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(54) **Title**: FORMULATION

(57) **Abstract**: The present invention relates to a high density polyethylene (HDPE) formulation comprising: high density polyethylene (HDPE) and one or more nucleating agents.

FORMULATION

The present invention relates to an improved high density polyethylene (HDPE) formulation and in particular, but not exclusively, to formulations for the manufacture of caps and closures, for example screw caps for drink containers. The present invention also relates to caps and closures manufactured from an improved high density polyethylene (HDPE) formulations, and the manufacture and uses thereof.

BACKGROUND

During manufacture of thermoplastic polymer based items, such as for example caps and closures, a thermoplastic polymer melt cools and during cooling spontaneous homogenous nucleation occurs to provide lamellae. The lamellae continue to grow to provide a complex macrostructure comprising spherulites within the thermoplastic polymer. The nucleation and the subsequent crystal growth is highly dependent on the temperature of the polymer melt and on the type of thermoplastic polymer. It has also been found that the number and size of the spherulites within the macrostructure has an importance influence over a number of physical and optical properties of the resultant thermoplastic polymer based item.

The size of the spherulites within the polymer is dependent on the number of nucleation sites within the thermoplastic polymer melt, on the temperature of the melt at nucleation, on the speed of cooling, on the speed of nucleation sites formation compared to speed of growth those crystalline microstructure. The presence of a nucleating agent for heterogeneous crystallization within the melt can help to increase the rate of crystallization of a thermoplastic polymer melt, and therefore have a direct influence on the number and size of the spherulites within the polymer. A number of studies have been carried out in relation to the use of nucleating agents for the heterogeneous crystallisation of polymers which are not high density polymers such thermoplastic polymers which have a low rate of crystallization, e.g. polypropylene.

High density polyethylene readily crystalizes so the present invention seeks to overcome difficulties with producing high density polyethylene for caps or closures so they can be manufactured to have one or more of: improved stiffness, improved opening force behaviour, improved shrinkage, improved shrinkage according to colors, improved warpage, reduced defects and/or reduction of blooming effect compared to conventional high density polyethylene caps or closures.

The present invention also provides a method of manufacturing high density polyethylene caps and closures with reduced associated cycle time compared to conventional methods of manufacturing high density polyethylene caps.

SUMMARY OF INVENTION

According to a first aspect, the present invention provides a high density polyethylene (HDPE) formulation comprising: high density polyethylene (HDPE) and one or more nucleating agents.

The term 'high density polyethylene' is used herein to refer to polyethylene having a density of at least 940 kg/m^3. Preferably, the high density polyethylene has a density of no more than 970 kg/m^3. For example, the high density polyethylene has a density of at least 945 kg/m^3, more preferably at least 950 kg/m^3. For example, the high density polyethylene has a density of no more than 965 kg/m^3, more preferably no more than 960 kg/m^3. The high density polyethylene may comprise a blend of two or more high density polyethylene fractions, each fraction having different densities.

The nucleating agent may be any suitable substance, or mixture of substances, that forms nuclei or provides nucleation sites for the formation and/or growth of crystals in high density polyethylene as it solidifies from a molten state. The nucleating agent may be any suitable substance(s) that raises the crystallization temperature of the high density polyethylene composition. The nucleating agent may be any suitable substance(s) that is capable of changing the orientation of crystalline lamellae and/or modifying the crystal size of high density polyethylene. High density polyethylene has a high rate of homogeneous nucleation. The nucleating agent may be any suitable substance(s) that is capable of enabling heterogeneous nucleation within the melt prior to homogeneous nucleation of the high density polyethylene.

The nucleating agent may comprise one or more soluble nucleating agents which are capable of dissolving in the molten polymer, in particular in molten high density polyethylene. As an alternative, the nucleating agent may comprise one or more insoluble nucleating agents which are not capable of dissolving in the molten polymer, in particular in molten high density polyethylene. As a further alternative, the nucleating agent may comprise a combination of soluble and insoluble nucleating agents.
Soluble nucleating agent(s) may include, but are not limited to, one or more of: acetal compounds that are the condensation product of a polyhydric alcohol and an aromatic aldehyde, including for example sorbitol acetals. The sorbitol acetals may include dibenzylidene sorbitol (DBS), bis (p-methyl-dibenzylidene sorbitol) (MDBS), bis(3,4-dimethyl-dibenzylidene sorbitol) (DMDBS), and derivatives thereof. Further soluble nucleating agent(s) may include triamide nucleating agents and polymeric nucleating agents

Insoluble nucleating agent(s) may include, but are not limited to, one or more of: mineral based nucleating agents (such as for example talc, mica, kaolin, and halloysite), organic acid salts such as alkali metal salts or organic acids and alkaline earth metal salts or organic acids, transition metal salts or organic acids and post-transition metal salts of organic acids, or any combination thereof.

