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(54) Title: FILM COMPOSITIONS WITH PERMANENT ANTI-FOG, ANTI-MIST AND ANTI-CLOUD PROPERTIES

(57) Abstract: The instant invention discloses a film composition with anti-fog, anti-mist and anti-cloud properties comprising (a) a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof, (b) an effective amount of at least one linear ethoxylated alcohol; and (c) an effective amount of at least one fluorine-containing surfactant. The films are useful as a greenhouse film for agricultural applications.

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Film compositions with permanent anti-fog, anti-mist and anti-cloud properties

This invention relates to film compositions with anti-fog, anti-mist and anti-cloud properties comprising (a) a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof, (b) an effective amount of at least one linear ethoxylated alcohol; and (c) an effective amount of at least one fluorine-containing surfactant, especially when employed as a greenhouse film for agricultural applications.

Agricultural films which are largely used in greenhouse culture or tunnel culture chiefly include soft ethylene resin films which are about 30 to 200 microns thick and which comprise, as a base resin, polyvinyl chloride (hereinafter abbreviated as PVC), branched low-density polyethylene (hereinafter abbreviated as LDPE), ethylene-vinyl acetate copolymers (hereinafter abbreviated as EVA), linear low-density polyethylene (hereinafter abbreviated as LLDPE), etc. Of the various properties required for the agricultural films, particularly important are weather resistance, anti-fogging properties, heat-retaining properties, and transparency. To cope with the recent situation confronting agriculture such as an increased cost and a shortage of labour, development of films having an extended duration of life before replacement is desired.

The atmosphere within greenhouses or tunnels surrounded by an agricultural film is saturated with water vapour which evaporates from the soil or plants, and the water vapour dropwise condenses on the inner surface of a cold film to cause fogging. Water droplets on the film not only greatly reduce the incident sunlight due to irregular reflection but the droplets fall on the plants resulting in frequent occurrence of diseases.

To avoid fogging, anti-fog treatments on the inner surface of an agricultural film converting the film into an anti-stick water film and preventing adhesion of water droplets have been used thereby assuring transmission of sunlight into the greenhouse or tunnel, raising the soil temperature and air temperature within the greenhouse or tunnel, accelerating photosynthesis of the plants, accelerating healthy growth of the plants, and controlling the occurrence of plant diseases.

Currently employed anti-fog treatments include incorporation of an anti-fogging agent (anti-fog additive) into a film-forming ethylene resin compound and coating of an anti-fogging agent on a film.

However, an anti-fogging film obtained by coating a soft plastic film with an anti-fogging agent has not yet been employed practically as an agricultural film for the following reasons. Because of their low surface energy, soft plastic films for agricultural use generally have poor wettability and adhesion when coated with surface active agents or hydrophilic high polymeric substances which have been used as anti-fogging agents. This tendency is particularly conspicuous with soft ethylene resin films of low polarity, e.g., LDPE, EVA, and LLDPE films. Therefore, where an anti-fogging agent is spray coated with a power atomiser onto a soft ethylene resin film, the anti-fogging agent needs to be used in a large quantity and this increases cost, and a large amount of time is required for spray coating operation. Further, spray coating cannot be effected uniformly with insufficient anti-fogging effects arising. Where an anti-fogging agent is applied using a coater, etc., a large quantity of a coating is consumed, and the coating speed cannot be increased, resulting in an increase of cost. In either case, the coated anti-fogging agent is washed away together with running water droplets due to poor adhesion resulting in a very short life for the anti-fogging properties. Furthermore, the coated film undergoes blocking due to the stickiness of the anti-fogging agent. As a result, it has been impossible to retain anti-fogging effects in a stable manner for a long duration of at least 1 year, more desirably, several years. Most of the state-of-the-art agricultural films exhibit anti-fogging properties for a period of only about 1 month.

Anti-fogging agents commonly incorporated into the films include non-ionic, anionic and cationic surface active agents.

Other methods for providing anti-fogging properties to agricultural films, in addition to the coating method and incorporation method, include chemical modification of the ethylene base resin or the ethylene resin film surface by introducing a polar group, such as a hydrophilic group. This technique, however, entails high cost at the present time and is difficult to apply to agricultural films.

