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(54) Title: USE OF SECONDARY STERICALLY HINDERED AMINES AS PROCESSING ADDITIVES IN ROTOMOLDING PROCESSES

(57) Abstract: The instant invention pertains to the use of secondary sterically hindered amines as processing additives in rotational molding processes. These additives increase process stability, since they provide a broader temperature range towards higher temperatures during the melt processing step.

Use of Secondary Sterically Hindered Amines as Processing Additives in Rotomolding Processes

The instant invention pertains to the use of secondary sterically hindered amines as processing additives in rotational molding processes. These additives increase process stability, since they provide a broader temperature range towards higher temperatures during the melt processing step.

Rotational molding is a highly versatile manufacturing option that allows for unlimited design possibilities with the added benefit of low production costs.

The rotational molding process (rotomolding process) starts with a good quality mold that is placed in a molding machine that has a loading, heating, and cooling area.

Several molds may be placed on the machine at the same time. Pre-measured plastic resin is loaded into each mold, and then the molds are moved into the oven where they are slowly rotated on both the vertical and horizontal axis. The melting resin sticks to the hot mold and coats every surface evenly. The mold continues to rotate during the cooling cycle so the parts retain an even wall thickness.

Once the parts are cooled, they are released from the mold. The rotational speed, heating and cooling times may be all controlled throughout the process.

Rotational molding offers design advantages over other molding processes. With proper design, parts that are assembled from several pieces can be molded as one part, eliminating expensive fabrication costs.

The process also has a number of inherent design strengths, such as consistent wall thickness and strong outside corners that are virtually stress free. If additional strength is required, reinforcing ribs can be designed into the part.

Rotational molding delivers the product the designer envisions. Designers can select the best material for their application, including materials that meet FDA requirements. Additives to help make the part weather resistant, flame retardant, or static free can be specified.

And because parts are formed with heat and rotation, rather than pressure, molds don't need to be engineered to withstand the high pressure of injection molding.

5 Production costs for product conversions are reduced because lightweight plastics replace heavier, often more costly materials, which makes rotational molding as cost effective for one-of-a-kind prototypes as it is for large production runs

10 Rotational molding is versatile and able to handle a vast variety of shapes and sizes. Many parts cannot be readily produced by any other method. Typical examples are specialty tanks and containers for fuel, water, and chemical processing, livestock feeders, drainage systems, food service containers, instrument housings, vending machines, highway barriers and road markers. Other application areas are consumer products, toys and transportation. Many aspects of the rotational molding process are, for example, described by R. J. Crawford and J. L. Throne in Rotational Molding Technology, Plastics Design Library, William Andrew  
15 Publishing, 2001.

As mentioned above rotational speed, heating and cooling times may be all controlled throughout the process. The maximum temperature of the air, which is reached inside the hollow molded article, depends strongly on the heating time. This temperature is also called  
20 peak internal air temperature (PIAT). It correlates with the temperature of the molten resin.

The concept of peak internal air temperature (PIAT) and the consequences, if a too low or too high PIAT is applied, is for example described by M. C. Cramez et al. in Proc. Instrn Mech. Engrs. Vol. 217 Part B: J. of Engineering Manufacture, 2003.  
25

The peak internal air temperature can influence the final properties of the molded product. For example, if the temperature becomes too high, a strong yellowing may occur and also the mechanical properties are negatively affected, for example, the impact strength decreases significantly. If the temperature remains too low the final properties can also be  
30 adversely affected because the resins have not been properly molten. In other words, there is only a small temperature range for achieving the desired final properties. It is therefore of high interest to widen this temperature range or processing window, within which almost constant mechanical properties are obtained.