The alkali metal salts are preferably lithium, sodium or potassium salts. The alkaline earth metal salts are preferably magnesium or calcium salts. The transition metal salts are preferably manganese or zinc salts. The post-transition metal salts are preferably aluminium salts.

Further example of suitable nucleating agents include, but are not limited to, aliphatic or aromatic salts, such as benzoic acid salts, phosphate ester salts (such as for example bisphenol phosphate ester salts), carboxylate salts, benzenesulfonic acid salts, mandelic acid salts, and combinations thereof.

Examples of suitable carboxylate salts may include may organocarboxylic acid salts, such as alicyclic organocarboxylic acid salts and bicyclic organodicarboxylic acid salts. Examples of suitable carboxylate salts preferably include bicyclic alkane dicarboxylate salts (such as for example disodium bicycle(2.2.1)heptane-2,3-dicarboxylate and calcium bicycle[2.2.1]heptane-2,3-dicarboxylate), cycloalkane dicarboxylate salts, organocarboxylic acid salts, such as alicyclic organocarboxylic acid salts. bicyclic alkane dicarboxylate salts (such as for example disodium bicycle(2.2.1)heptane-2,3-dicarboxylate and calcium bicycle[2.2.1]heptane-2,3-dicarboxylate), cycloalkane dicarboxylate salts, Preferably, the carboxylate salts include hexahydrophthalic acid, calcium salt (Hyperform® HPN-20E), sodium salt (Hyperform® HPN-68L), Hyperform ® being a zinc stearate and cyclohexanedicarboxylic acid, calcium salt.

Examples of other suitable nucleating agents include: 12H-Dibenzo[d, g] [1,3,2] dioxaphophocin, 2, 4, 8, 10-tetrakis (1,1-dimethylethyl)-6-hydroxy-6-oxide, sodium salt (ADK STAB NA11-UH); ADK STAB NA21; ADK STAB NA71; Hyperform® HPN-68L; and any combination thereof.

Preferably, the nucleating agent is selected from one or more of Hyperform® HPN-20E, ADK STAB NA11-UH, ADK STAB NA21; ADK STAB NA71, and Hyperform® HPN-68L, and any combination thereof.

The concentration of the nucleating agent(s) in the formulation will depend on the particular crystallization efficiency of the agent(s). The nucleating agents are preferably present within the formulation in an amount sufficient to initiate heterogeneous recrystallization of the high density polypropylene.

The nucleating agent(s) is preferably present within the formulation at a concentration of at least 50 ppm, more preferably at least 75 ppm, for example at least about 100ppm. The nucleating agent(s) is preferably present within the formulation at a concentration of no more than 800 ppm, more preferably no more than 500 ppm, for example no more than 250 ppm. The nucleating agent(s) is preferably present within the formulation at a concentration within the range of 50 ppm and 800 ppm; more preferably within the range of 100 ppm and 250 ppm. Preferably, the nucleating agent(s) is present within the formulation at a concentration of about 150 ppm.

According to a second aspect, the present invention provides a cap or closure comprising a high density polyethylene formulation comprising high density polyethylene (HDPE) and one or more nucleating agents.

The cap or closure of the present invention preferably includes, but is not limited to, screw caps, caps and closures with a living hinge, transparent caps and closures, glossy caps and closures. Preferably, the cap or closure is a screw cap.

The caps and closures of the present invention may be used in various packaging applications, including for example food packaging, medical packaging, cosmetic packaging, detergent packaging. Preferably, the cap or closure is a cap or closure of a drink container, such as for example a carbonated or still drink container.

According to a further aspect, the present invention provides a method for the manufacture of a HDPE formulation as herein described, the method comprising:

introducing one or more nucleating agents to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate heterogeneous crystallisation of the high density polyethylene.

According to a further aspect, the present invention provides a method for the manufacture of a cap or closure comprising:

Introducing one or more nucleating agents to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate heterogeneous crystallisation of the high density polyethylene; and

shaping the high density polyethylene formulation to provide the cap or closure.

Preferably, the method involves shaping the formulation by injection molding.

The method of manufacturing the caps or closures according to the present invention has improved efficiency compared to conventional methods of manufacturing HDPE caps or closures. In particular, the method of the present invention has improved efficiency due to the efficient nucleation generated by the presence of the nucleating agent(s) within the HDPE formulation. Cycle time reduction is also achieved as a result of inducing in the high density polyethylene melt a higher temperature of crystallisation which enables the molten polymer melt to harden at a higher temperature. As a result, the cooling time for the HDPE formulation is reduced compared to HDPE and the resultant caps or closures can be removed from the mold at a faster rate than would be possible without the presence of the nucleating agent(s).

Preferably, the cycle time of the method of manufacture of the caps or closures of the present invention is reduced by at least 5%, more preferably at least 10%, compared to conventional methods of manufacturing HDPE caps or closures.