Suitable inorganic hydrophilic colloidal substances include colloidal silica, colloidal alumina, colloidal $\text{Fe}(\text{OH})_2$, colloidal $\text{Sn}(\text{OH})_4$, colloidal TiO_2 , colloidal BaSO_4 , and colloidal lithium

silicate, with colloidal silica and colloidal alumina most generally used. Suitable hydrophilic organic compounds include various non-ionic, anionic or cationic surface active agents; graft copolymers mainly comprising a hydroxyl-containing vinyl monomer unit and from 0.1 to 40% by weight of a carboxyl-containing vinyl monomer unit or a partial or complete neutralisation product thereof; and sulfo-containing polyester resins.

Coating type anti-fogging agents used with this new film type have markedly improved wettability and adhesion and coated agricultural films exhibiting anti-fogging properties for a duration of about a half year to about 1 year are provided.

Under these circumstances, none of the state-of-the-art polyolefin-based agricultural films satisfies the requirements of long lasting anti-fogging and anti-clouding properties.

In the field of packaging, whereby polymer films are used for covering or enclosing items of sale, and where film clarity or good optical properties are desired, there is a recognised need for polymer films which resist fogging when exposed to conditions of temperature and humidity which can produce condensation on the film. This condensation is especially troublesome when the interior of the package contains enough moisture to produce fogging of the interior surface of the film.

EP-A-0 933 400 discloses a synthetic resin film for agriculture which contains incorporated therein: (a) at least one compound selected from the group consisting of (1) an ester of sorbitan with acid wax mainly derived from montan wax, i.e., higher fatty acids mainly containing 24 to 34 carbon atoms (hereinafter referred to as "montanic acid wax", (2) an ester of glycerin with montanic acid wax, (3) an alkylene oxide adduct to the ester of sorbitan with montanic acid wax, (4) an alkylene oxide adduct to the ester of glycerin with montanic acid wax, and (5) an ester of polyoxyalkylene and montanic acid wax; and (b) a fluorine-containing surfactant.

EP-A-1 152 027 discloses a fog-resistant polyolefin film composition comprising (a) a polyolefin film; and (b) a compound of the formula $\text{CH}_3\text{CH}_2(\text{CH}_2\text{CH}_2)_a \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_b\text{OH}$, wherein a is 9 to 25 and b is 1 to 10.

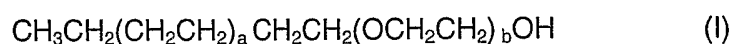
These known additives do not in every respect satisfy the high requirements to be met by an additive mixture, especially as regards to polyolefin films with anti-fog, anti-mist and anti-cloud properties.

It has now been found that an additive mixture comprising an effective amount of at least one linear ethoxylated alcohol, and an effective amount of at least one fluorine-containing surfactant is especially suitable for the preparation of a film containing a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof with anti-fog, anti-mist and anti-cloud properties.

The present invention accordingly relates to a film composition with anti-fog, anti-mist and anti-cloud properties comprising

- a) a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof,
- b) an effective amount of at least one linear ethoxylated alcohol; and
- c) an effective amount of at least one fluorine-containing surfactant.

Of interest are compositions wherein component (b) is a compound of formula I



wherein a is 9 to 25 and b is 1 to 10.

In the compounds of the formula I, the term "a" is for example 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24 or 25. The term "b" is for example 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10.

Likewise of interest are compositions wherein component (b) is a compound of formula I, wherein a is 12 to 18 and b is 1 to 3.

The compounds of the formula I are known in the literature and most of them commercially available as Brij (RTM) [from Uniquema] or Atmer (RTM) [from Ciba Specialty Chemicals Inc.]. An example of these Atmer (RTM) products is Atmer 502 (RTM).