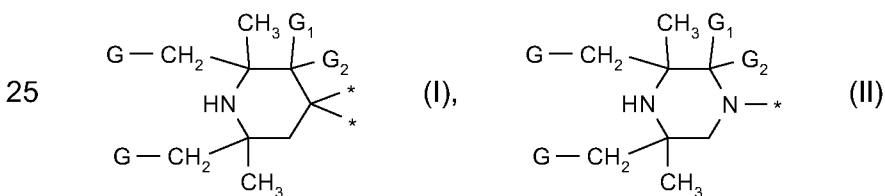
Botkin et al in "An additive approach to cycle time reduction in rotational molding" Rotational Molding by Design Conference, Society of Plastics Engineers, 2004 have demonstrated that by using a proprietary process stabilizer, the PIAT can be shifted towards lower temperatures maintaining good impact strength. This corresponds to broadening the processing window towards lower temperatures.

Surprisingly it has now been found that when a secondary hindered amine compound is added to the resin formulation a significantly broader processing window towards higher temperatures is achieved without adversely affecting color and mechanical properties of the molded article.

Consequently one aspect of the invention is the use of a secondary sterically hindered amine compound as processing additive for enlarging the processing window towards higher peak internal air temperatures in rotational molding processes of thermoplastic polymers.

Under processing window there is understood the temperature range, as measured by the peak internal air method (PIAT), within which the mechanical properties and/or the color of the molded article remain essentially the same. A particularly suitable mechanical property to measure is impact strength, for example at low temperatures. Low temperature means in this context from 0° to -50° C, particularly -20° C to -40° C.

For example the sterically hindered amine is a compound containing at least one group of the formula (I) or (II)



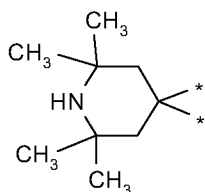
in which

\* indicates a bond

G is hydrogen or methyl, and

30 G<sub>1</sub> and G<sub>2</sub>, independently of one another, are hydrogen, methyl or together are a substituent =O.

For instance the sterically hindered amine is a compound containing at least one group of formula (Ia).



(Ia).

- 5 The sterically hindered amine compounds are known and widely used as thermal or light stabilizers for polymers. They are either commercially available or can be prepared as described, for example, in  
 US-A-5,679,733, US-A-3,640,928, US-A-4,198,334, US-A-5,204,473,  
 US-A-4,619,958, US-A-4,110,306, US-A-4,110,334, US-A-4,689,416,  
 10 US-A-4,408,051, SU-A-768,175 (Derwent 88-138,751/20), US-A-5,049,604,  
 US-A-4,769,457, US-A-4,356,307, US-A-4,619,956, US-A-5,182,390,  
 GB-A-2,269,819, US-A-4,292,240, US-A-5,026,849, US-A-5,071,981,  
 US-A-4,547,538, US-A-4,976,889, US-A-4,086,204, US-A-6,046,304,  
 US-A-4,331,586, US-A-4,108,829, US-A-5,051,458, WO-A-94/12,544 (Derwent  
 15 94-177,274/22), DD-A-262,439 (Derwent 89-122,983/17), US-A-4,857,595,  
 US-A-4,529,760, US-A-4,477,615, CAS 136,504-96-6, US-A-4,233,412,  
 US-A-4,340,534, WO-A-98/51,690 and EP-A-1,803, the disclosures of which are  
 incorporated by reference.

- 20 Preferred are the following commercial compounds.

Chimassorb 2020®, Chimassorb 944®, Tinuvin 770® and Tinuvin 783®, Cyasorb UV 3346®,  
 Cyasorb UV 3581®, Dastib 845®, Dastib 1082®, Diacetam 5, Fero 806-X®, Goodrite 3034®,  
 Goodrite 3150®, HALS IC-TAM, Hostavin N 20®, Hostavin N 24®, Hostavin N 30®, Hüls S-  
 25 95®, ICI PA 500®, Lichtschutzstoff UV 31, Luchem HA-B 18®, Mark LA 55®, Mark LA 57®,  
 Mark LA 67®, Mark LA 68®, Sanduvor 3050®, Sumilizer 61®, Sumilizer 70®, Suimisorb TM  
 61®, UVASORB HA 88®, Uvinul 4049®, Uvinul 5050®, Uvasil 299®, Uvasil 125®.