The presence of the nucleating agent(s) within the formulation also increases the demoulding temperature of the cap or closure. As a result, it has been found that the cap or closure manufactured from a formulation comprising HDPE and a nucleating agent(s) is more robust and less likely to demonstrate quality issues, associated with for example broken bridges during demolding.

The present invention also provides a HDPE cap or closure with improved functional performance compared to conventional HDPE caps or closures. Furthermore, the HDPE cap or closure of the present invention has a controlled opening torque in an acceptable range, such as for example. The HDPE cap or closure of the present invention has also been found to have improved stiffness compared to conventional HDPE caps or closures. As a result, the HDPE cap or closures of the present invention provide a reduced blooming effect, and as such are suitable for use with pressurised containers, such as for example carbonated drink containers.

In accordance with a further aspect, the present invention provides a HDPE formulation comprising:

high density polyethylene (HDPE);
at least one nucleating agent; and
a slip agent formulation.

The slip agent formulation preferably comprises: at least one of an unsaturated slip agent and/or a saturated slip agent, or any combination thereof.

The slip agent formulation preferably further comprises at least one of:

at least one filler;
at least one process stabiliser;
at least one primary antioxidant;
at least one secondary antioxidant; and/or
at least one UV absorber; and
any combination thereof.

The slip agent may comprise any suitable conventional slip agent such as for example aliphatic saturated and/or unsaturated fatty acid containing between 16 and 22 carbon atoms. For example, the slip agent(s) may comprise one or more primary fatty acid amides, including for example erucamide, behenamide and oleamide; and/or one or more secondary fatty acid amides, including for example stearyl erucamide, oleyl palmitamide, erucyl erucamide and stearyl stearamide; and/or one or more branched fatty acid amides; and/or one or more saturated bis amides, including for example ethylene bid stearamide. Preferably, the slip agent(s) comprises erucamide (13-cis-docosenamide) and/or behanamide. Preferably, the slip agent comprises erucamide.

The slip agent may be present at any suitable concentration within the slip agent formulation. The saturated and unsaturated slip agent are preferably each present within the slip agent formulation at a

concentration in the range of between 0 and 3000 ppm. Preferably, the or each of the saturated and/or unsaturated slip agent are present within the slip agent formulation at a concentration of at least 50 ppm, preferably at least 500 ppm, more preferably at least 1000 ppm, or for example at least 1500 ppm. Preferably, the or each of the saturated and/or unsaturated slip agent are present within the slip agent formulation at a concentration of at no more than 3000 ppm, more preferably no more than 2750 ppm, for example no more than 2500 ppm. The or each of the saturated and/or unsaturated slip agent may be present within the formulation at a concentration within the range of between 500 ppm and 2500 ppm, for example between 1000 ppm and 2500 ppm, 1000ppm to 2000ppm, or between 1800 ppm and 2200 ppm. The or each of the saturated and/or unsaturated slip agent may, for example, be present within the formulation at a concentration of approximately 1000ppm or 2000 ppm.

The filler may comprise any number of suitable fillers for the slip agent formulation. For example, the filler may comprise one or more of calcium stearate and/or zinc stearate. Preferably, the filler comprises calcium stearate. The filler may be present within the formulation at any suitable concentration. The total filler concentration within the slip agent formulation is preferably at least 100 ppm, more preferably at least 250 ppm, or for example at least 500 ppm. The total filler concentration in the slip agent formulation is preferably no more than 2500 ppm, more preferably no more than 2200 ppm. The total filler concentration in the slip agent formulation is preferably in the range of 500 to 2500, more preferably between 1000 ppm and 2500 ppm, especially preferably between 1800 ppm and 2200 ppm, for example 2000 ppm.

The stabiliser may comprise any suitable process stabiliser or combination of process stabilisers. The stabiliser is preferably a heat stabiliser. For example, the stabiliser may comprise tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168) or use another to describe a solution that we do not use. The slip agent formulation preferably comprises a total stabiliser concentration of no more than 1000 ppm, preferably no more than 900 ppm, for example no more than 660 ppm. The slip agent formulation preferably comprises a total stabiliser concentration of at least 200 ppm, preferably at least 250 ppm, more preferably at least 540 ppm. The total stabiliser concentration is preferably in the range of between 200 ppm and 1000 ppm, more preferably in the range of between 250 ppm and 1000 ppm, more preferably in the range of from 200 ppm to 900 ppm, especially preferably in the range of from 540 ppm to 660 ppm. The total stabiliser concentration is preferably about 600 ppm.

