</td>
<td>20 g - (2000 ppm)</td>
</tr>
<tr>
<td>Ondina 941 white mineral oil</td>
<td>47 g - (4700 ppm)</td>
</tr>
</tbody>
</table>

Irganox 1076, Irgafos 38, UV stabiliser, Zn-stearate together with Ondina 941 mineral oil were heated to 120-140°C under a nitrogen atmosphere. In a mechanically
fluidised bed mixer, e.g. a Forberg mixer, the hot additives were sprayed onto a circulating polyethylene powder prepared as described in Example 1, the powder having a temperature of 60°C. Zinc stearate powder (9 g) was added and the mixture blended for another five minutes. The mixture was blended for another five minutes. Rotomoulding was effected as described in Example 3.

The yellowness index of the resulting articles was measured. Percentage retained mechanical properties after 3000 hours in wheather-o-meter C165 were measured according to ISO 4892.

<table>
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<tr>
<th>UV stabiliser</th>
<th>YI₈</th>
<th>Elongation to break, ISO 527-5A</th>
</tr>
</thead>
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<td>65% retained mechanical properties after 3000 hours in WOM</td>
</tr>
<tr>
<td>Cyasorb 3364</td>
<td>-6.8</td>
<td>70% retained mechanical properties after 3000 hours in WOM</td>
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<td>Cyasorb 4042</td>
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<tr>
<td>Cyasorb 4611</td>
<td>-5.2</td>
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</tbody>
</table>

Example 6

Influence of phosphites/phosphonites on properties of rotationally moulded article.

PE powder from Example 1 10 kg (to 100 wt%)
Irganox 1076 6 g - (600 ppm)
Phosphite 12 g - (1200 ppm)
Chimassorb 2020 20 g - (2000 ppm)
Ondina 941 white mineral oil 47 g - (4700 ppm)
Zinc Stearate 9 g - (900 ppm)

Rotomoulded articles were prepared following the
experimental procedure described in Example 5.

The yellowness index of the resulting articles was measured.

<table>
<thead>
<tr>
<th>Phosphite</th>
<th>YI₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgafos 38</td>
<td>-6.5</td>
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<tr>
<td>Irgafos P-EPQ</td>
<td>-7.7</td>
</tr>
<tr>
<td>Ultranox 641</td>
<td>-7.8</td>
</tr>
</tbody>
</table>

The YI values for the rotomoulded articles made in Examples 5 and 6 are lower than those associated with conventional rotomoulded articles. The mechanical property values determined are comparable with conventional rotomoulded articles showing that the process of the invention does not detrimentally affect mechanical properties.

**EXAMPLE 7**

<table>
<thead>
<tr>
<th>PE powder from Example 1 = 10 kg (to 100 wt%)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Irganox 1076</td>
<td>6g</td>
</tr>
<tr>
<td>Irgafos 38</td>
<td>12g</td>
</tr>
<tr>
<td>Chimassorb 2020</td>
<td>17g</td>
</tr>
<tr>
<td>Dimodan PVP</td>
<td>47g</td>
</tr>
<tr>
<td>Zinc Stearate</td>
<td>9g</td>
</tr>
</tbody>
</table>

Irganox 1076 (6 g), Irgafos 38 (12 g), Chimassorb 2020 (17 g) together with Dimodan (47 g available from the Danisco Cultor) were heated to 100-130°C under a nitrogen atmosphere. In a mechanically fluidised bed mixer, e.g. a Forberg mixer, the hot additives were sprayed onto a circulating polyethylene powder prepared as described in Example 1, the powder having a temperature of 60°C. Zinc Stearate powder was added and the mixture blended for another five minutes.
EXAMPLE 8

PE powder from Example 1 =10kg (to 100 wt%)
Irganox 1076 6g
5 Irgafos 38 12g
Chimassorb 2020 17g
Armostat 2000 47g
Zinc Stearate 9g

10 Irganox 1076 (6 g), Irgafos 38 (12 g), Chimassorb 2020 (17 g) together with Armostat (47 g available from Akzo Nobel) were heated to 90°C under a nitrogen atmosphere. In a mechanically fluidised bed mixer, e.g. a Forberg mixer, the hot additives were sprayed onto a circulating polyethylene powder prepared as described in Example 1, the powder having a temperature of 60°C. Zinc Stearate powder was added and the mixture blended for another five minutes.
Claims

1. A process for the preparation of a polymer moulding powder for rotational moulding, said process comprising:
   (i) obtaining a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 μm;
   (ii) heating a mixture of:

   A) at least one phenolic antioxidant;
   B) at least one organic phosphite or phosphonite antioxidant;
   C) at least one UV-stabiliser selected from [1,6-Hexanediame, N,N'-bis(2,2,6,6-tetramethyl-4-piperidiny1)-, polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with, N-butyl-1-butanimine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine] (e.g. Chimassorb 2020), [Poly((6-morpholino-s-triazine-2,4-diyl)(2,2,6,6-tetramethyl-4 piperidyl)imino)hexamethylene (2,2,6,6-tetramethyl-4-piperidyl)imino)]) (e.g. Cyasorb UV 3346), [Poly((6-((1,1,3,3-tetramethylbutyl)amino)-1,3,5-triazine-2,4-diyl)(2,2,6,6-tetramethyl-4-piperidyl)imino)-1,6-hexanediy1((2,2,6,6-tetramethyl-4-piperidyl)imino)]) (e.g. Chimassorb 944), Cyasorb 4042 or Cyasorb 4611;
   D) a diluent; and optionally
   E) a metal stearate;

   to a temperature of between 20 and 200°C;
   (iii) depositing the mixture onto said polyolefin polymer particles; and optionally
   (iv) blending a metal stearate to the resulting polyolefin polymer particles if component E was not present in said mixture.