These compounds are commercially available and described in: US-A-5,679,733, US-A-  
 30 3,640,928, US-A-5,204,473, US-A-4,619,958, US-A-4,110,306, US-A-4,110,334, US-A-  
 4,689,416, US-A-4,408,051, SU-A-768,175 (Derwent 88-138,751/20), US-A-5,049,604, US-

A-4,769,457, US-A-4,356,307, US-A-4,619,956, US-A-5,182,390, GB-A-2,269,819, US-A-4,292,240, US-A-5,026,849, US-A-5,071,981, US-A-4,547,538, US-A-4,976,889, US-A-4,086,204, US-A-6,046,304, US-A-4,331,586, US-A-4,108,829, US-A-5,051,458, WO-A-94/12,544 (Derwent 94-177,274/22), DD-A-262,439 (Derwent 89-122,983/17), US-A-4,857,595, US-A-4,529,760, US-A-4,477,615 (CAS 136,504-96-6), US-A-4,340,534, WO-A-98/51,690, EP-A-1,803, the disclosures of which are incorporated by reference,

The sterically hindered amine compound according to the invention is preferably added in an amount from 0.01 to 5%, more preferably from 0.05 to 2% and most preferably from 0.1 to 1% by weight, based on the weight of the thermoplastic polymer.

For instance the thermoplastic polymer is a polyolefin, a polyvinylchloride or a polyamide. Examples are given below.

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyvinylcyclohexane, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

a) radical polymerisation (normally under high pressure and at elevated temperature).

b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either  $\pi$ - or  $\sigma$ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These

catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

5

10 2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

15

3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, ethylene/vinylcyclohexane copolymers, ethylene/cycloolefin copolymers (e.g. ethylene/norbornene like COC), ethylene/1-olefins copolymers, where the 1-olefin is generated in-situ; propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/vinylcyclohexene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

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4. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides

starting from m-xylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides  
5 with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; as well as polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems).

10 Particular preference is given to polyethylene preferably linear low density polyethylene (LLDPE).

For example the peak internal air temperature range in rotational molding processes is enlarged up to 10 to 50° C, preferably up to 15 to 40° C towards higher temperatures. The  
15 reference being without the addition of a sterically hindered amine.

Preferably the peak internal air temperature range is from 210 to 250° C, more preferably from 215 to 250° C and most preferably from 220 to 250° C.

20 The above temperature range corresponds to the preferred processing window, within which the mechanical properties and/or the color of the article are not adversely affected.

In a specific embodiment of the invention an additional stabilizer selected from the group consisting of a UV-absorber, a sterically hindered amine, different from that of formula (I) or  
25 (II), a phenolic antioxidant, a phosphite or phosphonite and a benzofuranone or indolinone is present.

Examples for the above mentioned additives are given below.

### 30 1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-( $\alpha$ -methylcyclohexyl)-4,6-dimethyl-

phenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  $\delta$ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)-disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-( $\alpha$ -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-( $\alpha,\alpha$ -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-

butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane,  
5 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-  
10 tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, di-  
15 dodecylmercaptoethyl-2,2-bis (3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.  
20

1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris-  
25 (3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.  
30

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

5 1.13. Esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

15 1.14. Esters of  $\beta$ -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; 3,9-bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane.