The primary antioxidant preferably comprises any suitable antioxidant, or combination of antioxidants, capable of providing processing and long term thermal stabilization of the formulation. Preferably the primary antioxidant comprises at least one phenolic antioxidant. The primary antioxidant preferably comprises Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076). An alternative would be

Pentaerythritol Tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (Irganox 1010)

The slip agent formulation preferably comprises a total primary antioxidant concentration of no more than 150 ppm, and more preferably no more than 110 ppm. The slip agent formulation preferably comprises a total primary antioxidant concentration of at least 30 ppm, more preferably at least about 50 ppm, for example at least about 90 ppm. The slip agent formulation preferably comprises a total primary antioxidant concentration in the range of between 30 ppm and 150 ppm, preferably in the range of from 50 ppm and 150 ppm, especially preferably in the range of between 90 ppm and 110 ppm, for example 100 ppm.

The secondary antioxidant may be any suitable antioxidant, or combination of antioxidants, for providing light protection, low volatility and minimal migration of the slip agent formulation. The secondary antioxidant may be any suitable antioxidant further providing long term heat stability of the slip agent formulation. The secondary antioxidant preferably comprises butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tatramethyl-1-piperidine ethanol (Tinuvin 622 LD).

The secondary antioxidant may be present at any suitable concentrations within the slip agent formulation to provide the necessary protection discussed above. The slip agent formulation preferably comprises a total secondary antioxidant concentration of up to 1500 ppm, preferably up to 1000 ppm, more preferably up to 800 ppm, for example up to 550 ppm. The slip agent formulation preferably comprises a total secondary antioxidant concentration of at least 300 ppm, more preferably at least 450 ppm. The slip agent formulation preferably comprises a total secondary antioxidant concentration of between 300 ppm and 1500 ppm, more preferably between 300 ppm and 800 ppm, especially preferably between 450 and 550 ppm, for example 500 ppm.

The slip agent formulation may comprise any suitable UV absorber, or combination of UV absorbers. For example, the slip agent formulation may comprise 2-(5-chloro(2H)-benzotrazole-2-yl)-4-methyl-6-(tert-butyl)phenol (Tinuvin 326). The slip agent formulation may comprise a total concentration of UV absorber of up to 900 ppm, more preferably up to 800 ppm, for example of up to 550 ppm. The slip agent formulation may comprise a total UV absorber concentration of at least 200 ppm, more preferably at least 450 ppm. The slip agent formulation preferably comprises a total UV absorber concentration in the range of between 200 ppm and 900 ppm, more preferably between 200 ppm and 800 ppm; especially preferably in the range of between 450 and 550 ppm, for example 500 ppm.

The slip agent formulation preferably comprises:

a slip agent selected from erucamide and/or behenamide and/or Incroslip™ SL or any combination thereof, and at least one of:

at least one filler selected from: calcium stearate and/or zinc stearate, or any combination thereof;

a process stabiliser comprising tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168);

a primary antioxidant comprising octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076);

a secondary antioxidant selected from butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol (Tinuvin 622); and

a UV absorber comprising 2-(5-chloro(2H)-benzotrazole-2-yl)-4-(methyl)-6-(tert-butyl)phenol (Tinuvin 326).

Preferably, the slip agent is erucamide and behenamide or Incroslip™ SL (a slip agent and torque release agent.). Preferably, the slip agent formulation comprises erucamide.

According to a second aspect, the present invention provides a cap or closure comprising a high density polyethylene formulation comprising high density polyethylene (HDPE), at least one nucleating agents, and a slip agent formulation.

The cap or closure preferably includes, but is not limited to, screw caps, caps and closures with a living hinge, transparent caps and closures, glossy caps and closures. Preferably, the cap or closure is a screw cap.

According to a further aspect, the present invention provides a method for the manufacture of a HDPE formulation as herein described, the method comprising:

introducing at least one nucleating agent, and a slip agent formulation, to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate heterogeneous crystallisation of the high density polyethylene.

According to a further aspect, the present invention provides a kit for the manufacture of a HDPE formulation as herein described, the kit comprising:

a first container comprising high density polyethylene; and

a second container comprising at least one nucleating agent.

One of the first and second containers may additionally comprise the slip agent formulation. For example, the first container may comprise the slip agent formulation. Alternatively, the second container may comprise the slip agent formulation.

According to a still further aspect, the present invention provides a kit for the manufacture of a HDPE formulation as herein described, the kit comprising:

a first container comprising high density polyethylene and at least one nucleating agent; and

a second container comprising a slip agent formulation.

The contents of the second container, i.e. the nucleating agent and optionally the slip agent formulation, may be introduced to the contents of the first container (i.e. high density polyethylene and optionally one of the nucleating agent(s) and slip agent formulation) via master batch on the injection machine.

The caps or closures of the present invention are preferably screw caps. The cap or closure of the present invention may be formed by any suitable method.

According to a still further aspect, the present invention provides a method for the manufacture of HDPE caps or closures as herein described, the method comprising:

introducing at least one nucleating agent and a slip agent formulation, to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate heterogeneous crystallisation of the high density polyethylene; and

injection molding the high density polyethylene formulation to provide the cap or closure.

The at least one nucleating agent and slip agent formulation may be introduced simultaneously or separately to the high density polyethylene.

