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(54) Title: UV ABSORBING COMPOSITION

(57) **Abrégé/Abstract:**

A UV absorbing polymeric composition has an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4, and contains an organic resin and zinc oxide particles. The composition is particularly suitable for use in producing an end-use product, preferably in the form of a polymeric film, exhibiting UV absorbing properties and improved transparency. In one embodiment, the composition may be produced from a masterbatch composition containing an organic resin, an organic dispersing medium and zinc oxide particles. The masterbatch is preferably prepared by mixing a pre-dispersion of the zinc oxide particles in the organic dispersing medium, with the organic resin.



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(54) Title: UV ABSORBING COMPOSITION

(57) Abstract: A UV absorbing polymeric composition has an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4, and contains an organic resin and zinc oxide particles. The composition is particularly suitable for use in producing an end-use product, preferably in the form of a polymeric film, exhibiting UV absorbing properties and improved transparency. In one embodiment, the composition may be produced from a masterbatch composition containing an organic resin, an organic dispersing medium and zinc oxide particles. The masterbatch is preferably prepared by mixing a pre-dispersion of the zinc oxide particles in the organic dispersing medium, with the organic resin.



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UV Absorbing Composition

Field of Invention

- 5 The present invention relates to a UV absorbing polymeric composition, and in particular to one formed using a masterbatch composition comprising an organic resin, an organic dispersing medium and zinc oxide particles.

Background

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Plastics masterbatch compositions are well known. They normally contain an organic resin and pigment suitable for use as pigment concentrate for dilution or "let down" into various non-pigmented plastics or polymeric materials. The masterbatch or pigment concentrate is designed to be diluted into bulk plastics to add opacity and, if
15 necessary, colour or other functionality to the final composition.

Masterbatch techniques are frequently used as a method to incorporate additives such as antiblocks, biocides, heat stabilisers, light stabilisers, pigment and UV absorbers in to plastics. Such additives are necessary to overcome physical
20 limitations of plastic materials such as light induced breakdown.

As an alternative to the use of a masterbatch, liquid carrier systems may be used to introduce the aforementioned additives into polymers, e.g. during injection and blow moulding. The additive is pre-dispersed into a liquid carrier usually in the presence of
25 a compatibilising agent, prior to incorporation into the polymeric resin.

Many applications require plastics to be used in exposed conditions, such as outdoors. In these environments, plastics without additive stabilisers will degrade and discolour due to a mixture of heat instability, light instability, weathering (e.g. water ingress) and other chemical attack (e.g. acid rain). Such degradation will have a deleterious effect on both aesthetic and function of the polymer employed. Light stabilisers are a class of additive that are frequently employed to retard the rate of visible and especially UV light induced degradation in non-opaque (semi/transparent or clear) plastics where other protective materials (e.g. pigmentary titanium dioxide)
30 cannot be employed. In applications where a thin cross section of plastic is used,
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such as films, light stability is often difficult to achieve, as the levels of light stabiliser required often have negative effects on the physical properties of the films either during manufacture or in use. Moreover, the nature of organic light stabiliser compounds is to be chemically stable which can be a negative property when toxicity or biodegradability is considered, especially for biodegradable polymers.

Metal oxides such as zinc oxide have been employed as attenuators of ultraviolet light in applications such as plastics films and resins, but existing materials either have insufficient UV absorption and/or lack of transparency and/or do not maintain these properties over time.

Consequently, there is a need for a polymeric material that exhibits and maintains both effective UV absorption and transparency, is low or non-toxic in use and/or sufficiently biodegradable.

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Summary of the Invention

We have now surprisingly discovered an improved polymeric and masterbatch composition, which overcomes or significantly reduces at least one of the aforementioned problems.

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Accordingly, the present invention provides a UV absorbing polymeric composition having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4 which comprises an organic resin and zinc oxide particles.

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The invention also provides a masterbatch composition comprising an organic resin, an organic dispersing medium and zinc oxide particles.

The invention further provides a method of producing a masterbatch composition which comprises mixing a dispersion of zinc oxide particles in an organic dispersing medium, with an organic resin.