20 1.15. Esters of  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

30 1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Nau-  
5 gard<sup>®</sup>XL-1, supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- and dialkylated tert-butyl-diphenylamines, a mixture of mono- and dialkylated tert-butyl-diphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octyl-phenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene.  
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2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-( $\alpha,\alpha$ -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300;  $\left[ \text{R}-\text{CH}_2\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_2 \right]_2$ , where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'-( $\alpha,\alpha$ -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)-phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-( $\alpha,\alpha$ -dimethylbenzyl)-phenyl]benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylate, isooctyl  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylate, methyl  $\alpha$ -carbomethoxycinnamate, methyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxycinnamate, butyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxy-cinnamate, methyl  $\alpha$ -carbomethoxy-p-methoxycin-

namate, N-( $\beta$ -carbomethoxy- $\beta$ -cyanovinyl)-2-methylindoline, neopentyl tetra( $\alpha$ -cyano- $\beta$ , $\beta$ -di-phenylacrylate).

5 2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis[4-(1,1,3,3-tetramethyl-butyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenylundecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or with-  
10 out additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetra-carboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearlyoxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)-malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearlyoxy-2,2,6,6-tetramethylpiperidine, a condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No.  
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[136504-96-6]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro-  
5 [4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxo-spiro-[4,5]decane and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl)oxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine, a diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, a reaction product of maleic acid anhydride- $\alpha$ -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine, 2,4-bis[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidine-4-yl)-N-butylamino]-6-(2-hydroxyethyl)amino-1,3,5-triazine, 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 5-(2-ethylhexanoyl)oxymethyl-3,3,5-trimethyl-2-morpholinone, Sanduvor (Clariant; CAS  
10 Reg. No. 106917-31-1), 5-(2-ethylhexanoyl)oxymethyl-3,3,5-trimethyl-2-morpholinone, the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidine-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine), 1,3,5-tris(N-cyclohexyl-N-(2,2,6,6-tetramethylpiperazine-3-one-4-yl)amino)-s-triazine, 1,3,5-tris(N-cyclohexyl-N-(1,2,2,6,6-pentamethylpiperazine-3-one-4-yl)amino)-s-triazine.

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2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted  
25 oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-

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(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(4-[2-ethylhexyloxy]-2-hydroxyphenyl)-6-(4-methoxyphenyl)-1,3,5-triazine.

10 3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

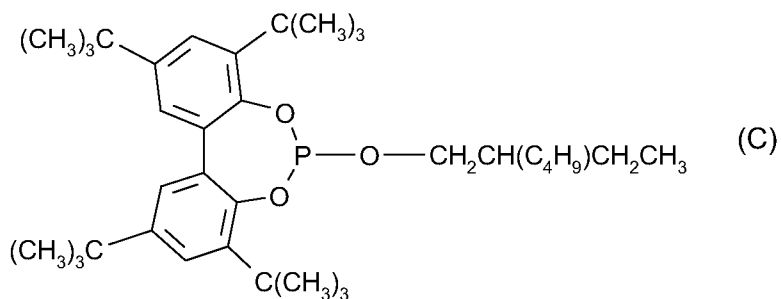
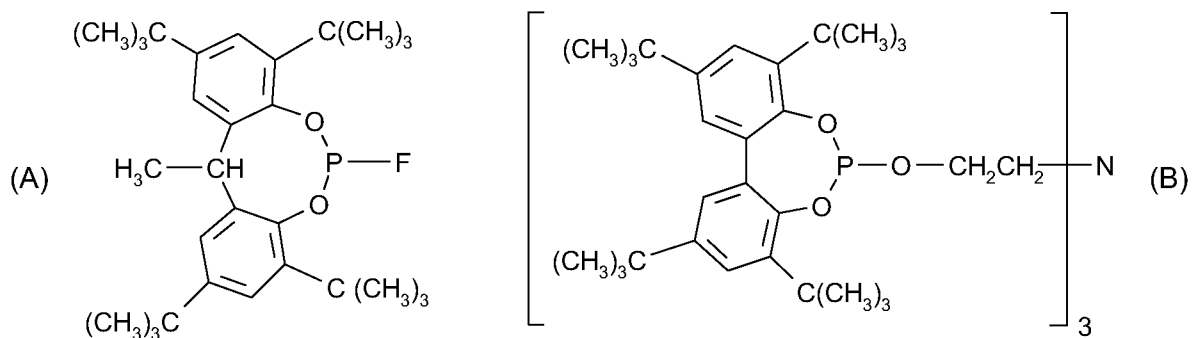
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4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,4-dicumylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)-pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite, tristea-  
 20 ryl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isoctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitri-  
 25 [triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