The present invention provides HDPE caps and closures with excellent slip properties. Furthermore, the present invention provides HDPE caps and closures with increased UV protection. In particular, the present invention provides HDPE caps and closures with low, preferably substantially no, UV degradation. Furthermore, the nucleating agent(s), and optionally the slip agent formulation, do not impart any undesirable taste into the HDPE article, such as caps or closures. The HDPE caps or closures prepared according to the methods of the present invention exhibit higher stiffness and good opening force behaviour.

It has also been found that by including both at least one nucleating agent together with a slip agent formulation as herein described within the HDPE formulation the cycle time for the production of the caps or closures is significantly reduced. The cycle time for the production of HDPE caps or closures using an HDPE formulation comprising nucleating agent(s) and slip agent formulation is reduced by preferably at least 10%, more preferably at least 15%, for example at least 20% when compared to the cycle time for production of HDPE caps or closures using HDPE prepared using homogeneous crystallization. For example, the cycle time for the production of HDPE caps or closures using an HDPE formulation comprising nucleating agent(s) and slip agent formulation is reduced by between 12 and 20% compared to the cycle time for production of HDPE caps or closures using HDPE prepared using homogeneous crystallization.

The cycle time for the production of the HDPE caps or closures of the present invention using a HDPE formulation comprising nucleating agent(s) and slip agent formulation is significantly reduced compared to the cycle time associated with the production of HDPE caps or closures using HDPE formulations comprising nucleating agent(s) alone. The cycle time for the production of HDPE caps or closures using an HDPE formulation comprising nucleating agent(s) and slip agent formulation is reduced by at least 5%, preferably at least 10% when compared to the cycle time for production of HDPE caps or closures using HDPE formulations comprising nucleating agent(s) alone.

In one aspect the present invention relates to PEHD and a nucleating agent, with or without a slip agent package.

In some embodiments the improved efficiency of nucleating agent leads to an increase of demoulding temperature associated with a better resistance of frangible tamper-evident bridges which leads to:

- Decrease of quality problem bound to broken bridges (moulded bridges were previously more fragile during demoulding)
- Increase of productivity (cooling time is reduced by 0.7 s minimum).
- Decrease of dimensions variations from one colour MB to another
- Decrease in blooming

The invention may comprise a PEHD formulation including:

- A nucleating agent typically Calcium, Lithium, Sodium, Aluminium salt (aliphatic or aromatic) in a content between 50 and 800 ppm (especially between 100 and 250 ppm); and
- An additive package including an unsaturated slip agent (for example Erucamide) associated with UV stabilizer and other additives like antistatic, heat stabilizer, anti-oxidant.

The use of the combination can be done in different ways, for example:

- fully formulated materials
- Polymer matrix compounded with slip additive package on which the nucleating agent is added via master batch on the injection machine
- Polymer matrix on which the nucleating agent and the slip additive package are added via master batch on the injection machine
- Polymer matrix compounded with the nucleating agent on which slip additive package is added via master batch on the injection machine

Some other combination should exist with the colour master batch.

In some aspects and embodiments the invention consists in caps injected in PEHD. The composition of PEHD may use :

- Either simultaneously in the same formulation a combination of nucleating agent and slip agent package;
- Or nucleating agent alone

This simultaneous use leads to a large increase of cycle time until 20% and allows good functional performance like increased stiffness and controlled opening force with reduced blooming effect.

In some aspects and embodiments the use of the combination leads to a synergy which leads to:

- A decrease of 12 to 20% of the cycle time mainly related to cooling time
- A higher stiffness and a good opening force behaviour
- A reduction of blooming effect compared to behenamide solution

Table 1 - Slip agent package

Kind of additive	Additives	Window
Filler	Calcium stearate Zinc stearate	 500 to 2500 Level 3
Process stabiliser	 Tris(2,4-di-tert-butylphenyl)phosphite Define with chemical name with CAS n° 31570-04-4	540 – 660 ppm 250 to 1000 ppm Necessary Level 2
(Phenolic) Primary anti-oxidant for processing and long-term thermal stabilization..	Define with chemical name with Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate CAS n°2082-79-3	90 - 110 ppm Level 3 30 - 150
Slip agent (unsaturated) and slip agent (saturated) like behenamide	Erucamide (13-cis-docosenamide) with CAS n°112-84-5	 0 to 3000 ppm Level 2
Light protection Low volatility and minimal migration providing anti-oxidant properties and contributing significantly to the long term heat stability,	Tinuvin 622 LD Butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol Casn° 65447-77-0	450 – 550 ppm Level 4 300 – 1500 ppm
UV Absorber	Tinuvin 326 2-(5-chloro(2H)-benzotrazole-2-yl)-4-(methyl)-6-(tert-butyl)phenol Casn° 3896-11-05	450 – 550 ppm Level 4 200 - 800

The additive package provides, for example, on beverage screw caps, excellent slip properties and UV protection (no UV degradation and not creating off-taste).