2. A process as claimed in claim 1 wherein said at
least one phenolic antioxidant is selected from
[Octadecyl 3-(3',5'-di-tert. butyl-4-
hydroxyphenyl)propionate] (e.g. Irganox 1076) or
[Pentaerythritol-tetrakis(3-(3',5'-di-tert. butyl-4-
hydroxyphenyl)-propionate] (e.g. Irganox 1010).

3. A process as claimed in claim 1 or 2 wherein said
at least one organic phosphite or phosphonite
antioxidant is selected from [Bis(2-methyl-4,6-bis(1,1-
dimethylethyl)phenyl)phosphorous acid ethylester] (e.g.
Irgafos 38), [Tris(2,4-di-t-butylphenyl)phosphate] (e.g.
Irgafos 168), tris-nonylphenyl phosphate, [Tetrakis-
(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite]
(e.g. Irgafos P-EPQ) or [Phosphorous acid- cyclic
butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester]
(e.g. Ultranol 641).

4. A process as claimed in any one of claims 1 to 3
wherein said polyolefin polymers particles are
polyethylene or polypropylene homo or copolymer
particles.

5. A process as claimed in any one of claims 1 to 4
wherein said UV stabiliser is [1,6-Hexanediame, N,N'-
bis(2,2,6,6-tetramethyl-4-piperidinyl)-, polymer with
2,4,6-trichloro-1,3,5-triazine, reaction products with,
N-butyl-1-butramine and N-butyl-2,2,6,6-tetramethyl-4-
piperidinamine].

6. A process as claimed in any one of claims 1 to 5
wherein said phenolic antioxidant is [Octadecyl 3-
(3',5'-di-tert. butyl-4-hydroxyphenyl)propionate].

7. A process as claimed in any one of claims 1 to 6
wherein said at least one organic phosphite or
phosphonite antioxidant is [Bis(2-methyl-4,6-bis(1,1-
dimethylethyl)phenyl)phosphorous acid ethylester].
8. A process as claimed in any one of claims 1 to 7 wherein said metal stearate is zinc stearate.

9. A process as claimed in any one of claims 1 to 8 wherein said diluent is selected from mineral oil, silicon oil, waxes e.g. polyethylene wax, epoxidised soybean oil, antistatic agents, glyceryl monocarboxylic ester, and N,N-bis(2-hydroxyethyl) dodecanamide.

10. A process as claimed in any one of claims 1 to 9 wherein said mixture comprises 0.01 to 0.5 wt% organic phosphite or phosphonite antioxidant, 0.01 to 0.5 wt%, phenolic antioxidant, 0.01 to 2 wt% UV stabiliser, 0.01 to 0.05 wt%, metal stearate and 0.02 to 3 wt%, diluent.

11. A process as claimed in any one of claims 1 to 10 wherein all the components of said mixture are approved for contact with food.

12. A process as claimed in any one of claims 1 to 11 wherein said polyolefin polymer particles have a mean particle size of 100 to 500 μm.

13. A process as claimed in any one of claims 1 to 12 wherein said polyolefin polymer particles have a bulk density of 300 to 500 kg/m³.

14. A polymer moulding powder for rotational moulding obtainable by a process as claimed in any one of claims 1 to 13.

15. A process for the preparation of a moulded polymer item, said process comprising:

(i) obtaining a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 μm;
(ii) heating a mixture of:
A) at least one phenolic antioxidant;
B) at least one organic phosphite or phosphonite antioxidant;
C) at least one UV-stabiliser;
D) a diluent; and optionally
E) a metal stearate;

to a temperature of between 20 and 200°C;
(iii) depositing the mixture onto said polyolefin polymer particles; optionally
(iv) blending a metal stearate to the resulting polyolefin polymer particles if component E was not present in said mixture; and
(v) rotomoulding said particles.

16. A rotomoulded article obtainable by a process as described in claim 15.

17. Use of a plurality of polyolefin polymer particles having a mean particle size of 1 to 2000 μm coated with a mixture of:

A) at least one phenolic antioxidant;
B) at least one organic phosphite or phosphonite antioxidant;
C) at least one UV-stabiliser;
D) a diluent; and optionally
E) a metal stearate;
in rotomoulding.

18. Moulded polymer items obtainable by a process in which a polymer moulding powder as claimed in claim 14 is rotomoulded.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C08K3/20  C08K5/00  C08K5/134  C08K5/52  C08K5/34  C08K5/098  C08L23/02

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 7 C08J  C08K  C08L

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

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

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>WO 00 11065 A (BOREALIS AS ; COCKBAIN JULIAN (GB); FATNES ANNE MARIE (NO); FROEHAU) 2 March 2000 (2000-03-02) cited in the application example C</td>
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<td>EP 0 411 628 A (HIMONT INC) 6 February 1991 (1991-02-06) example 9</td>
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</table>

Further documents are listed in the continuation of box C. Patent family members are listed in 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 document but published on or after the international filing date

*L* document which may throw doubts on priority claiming or which is cited to establish the publication date of another citation or other special reason (as specified)

*O* document referring to an oral disclosure, use, exhibition or other means

*P* document published prior to the international filing date but later than the priority date claimed

*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

*Z* document member of the same patent family

Date of the actual completion of the international search

9 May 2001

Date of mailing of the international search report

19/07/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (31-70) 345-2040, Tx. 31 651 epc nl, FAX (31-70) 340-3316

Authorized officer

Schmidt, H
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