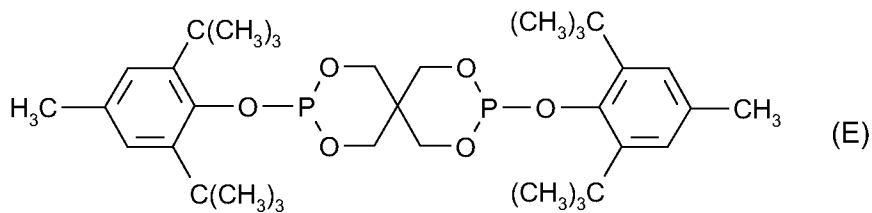
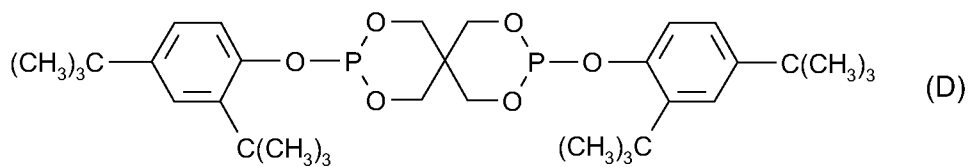
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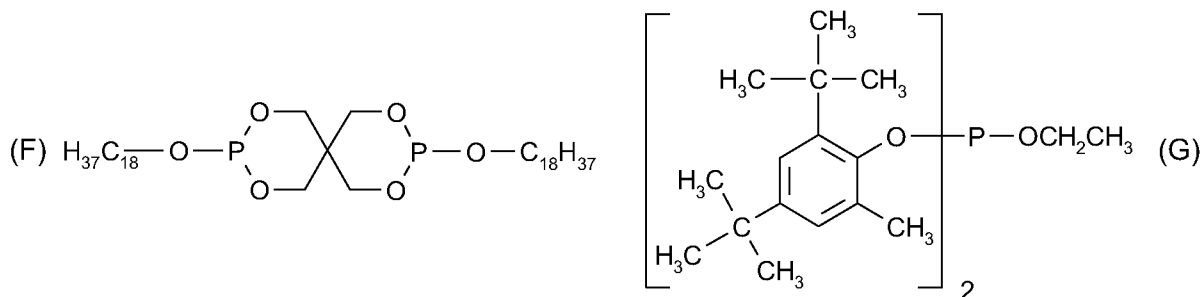
The following phosphites are especially preferred:

Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos<sup>®</sup> 168, Ciba Specialty Chemicals Inc.), tris(nonylphenyl) phosphite,



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5 5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

10 6. Nitrones, for example, N-benzyl-alpha-phenylnitronone, N-ethyl-alpha-methylnitronone, N-octyl-alpha-heptylnitronone, N-lauryl-alpha-undecylnitronone, N-tetradecyl-alpha-tridecylinnitronone, N-hexadecyl-alpha-pentadecylnitronone, N-octadecyl-alpha-heptadecylnitronone, N-hexadecyl-alpha-heptadecylnitronone, N-octadecyl-alpha-pentadecylnitronone, N-heptadecyl-alpha-heptadecylnitronone, N-octadecyl-alpha-hexadecylnitronone, nitronone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

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7. Thiosynergists, for example dilauryl thiodipropionate, dimistryl thiodipropionate, distearyl thiodipropionate or distearyl disulfide.

20 8. Peroxide scavengers, for example esters of  $\beta$ -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis( $\beta$ -dodecylmercapto)propionate.