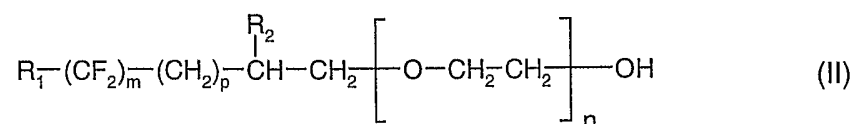
Of interest are compositions wherein component (c) is an anionic fluorine-containing surfactant, a cationic fluorine-containing surfactant, an amphoteric fluorine-containing surfactant, a

nonionic fluorine-containing surfactant as disclosed in EP-A-0 933 400, page 4, line 45 to page 5, line 54 which are incorporated by reference.

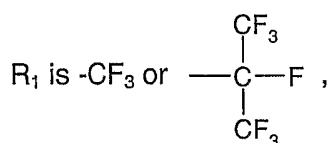
Of interest are also compositions wherein component (c) is an ethoxylated fluorine-containing alcohol or a fluorine-containing acrylate or methacrylate copolymer.

Preferred fluorine-containing surfactants are those disclosed for example in EP-A-0 933 400, page 4, line 43 to page 6, line 9.

Of special interest are compositions wherein component (c) is a compound of formula II



wherein



R_2 is hydrogen or hydroxyl,

m is 3, 4, 5, 6, 7 or 8,

n is 1 to 10, and

p is 0, 1 or 2.

A lot of the fluorine-containing surfactants are commercially available like for example Unidyne DS 403 (RTM) [C.A. Reg. No. 148919-89-5; Daikin, Japan]; Unidyne DS 451 (RTM) [C.A. Reg. No. 110069-68-6; Daikin, Japan]; Fulorad FC-95 (RTM) [Sumitomo 3M K.K.]; Fulorad FC-98 (RTM) [Sumitomo 3M K.K.]; Fulorad FC-135 (RTM) [Sumitomo 3M K.K.]; Fulorad FC-170C (RTM) [Sumitomo 3M K.K.]; Zonyl (RTM) surfactants [DuPont] or Fluorolink (RTM) [Solvay Solexis].

Examples of component (a) according to the invention are:

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 π - or σ -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).

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).

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.

4. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine; as well as their copolymers with olefins mentioned in 1) above.

Of special interest is a composition wherein component (a) is polyethylene, polyvinylalcohol, polyvinyl acetate or ethylene/vinyl acetate copolymer or mixtures thereof.

It is also contemplated within the purview of the present invention to employ ethylene polymers which contain other comonomers, such as acrylic acid, methacrylic acid, alkyl acrylates, vinyl esters, and carbon monoxide. These type of monomers, which contain oxygen atoms, are employed using a free-radical initiator, but are not very well suitable when co-ordination catalysts are employed. The co-ordination catalysts, which generally contain metal-carbon bonds, are usually poisoned or deactivated by compounds containing oxygen-carbon bonds or hydrogen-oxygen bonds when employed in quantities such as are involved in copolymeri-

sation thereof. On the other hand, copolymerisation of ethylene with the higher hydrocarbon olefins is best done using a co-ordination type catalyst.

In the present invention, it is preferred that the ethylene polymer be of the LLDPE variety, especially those which have a melt flow value in the range of about 0.1-10 and enough comonomer units to give a density in the range of about 0.9 to about 0.935 g/cc, such comonomer units being an aliphatic hydrocarbon olefin of from 4 to 8 carbon atoms, including isomers in that range. These LLDPE polymers are recognised in the art as having excellent strength, resistance to tear propagation as shown by Dart Impact and Elmendorf Tear, and exhibit good resistance to tearing or puncturing when stressed against articles having protuberances.

Preferably, component (b) is added to component (a) in an amount of from 0.01 to 4 %, for example from 0.1 to 4 %, preferably from 0.5 to 3 %, based on the weight of component (a).

Advantageously, component (c) is added to component (a) in an amount of from 0.01 to 4 %, for example from 0.1 to 4 %, preferably from 0.5 to 3 %, based on the weight of component (a).

The present compositions may comprise other known anti-fog additives, such as sorbitan esters, polyoxyalkylene fatty acid esters, alkoxyated phenols, mixed mono-, di-, or triglycerides, fatty acid esters of polyhydroxy alcohols, other polyalkoxyated compounds and the like.