Table 2 - Nucleating agent

Kind of additive	Additives	Window
Nucleating agent : salt of metal (e.g. Li; Al; So; Ca)	Example Hyperform® HPN- 20E	50 and 800 ppm (especially between 100 and 250 ppm)

Different aspects and embodiments of the invention may be used separately or together.

Further particular and preferred aspects of the present invention are set out in the accompanying independent and dependent claims. Features of the dependent claims may be combined with the

features of the independent claims as appropriate, and in combination other than those explicitly set out in the claims.

The following examples illustrate embodiments of the present invention.

Example 1 – High Density Polyethylene Formulation with Nucleating Agent

The high density polyethylene formulation comprises high density polyethylene and Hyperform ® HPN-20E as the nucleating agent. Hydroform ® HPN-20E is present at within the HDPE formulation at a concentration of 150 ppm.

The high density polyethylene formulation was used to manufacture a cap by injection molding. The cycle time for producing the cap was reduced by 10% compared to conventional processes for manufacturing caps using HDPE formed by homogeneous crystallization.

Example 2 – High Density Polyethylene Formulation with Nucleating Agent and Slip Agent Formulation

The high density polyethylene formulation comprises:

high density polyethylene;

Hyperform ® HPN-20E as the nucleating agent. Hydroform ® HPN-20E is present at within the HDPE formulation at a concentration of 150 ppm; and

a slip agent formulation comprising:

a slip agent comprising erucamide and behenamide. The total concentration of slip agent present within the slip agent formulation at a concentration of 2000 ppm;

a filler comprising calcium stearate at a concentration of 2000 ppm within the slip agent formulation;

a process stabiliser comprising tris(2,4-di-tert-butylphenyl)phosphite, the concentration of stabiliser within the slip agent formulation is 600 ppm;

a primary antioxidant comprising octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and the total concentration of primary antioxidant within the formulation is 100 ppm;

a secondary antioxidant comprising butanedioic acid dimethylester polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, and the total concentration of secondary antioxidant within the formulation is 500 ppm; and

a UV absorber comprising 2-(5-chloro(2H)-benzotrazole-2-yl)-4-(methyl)-6-(tert-butyl)phenol, and the total concentration of UV absorber within the formulation is 500 ppm.

Example 3 – High Density Polyethylene Formulation with Nucleating Agent and Slip Agent Formulation

The high density polyethylene formulation comprises:

high density polyethylene;

Hyperform ® HPN-20E as the nucleating agent. Hydroform ® HPN-20E is present at within the HDPE formulation at a concentration of 150 ppm; and

a slip agent formulation comprising:

a slip agent comprising Incroslip™ SL. The total concentration of slip agent present within the slip agent formulation at a concentration of 1000 ppm;

a filler comprising calcium stearate at a concentration of 2000 ppm within the slip agent formulation;

a process stabiliser comprising tris(2,4-di-tert-butylphenyl)phosphite, the concentration of stabiliser within the slip agent formulation is 600 ppm;

a primary antioxidant comprising octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and the total concentration of primary antioxidant within the formulation is 100 ppm;

a secondary antioxidant comprising butanedioic acid dimethylester polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, and the total concentration of secondary antioxidant within the formulation is 500 ppm; and

a UV absorber comprising 2-(5-chloro(2H)-benzotrazole-2-yl)-4-(methyl)-6-(tert-butyl)phenol, and the total concentration of UV absorber within the formulation is 500 ppm.

The high density polyethylene formulation was used to manufacture a cap by injection molding. The cycle time for producing the cap was reduced by 20% compared to conventional processes for manufacturing caps using HDPE formed by homogeneous crystallization. This cycle time reduction is far greater than the cycle time reduction provided by HDPE formulations comprising nucleating alone, as demonstrated in Example 1.

CLAIMS

1. A high density polyethylene (HDPE) formulation comprising: high density polyethylene (HDPE) and one or more nucleating agents.

2. A formulation as claimed in claim 1, in which the high density polyethylene has a density of at least 940 kg/m^3.

3. A formulation as claimed in either of claims 1 and 2, in which the nucleating agent(s) comprises one or more nucleating agents selected from acetal compounds, triamide nucleating agents, polymeric nucleating agents, mineral based nucleating agents, aliphatic or aromatic salts, phosphate ester salts, carboxylate salts, organic acid salts of alkali metals, alkaline earth metals, transition metals or post-transition metals, and any combination thereof.

4. A formulation as claimed in any preceding claim, in which the nucleating agent(s) comprises one or more sorbital acetals.

5. A formulation as claimed in claim 4, in which the nucleating agent(s) comprises one or more of: dibenzylidene sorbital (DBS), bis (p-methyl-dibenzylidene sorbitol) (MDBS), bis(3,4-dimethyl-dibenzylidene sorbitol) (DMDBS), and derivatives thereof.