25 9. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilizers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali

metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

5 11. Nucleating agents, for example inorganic substances, such as talcum, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds, such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate  
10 or sodium benzoate; polymeric compounds, such as ionic copolymers (ionomers). Especially preferred are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyl-dibenzylidene)sorbitol, and 1,3:2,4-di(benzylidene)sorbitol.

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass beads, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.  
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13. Other additives, for example plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.  
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14. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839, EP-A-0591102; EP-A-1291384 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butylbenzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2-acetyl-5-isooctylphenyl)-5-isooctylbenzofuran-2-one.  
25  
30

The above additives are in general applied in an amount between 0.01 and 2% by weight based on the weight of the thermoplastic polymer.

A further aspect of the invention is a method for enlarging the optimal peak temperature range in rotational molding processes of thermoplastic polymers by the use of a secondary sterically hindered amine compound as processing additive.

5 Accordingly disclosed is a method for enlarging the processing window towards higher peak internal air temperatures in rotational molding processes of thermoplastic polymers, which method comprises incorporating a secondary sterically hindered amine into a thermoplastic polymer and subjecting the polymer to a rotational molding process..

10 Yet another embodiment of the invention is a process for the production of thermoplastic hollow articles, which process comprises

mixing a thermoplastic polymer with a secondary sterically hindered amine and  
subjecting this mixture to a rotational molding process where the peak internal

temperature range is from about 215 to about 250C,

15 wherein when the thermoplastic polymer is polyethylene, the hindered amine is not a linear or cyclic condensate of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine.

Definitions and preferences given above apply also for the other aspect of the invention.

20

The following examples illustrate the invention.

Example 1: Preparation of Polyolefin Hollow Articles by a rotational molding process

100 parts medium density polyethylene, copolymerized with hexene (nominal melt index 3.3  
25 g/10 min., density 0.938 g/cm<sup>3</sup>) are dry blended with 0.050 parts of zinc stearate and a combination of additional stabilizers as given in Table 1. The mixtures are melt compounded into pellets at 190 °C in a Superior/MPM extruder using a 24:1 L/D screw with Maddock mixing head at 100 rpm. The compounded pellets are ground to a uniform particle size (150-  
30 500 µm) prior to the rotational molding process. This grinding step increases the surface area of the particles leading to faster heat absorption, and thus reducing overall energy consumption. The rotational molding process is performed in laboratory scale equipment FSP M20 "Clamshell". The ground resin is placed in an aluminum mold, which is rotated biaxially in a gas fired oven. Hot air is circulated by blowers in the chamber while the temperature is increased to 274°C. This temperature is maintained for a specific time, which

will give a certain peak internal air temperature (PIAT) as given in Table 2. Subsequently, the oven is opened and while still rotating, the mold is cooled with forced air circulation for 7.3 minutes, followed by water spray mist for 1.5 minutes, air cooling for 2 minutes, water spray 2.9 minutes and air cooling 4.4 minutes. Throughout the entire heating and cooling cycles, the speed of the major axis is maintained at 6 rpm with a 4 : 1 ratio of rotation. After the cooling cycles, the mold is opened and the hollow object removed.

The processing range is defined as peak internal air temperature range (PIAT) in which a part with high impact strength can be produced. The impact strength is measured with the Dynatup Falling weight method (25lb/20") according to ASTM D-3763 at -40° C.

10 Table 1

Additives	01	02	03	04 comparative	05 comparative	06
Zn-stearate	0.05	0.05	0.05	0.05	0.05	0.05
®Irgastab FS042	0.05	0.05	0.05	0.05	0.05	0.05
®Irgafos 168	0.12	0.12	0.12	0.12	0.12	0.12
®Tinuvin 622				0.12		
®Cyasorb UV 3346	0.2					
®Chimassorb 944		0.2				0.15
®Chimassorb 2020			0.2			
®Chimassorb 119				0.08		
®Hostavin N 30					0.2	
®Tinuvin 770						0.05

Table 2: Results

	01	02	03	04 comp.	05 comp.	06
Upper end of processing window PIAT [°C]	227	229	229	216	219	238
Total Impact Energy at -40 °C	44	45	47	46	50	43
Sterically hindered amine	Sec.	Sec.	Sec.	Tertiary	Tertiary	Sec.