WO-A-01/57124, incorporated herein by reference, discloses plastic films for food protection that comprise ultraviolet light absorbers. The present films with fog, mist and cloud resistance may also contain further appropriate additives such as ultraviolet light absorbers, hindered amine light stabilizers, antioxidants, processing aids and other additives as disclosed in WO-A-01/57124.

For example, the compositions of the invention may optionally also contain from 0.01 to 10%, preferably from 0.025 to 5%, and especially from 0.1 to 3% by weight of various conventional stabilizer coadditives, such as the materials listed below, or mixtures thereof.

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-(α -methylcyclohexyl)-4,6-dimethylphenol, 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 α -tocopherol, β -tocopherol, γ -tocopherol, δ -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)-isulfide.

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-(α -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-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -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-methylphenyl)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, 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-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-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.

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(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.

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.

1.13. Esters of β -(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.

1.14. Esters of β -(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.

1.15. Esters of β -(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.

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 β -(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-gard[®]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-butyrylamino-phenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, 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/iso-hexyldiphenylamines, 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-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethyl-

piperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

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-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 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(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonyl)ethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-yl]phenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl)ethyl)-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-yl]phenyl, 2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -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-butylphenyl 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-hydroxybenzo-

ate, 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 α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)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 without 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)nitrioltriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-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)pyr-

rolidine-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-stearoyloxy-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. [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[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[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- α -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

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 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-(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-hy-

droxy-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.

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.

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-di-cumylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyl oxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentaerythritol diphosphite, tristearyl 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''-nitrilo[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.

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.

6. Nitrones, for example, N-benzyl-alpha-phenylnitron, N-ethyl-alpha-methylnitron, N-octyl-alpha-heptylnitron, N-lauryl-alpha-undecylnitron, N-tetradecyl-alpha-tridecylnitron, 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.

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

8. Peroxide scavengers, for example esters of β -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(β -dodecylmercapto)propionate.

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

10. Basic co-stabilisers, 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.

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 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 bulbs, 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.

13. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

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 or EP-A-0591102 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.

The mixing of the anti-fog agents into component (a) is done by mixing it into molten component (a) by commonly used techniques such as roll-milling, mixing in a Banbury type mixer, or mixing in an extruder barrel and the like. The heat history (time at which held at elevated temperature) can be shortened by mixing the anti-fog agent with unheated component (a) particles so as to achieve substantially even distribution of the agent in the mass of component (a), thereby reducing the amount of time needed for intensive mixing at molten temperature.

Conveniently, the anti-fog agent can also be added substantially simultaneously or sequentially with any other additives (colorants, tackifiers, slip agents, block agents, and the like) which may be desired in certain instances. The anti-fog agents may also be preblended with other additives and the blend then added to the polymer. It is contemplated that in some instances these anti-fog agents should have the additional benefit of aiding the other additives to become more easily or evenly dispersed or dissolved in component (a). For easier batch-to-batch control of quality, it may be preferred to employ concentrated masterbatches of component (a)/agent blends which are subsequently blended, as portions, to additional quantities of component (a) to achieve the final desired formulation. The masterbatch, or the neat additives, may be injected into freshly prepared component (a) while component (a) is still molten and after it leaves the polymerisation vessel or train, and blended therewith before the molten component (a) is chilled to a solid or taken to further processing.

The making of films is well-known and includes the techniques of casting films as thin sheets through narrow slit dies, and the blown-film technique wherein an extruded tube of molten polymer is inflated to the desired "bubble" diameter and/or film thickness before being cooled and collected or further processed. These present formulations are also suitable in coextrusion fabrication of films wherein two or more films comprise a multi-layer structure. The anti-fog agents of the present invention can exude through an adjacent film layer which does not contain the anti-fog agent, thereby rendering the adjacent layer resistant to fogging.

The films of this invention with anti-fog, anti-mist and anti-cloud properties are preferably used for greenhouse films.

The present invention relates also to a process for the preparation of a film containing a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof with anti-fog, anti-mist and anti-cloud properties which comprises incorporating in or applying to said film an effective amount of at least one linear ethoxylated alcohol and an effective amount of at least one fluorine-containing surfactant.