6. A formulation as claimed in any preceding claim 1 to 3, in which the nucleating agent(s) comprises at least one alkali metal salt selected from lithium, sodium or potassium salts, or any combination thereof.

7. A formulation as claimed in any preceding claim, in which the nucleating agent(s) comprises at least one carboxylate salt.

8. A formulation as claimed in claim 7, in which the carboxylate salt(s) is selected from bicyclic alkane dicarboxylate salts, cycloalkane dicarboxylate salts, organocarboxylic acid salts, bicyclic alkane dicarboxylate salts, cycloalkane dicarboxylate salts, and any combination thereof.

9. A formulation as claimed in any preceding claim, in which the at least one nucleating agent comprises a calcium salt of hexahydrophthalic acid (Hyperform® HPN-20E).

10. A formulation as claimed in any preceding claim, in which the nucleating agent(s) is present within the formulation at a concentration of at least 50 ppm.

11. A formulation as claimed in any preceding claim, in which the nucleating agent(s) is present within the formulation at a concentration of no more than 800 ppm.

12. A cap or closure comprising a high density polyethylene formulation comprising high density polyethylene (HDPE) and one or more nucleating agents.

13. A cap or closure as claimed in claim 12, in which the cap or closure is a screw cap.

14. A method for the manufacture of a high density polyethylene (HDPE) formulation as claimed in any one of claims 1 to 11, the method comprising:

introducing one or more nucleating agents to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate crystallisation of the high density polyethylene.

15. A method for the manufacture of a cap or closure, comprising:
manufacturing a HDPE formulation in accordance with the method of claim 14; and shaping the formulation to provide the cap or closure.

16. A method as claimed in claim 15, in which the formulation is shaped by injection molding.

17. A HDPE formulation comprising:
high density polyethylene (HDPE);
at least one nucleating agent; and
a slip agent formulation.

18. A formulation as claimed in claim 17, in which the slip agent formulation comprises: at least one of an unsaturated slip agent and/or a saturated slip agent, or any combination thereof.

19. A formulation as claimed in claim 18, in which the slip agent formulation further comprises at least one of:
at least one filler;
at least one process stabiliser;
at least one primary antioxidant;
at least one secondary antioxidant; and/or
at least one UV absorber;
and any combination thereof.

20. A formulation as claimed in either of claims 18 and 19, in which the slip agent is selected from: erucamide, behenamide, Incroslip™ SL and oleamide, and any combination thereof.

21. A formulation as claimed in claim 20, in which the slip agent comprises erucamide.

22. A formulation as claimed in any one of claims 17 to 21, in which the slip agent is present within the slip agent formulation at a concentration in the range of between 0 ppm and 3000 ppm, for example up to 1000ppm, up to 2000ppm or up to 3000ppm.

23. A formulation as claimed in any one of claims 19 to 22, in which the filler comprises one or more of calcium stearate and/or zinc stearate.

24. A formulation as claimed in any one of claims 19 to 23, in which the total filler concentration in the slip agent formulation is in the range of 500 to 2500.

25. A formulation as claimed in any one of claims 19 to 24, in which the stabiliser comprises tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168).

26. A formulation as claimed in any one of claims 19 to 25, in which the total stabiliser concentration is in the range of between 200 ppm and 900 ppm.

27. A formulation as claimed in any one of claims 19 to 26, in which the primary antioxidant comprises at least one phenolic antioxidant.

28. A formulation as claimed in claim 27, in which the primary antioxidant is octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076).

29. A formulation as claimed in any one of claims 19 to 28, in which the total primary antioxidant concentration within the slip agent formulation is in the range of between 50 ppm and 150 ppm.

30. A formulation as claimed in any one of claims 19 to 29, in which the secondary antioxidant comprises butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tatramethyl-1-piperidine ethanol (Tinuvin 622 LD).

31. A formulation as claimed in any one of claims 19 to 30, in which the total secondary antioxidant concentration within the slip agent formulation is between 300 ppm and 1500 ppm.

32. A formulation as claimed in any one of claims 19 to 31, in which the UV absorber comprises 2-(5-chloro(2H)-benzotrazole-2-yl)-4-methyl-6-(tert-butyl)phenol (Tinuvin 326).

33. A formulation as claimed in any one of claims 19 to 32, in which the total UV absorber concentration within the slip agent formulation is in the range of between 200 ppm and 900 ppm.

34. A formulation as claimed in any one of claims 19 to 33, comprising

a slip agent selected from erucamide and behenamide, or any combination thereof, and at least one of:

at least one filler selected from: calcium stearate and/or zinc stearate, or any combination thereof;

a process stabiliser comprising tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168);

a primary antioxidant comprising octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076);

a secondary antioxidant selected from butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol (Tinuvin 622); and

a UV absorber comprising 2-(5-chloro(2H)-benzotrazole-2-yl)-4-(methyl)-6-(tert-butyl)phenol (Tinuvin 326).