The data clearly indicate that the useful process range can be significantly shifted towards higher temperatures by the use of secondary sterically hindered amine compounds without sacrificing the impact strength.

#### Example 2: Preparation of Polyolefin Hollow Articles by a rotational molding process

The procedure given in example 1 has been repeated with further additives as outlined in Table 3. The results are presented in Table 4

Table 3

<b>Additives</b>	<b>00</b>	<b>07</b>	<b>08</b>
Zn-stearate	0.05	0.05	0.05
®IRGANOX 3114	0.05	0.05	0.05
®IRGAFOS 168	0.1	0.1	0.1
®TINUVIN 622	None	0.2	None
®TINUVIN 783	None	None	0.2

Table 4

	<b>00</b>	<b>07</b>	<b>08</b>
Upper end of processing window PIAT [°C]	198	210	221
Total Impact Energy at -40 °C [J]	45	42	42
HALS	NONE	tertiary	secondary /tertiary

5 Whereas the processing temperature, as measured by the peak internal air temperature, (PIAT) should not exceed 198° C if no sterically hindered amine is present, 210° are acceptable when a tertiary sterically hindered amine is present. However, this temperature can further be extended up to 221° C, when, according to the invention, a secondary sterically hindered amine has been added.

10

®Irganox 3114 is a phenolic antioxidant from Ciba Specialty Chemicals,

®Irgastab FS042 is N,N-di(tallow alkyl)hydroxylamine from Ciba Specialty Chemicals,

®Irgafos 168 is a trisaryl phosphite from Ciba Specialty Chemicals,

®Tinuvin 622 is a tertiary sterically hindered amine from Ciba Specialty Chemicals,

15 ®Cyasorb UV 3346 is a secondary sterically hindered amine from Cytech Industries,

®Chimassorb 944 is a secondary sterically hindered amine from Ciba Specialty Chemicals,

®Chimassorb 2020 is a secondary sterically hindered amine from Ciba Specialty Chemicals,

®Chimassorb 119 is a tertiary sterically hindered amine from Ciba Specialty Chemicals,

®Hostavin N 30 is a tertiary sterically hindered amine from Clariant,

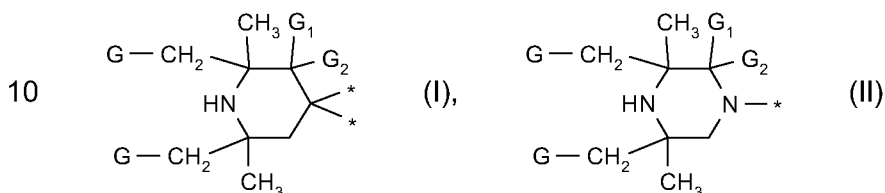
20 ®Tinuvin 770 is a secondary sterically hindered amine from Ciba Specialty Chemicals,

®Tinuvin 783 is a mixture of a secondary and tertiary sterically hindered amine from Ciba Specialty Chemicals.

Claims

1. Use of a secondary sterically hindered amine compound as processing additive for enlarging the processing window towards higher peak internal air temperatures in rotational  
5 molding processes of thermoplastic polymers.

2. Use according to claim 1 wherein the sterically hindered amine is a compound containing at least one group of the formula (I) or (II)



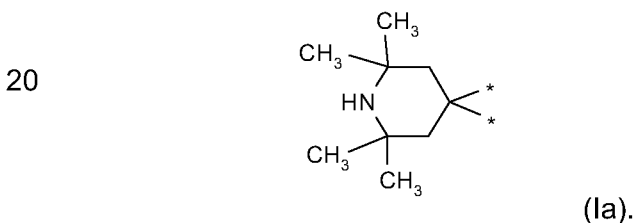
in which

\* indicates a bond

G is hydrogen or methyl, and

15 G<sub>1</sub> and G<sub>2</sub>, independently of one another, are hydrogen, methyl or together are a substituent =O.

3. Use according to claim 2 wherein the sterically hindered amine is a compound containing at least one group of formula (Ia).