A preferred embodiment of the present invention is likewise the use of a mixture of components (b) and (c) for the preparation of a film containing a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof with anti-fog, anti-mist and anti-cloud properties.

The preferred components (b) and (c) for the use for the preparation and the process for the preparation of a film containing a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof with anti-fog, anti-mist and anti-cloud properties are the same as those described for the compositions comprising components (a), (b) and (c).

The following examples illustrate the invention further. Parts or percentages relate to weight.

Example 1:

In order to evaluate the anti-fogging properties of the claimed compounds in LDPE films, they are incorporated in the polymer according the following procedure: Appropriate amounts of each compound are weighed and added to LDPE pellets (Riblene FF 29, supplied by Poli-

meri Europa, Milan, Italy), characterized by a density of 0.921 g/cm³ and a melt flow index of 0.6 at 190°C, 2.16 kg, in order to obtain formulations containing 2% by weight of linear ethoxylated alcohol [98-0218 as described in EP-A-1 152 027, page 11, Table 1 (component (b) according to the invention)] and 0.15% respectively 0.3% of a fluorine-containing surfactant (component (c) according to the invention). The granules so obtained are blown in a semi-industrial Dolci blow-extruder at a maximum temperature of 210°C to give films of 150µm thickness.

Test Method: The initial Anti-Fog rating of the films is evaluated according to the hot fog test: A 250 ml glass beaker, containing about 50 ml of water and covered with the film to be evaluated, is immersed to about ½ of its height in a water bath at 60°C. Films are observed and a conventional notation ranging from A to E is assigned. The accelerated Anti-Fog rating as well as the Anti-Mist rating of the films are evaluated as described in EP-A-0 933 400, page 7, lines 9 to 24. It is seen that blends of components (b) and (c) according to the invention provide superior anti-fog and anti-mist results. The results are summarized in Table 1.

Rating Hot Fog Test:

Description	Performance	Rating	Comments
An opaque layer of small fog droplets	none	A	Zero visibility, poor light transmission
An opaque layer of large droplets	none	B	Zero visibility, poor light transmission
A complete layer of large dripping transparent droplets	poor	C	Poor visibility, lens effect
Radomly scattered large transparent droplets	fair	D	Discontinuous film of water
Few small or large transparent droplets	good	D/E	Discontinuous film of water, mostly transparent
A transparent film displaying no visible water	excellent	E	Completely transparent

Rating Anti-Mist Test:

Description	Performance	Rating
Generation of fog was seriously observed	none	A
Generation of fog was clearly observed	poor	B
Generation of fog was slightly observed	good	C
Generation of fog was scarcely observed	excellent	D

Table 1:

Example	Additive	90 days of accelerated Anti-Fog Rating at 60°C	90 days of accelerated Anti-Mist Rating at 60°C
1a ^{a)}	none	B	A
1b ^{a)}	2.00 % 98-0218 ^{c)}	D/E	B
1c ^{a)}	0.20 % Unidyne DS-403 ^{d)}	B	A
1d ^{b)}	2.00 % 98-0218 ^{c)} 0.15 % Unidyne DS-403 ^{d)}	E	C
1e ^{b)}	2.00 % 98-0218 ^{c)} 0.30 % Unidyne DS-403 ^{d)}	E	D
1f ^{b)}	2.00 % 98-0218 ^{c)} 0.15 % Zonyl FSO-100 ^{e)}	E	C
1g ^{b)}	2.00 % 98-0218 ^{c)} 0.30 % Zonyl FSO-100 ^{e)}	E	D

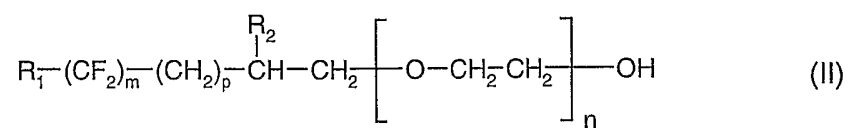
a) Comparative Example.

b) Example according to the invention.

c) 98-0218 is a linear ethoxylated alcohol as described in EP-A-1 152 027, page 11, Table 1 [component (b) according to the invention].

d) Unidyne DS-403 (RTM) (Daikin, Japan) is a fluorine containing surfactant of the formula II

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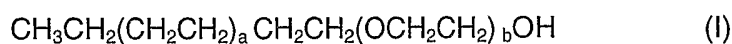
wherein R_1 is $\begin{array}{c} CF_3 \\ | \\ -C-F \\ | \\ CF_3 \end{array}$, R_2 is hydroxyl, m is 7, n is 1 to 10, and p is 2 [component (c)

according to the invention)].