35. A cap or closure comprising a high density polyethylene formulation comprising high density polyethylene (HDPE), at least one nucleating agents, and a slip agent formulation.

36. A cap or closure as claimed in claim 35, in which the cap or closure is a screw cap.

37. A method for the manufacture of a HDPE formulation as claimed in any one of claims 17 to 34 the method comprising:

introducing at least one nucleating agent, and a slip agent formulation, to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate heterogeneous crystallisation of the high density polyethylene.

38. A kit for the manufacture of a HDPE formulation as claimed in any one of claims 1 to 13 and 17 to 34, the kit comprising:

a first container comprising high density polyethylene; and

a second container comprising at least one nucleating agent.

39. A kit as claimed in claim 38, in which one of the first and second containers additionally comprises a slip agent formulation.

40. A kit for the manufacture of a HDPE formulation as claimed in any one of claims 17 to 34, the kit comprising:

a first container comprising high density polyethylene and at least one nucleating agent; and

a second container comprising a slip agent formulation.

41. A method for the manufacture of HDPE caps or closures as claimed in either of claims 35 and 36, the method comprising:

introducing at least one nucleating agent and a slip agent formulation, to high density polyethylene to provide a high density polyethylene formulation, in which the nucleating agent(s) is present within the formulation at a concentration sufficient to initiate heterogeneous crystallisation of the high density polyethylene; and

injection molding the high density polyethylene formulation to provide the cap or closure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2015/058384

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

17-37, 40, 41(completely); 38, 39(partially)

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/058384

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/06 C08K5/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L C08K

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 practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104 004 253 A (LUOHE GLOBAL SANITARY WARE ACCESSORIES CO LTD) 27 August 2014 (2014-08-27) examples 9,10,12,13,15,16,18	1-5, 10-16, 38,39
X	US 2015/061192 A1 (SUN DAVID DEZHOU [US]) 5 March 2015 (2015-03-05) paragraph [0045]; claims 18-23	17-41
X	US 2015/014879 A1 (SUN DAVID DEZHOU [US] ET AL) 15 January 2015 (2015-01-15) paragraph [0122]; claim 20	17-41
X	WO 2013/052273 A2 (EXXONMOBIL CHEM PATENTS INC [US]; ZHAO MOSHA H [US]; GARCIA-FRANCO CES) 11 April 2013 (2013-04-11) page 28 - page 30	17-23, 25-41

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

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of 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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 January 2016	18/01/2016

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/058384

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 402 391 A1 (BOREALIS AG [AT]) 4 January 2012 (2012-01-04) paragraph [0133] - paragraph [0134] -----	17-41

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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/058384

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 104004253 A	27-08-2014	NONE	
US 2015061192 A1	05-03-2015	TW 201521993 A	16-06-2015
		TW 201532782 A	01-09-2015
		TW 201536527 A	01-10-2015
		US 2015061192 A1	05-03-2015
		US 2015061193 A1	05-03-2015
		US 2015061194 A1	05-03-2015
		WO 2015031879 A1	05-03-2015
		WO 2015031880 A2	05-03-2015
		WO 2015031881 A1	05-03-2015
US 2015014879 A1	15-01-2015	TW 201512274 A	01-04-2015
		US 2015014879 A1	15-01-2015
		WO 2015006772 A1	15-01-2015
WO 2013052273 A2	11-04-2013	NONE	
EP 2402391 A1	04-01-2012	AU 2011273582 A1	20-12-2012
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		EP 2402391 A1	04-01-2012
		ES 2430856 T3	22-11-2013
		KR 20130029408 A	22-03-2013
		RU 2012155043 A	10-08-2014
		US 2013237652 A1	12-09-2013
		WO 2012000958 A1	05-01-2012

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 4, 5(completely); 1-3, 10-16, 38, 39(partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least an acetal compound

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2. claims: 1-3, 10-16, 38, 39(all partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least a triamide

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3. claims: 1-3, 10-16, 38, 39(all partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least a polymeric nucleating agent

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4. claims: 1-3, 10-16, 38, 39(all partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least a mineral based nucleating agent

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5. claims: 1-3, 10-16, 38, 39(all partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least an aliphatic or aromatic salt

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6. claims: 1-3, 10-16, 38, 39(all partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least a phosphate ester salt

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7. claims: 7, 8(completely); 1-3, 10-16, 38, 39(partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least a carboxylate salt

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8. claims: 6, 9(completely); 1-3, 10-16, 38, 39(partially)

   An HDPE formulation without slip agent where the nucleating agent comprises at least an organic acid salt of alkali metals, alkaline earth metals, transition metals or post-transition metals

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9. claims: 17-37, 40, 41(completely); 38, 39(partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An HDPE formulation with a slip agent and at least a nucleating agent

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