4. Use according to claim 1 wherein the sterically hindered amine compound is added in an amount from 0.01 to 5% by weight, based on the weight of the thermoplastic polymer.

25 5. Use according to claim 1 wherein the thermoplastic polymer is a polyolefin, polyvinylchloride or polyamide.

6. Use according to claim 1 wherein the thermoplastic polymer is polyethylene.

7. Use according to claim 1 wherein the peak internal air temperature range in rotational molding processes is enlarged up to 10 to 50° C towards higher temperatures.

5

8. Use according to claim 1 wherein the peak internal air temperature range is from 215 to 250° C

9. Use according to claim 1 wherein in the rotational molding process an additional stabilizer selected from the group consisting of a UV-absorber, a sterically hindered amine, different from that of formula (I) or (II), a phenolic antioxidant, a phosphite or phosphonite and a benzofuranone or indolinone is present.

10. A method for enlarging the processing window towards higher peak internal air temperatures in rotational molding processes of thermoplastic polymers, which method comprises incorporating a secondary sterically hindered amine into a thermoplastic polymer and subjecting the polymer to a rotational molding process.

11. A method of using a secondary sterically hindered amine compound as processing additive for enlarging the processing window towards higher peak internal air temperatures in rotational molding processes of thermoplastic polymers.

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**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2007/050678

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C08K5/3435 C08K5/3462 B29C41/04 B29C41/00

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)  
 C08K B29C

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, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 444 733 B1 (STADLER URS LEO) 3 September 2002 (2002-09-03) column 2, lines 23-29; claims 1,8; compounds H5,H8,H10,H12,H15,H16 column 17, lines 30-37 column 25, lines 53-67; example 2; tables 1,2 column 27, lines 50-55	1-11
A	EP 1 600 478 A (TOTAL PETROCHEMICALS RESEARCH FELUY) 30 November 2005 (2005-11-30) paragraphs [0006], [0051] - [0054], [0058], [0064], [0065]; claims 1,9 example 3; table II figure 1	1-11

Further documents are listed in the continuation of Box C.       See patent family annex.

\* Special categories of cited documents :

*A* document defining the general state of the art which is not considered to be of particular relevance	*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
*E* earlier document but published on or after the international filing date	*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
*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)	*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.
*O* document referring to an oral disclosure, use, exhibition or other means	*Z* document member of the same patent family
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  19 March 2007	Date of mailing of the international search report  26/03/2007
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Dury, Olivier
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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/050678

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	URS STADLER ET AL: "Stabilizer combinations for improving cycle times in the rotational molding process" RESEARCH DISCLOSURE, MASON PUBLICATIONS, HAMPSHIRE, GB, vol. 432, no. 108, April 2000 (2000-04), XP007125963 ISSN: 0374-4353 page 1, paragraphs 1,2 pages 6-12 -----	1-11
A	CRAMEZ M C ET AL: "Optimisation of rotational moulding of polyethylene by predicting antioxidant consumption" 2002, POLYMER DEGRADATION AND STABILITY, BARKING, GB, PAGE(S) 321-327 , XP004329673 ISSN: 0141-3910 the whole document -----	1-11
X	BOTKIN ET AL.: "An additive approach to cycle time reduction in rotational molding" 2004 ROTATIONAL MOLDING BY DESIGN CONFERENCE, SOCIETY OF PLASTICS ENGINEERS, 2004, XP009068875 the whole document -----	1-11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/050678

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EP 1600478	A	CA 2567568 A1	15-12-2005
		WO 2005118711 A1	15-12-2005