- e) Zonyl FSO-100 (RTM) (DuPont) is a fluorine containing surfactant of the formula II, wherein R_1 is CF_3 , R_2 is hydrogen, m is 6 to 8, n is 1 to 10, and p is 0 (zero) [component (c) according to the invention)].

What is claimed is:

1. A film composition with anti-fog, anti-mist and anti-cloud properties comprising
 - a) a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof,
 - b) an effective amount of at least one linear ethoxylated alcohol; and
 - c) an effective amount of at least one fluorine-containing surfactant.
2. A composition according to claim 1, wherein component (b) is a compound of formula I



wherein a is 9 to 25 and b is 1 to 10.

3. A composition according to claim 2, wherein a is 12 to 18 and b is 1 to 3.
4. A composition according to claim 1, wherein component (c) is an ethoxylated fluorine-containing alcohol or a fluorine-containing acrylate or methacrylate copolymer.
5. A composition according to claim 1, wherein component (a) is polyethylene, polyvinylalcohol, polyvinyl acetate or ethylene/vinyl acetate copolymer or mixtures thereof.
6. A composition according to claim 1, wherein the film is a greenhouse film.
7. A process for the preparation of a film containing a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof with anti-fog, anti-mist and anti-cloud properties which comprises incorporating in or applying to said film an effective amount of at least one linear ethoxylated alcohol and an effective amount of at least one fluorine-containing surfactant.
8. The use of a mixture of components (b) and (c) according to claim 1 for the preparation of a film containing a polyolefin, a polyvinylalcohol, a polyvinylester or mixtures thereof with anti-fog, anti-mist and anti-cloud properties.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/09543

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08K5/00 C08J5/18 C08L23/02 C08L29/04 C08L31/04
 //(C08K5/00, 5:06, 5:06)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08J C08K C08L

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

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

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; TASHIRO, TAKESHI ET AL: "Antifogging, antistatic, transparent polyolefin films for agriculture" retrieved from STN Database accession no. 132:3897 XP002230068 abstract	1,4-8
Y	& JP 11 322965 A (MITSUBISHI KAGAKU MKV K. K., JAPAN) 26 November 1999 (1999-11-26)	1-8
Y	EP 1 152 027 A (CIBA SC HOLDING AG) 7 November 2001 (2001-11-07) cited in the application claims 1-4	1-8
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance	*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	* & * 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 11 December 2003	Date of mailing of the international search report 29/12/2003
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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 Rose, E
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/09543

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YAMAMOTO, SANEHIRO: "Agricultural film with long-lasting antifogging effect and good dustproof property and toughness" retrieved from STN Database accession no. 131:338015 XP002230069 abstract & JP 11 310648 A (MITSUI CHEMICALS INC., JAPAN) 9 November 1999 (1999-11-09)</p>	1,4-8
A	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; KATO, NOBUKATSU ET AL: "Vinyl chloride resin film for agriculture" retrieved from STN Database accession no. 132:109109 XP002230070 abstract & JP 2000 026684 A (MITSUI CHEMICALS INC., JAPAN) 25 January 2000 (2000-01-25)</p>	1-8
A	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SAKATANI, YASUKAZU ET AL: "Transparent thermoplastic polymer agricultural films with good thermally insulating property" retrieved from STN Database accession no. 131:215485 XP002230071 abstract & JP 11 255909 A (SUMIKA PLASTIC K. K., JAPAN) 21 September 1999 (1999-09-21)</p>	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/09543

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JP 11310648	A	09-11-1999	NONE	
JP 2000026684	A	25-01-2000	NONE	
JP 11255909	A	21-09-1999	CN 1226573 A , B	25-08-1999