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The invention yet further provides a method of producing a UV absorbing polymeric composition having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4 which comprises an organic resin and zinc oxide particles, comprising the steps of providing

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(i) a masterbatch composition comprising an organic resin, an organic dispersing medium and zinc oxide particles, and mixing the masterbatch composition with a substrate organic resin, or (ii) a dispersion of zinc oxide particles in an organic dispersing medium, and incorporating the dispersion directly into a substrate organic resin.

The invention still further provides the use of a UV absorbing polymeric composition having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4, which comprises an organic resin and zinc oxide particles, as an antimicrobial agent.

In one embodiment of the present invention, the UV absorbing polymeric composition may be produced using a masterbatch composition as defined herein.

The organic resin which is present in the masterbatch composition according to the present invention can be any organic resin which is suitable for let-down into plastics or polymeric materials. It may be a thermoplastic resin or a thermosetting resin as will be familiar to the person skilled in the art.

Examples of suitable thermoplastic resins include poly(vinyl chloride) and co-polymers thereof, polyamides and co-polymers thereof, polyolefins and co-polymers thereof, polystyrenes and co-polymers thereof, poly(vinylidene fluoride) and co-polymers thereof, acrylonitrilebutadiene-styrene, polyoxymethylene and acetal derivatives, polybutylene terephthalate and glycolised derivatives, polyethylene terephthalate and glycolised derivatives, polyacrylamide nylon (preferably nylon 11 or 12), polyacrylonitrile and co-polymers thereof, polycarbonate and co-polymers thereof. Polyethylene and polypropylene, which may be modified by grafting of carboxylic acid or anhydride groups onto the polymer backbone, are suitable polyolefins. Low density polyethylene may be used. A poly(vinyl chloride) may be plasticised, and preferably is a homopolymer of vinyl chloride.

Examples of thermosetting resins which may be used are epoxy resins, polyester resins, hybrid epoxy-polyester resins, urethane resins and acrylic resins.

The organic resin is preferably a resin selected or polymerized from the following polymers or monomers that are frequently used for polymeric films either with or

without biodegradable qualities; alkyl vinyl alcohols, alkyl vinyl acetates, carbohydrates, casein, collagen, cellulose, cellulose acetate, glycerol, lignin, low density polyethylene, linear low density polyethylene, nylon, polyalkylene esters, polyamides, polyanhydrides, polybutylene adipate/terephthalate, polybutylene succinate, polybutylene succinate/adipate, polycaprolactone, polyesters, polyester carbonate, polyethylene succinate, polyethylene terephthalate, polyglycerol, polyhydroxyalkanoates, polyhydroxy butyrate, polypropylene, polylactates, polysaccharides, polytetramethylene adipate/terephthalate, polyvinyl alcohol polyvinylidene chloride, proteins, soy protein, triglycerides and variants or co-polymers thereof.

The organic resin preferably has a melting point greater than 40°C, more preferably in the range from 50 to 500°C, particularly 75 to 400°C, and especially 90 to 300°C. The organic resin preferably has a glass transition point (T_g) in the range from -200 to 500°C, more preferably -150 to 400°C, and particularly -125 to 300°C.

The concentration of organic resin is preferably in the range from 20 to 95%, more preferably 30 to 90%, particularly 40 to 80%, and especially 50 to 70% by weight, based upon the total weight of the masterbatch composition.

The particulate zinc oxide according to the present invention comprises primary particles suitably having a mean particle size (measured as described herein) of less than 120 nm, preferably less than 90 nm, more preferably in the range from 35 to 70 nm, particularly 40 to 60 nm, and especially 45 to 55 nm. The size distribution of the primary zinc oxide particles can also have a significant effect on the final properties of the masterbatch or UV absorbing polymeric composition. In a preferred embodiment of the invention suitably at least 50%, preferably at least 60%, more preferably at least 70%, particularly at least 80%, and especially at least 90% by number of particles have a particle size within the above preferred ranges given for the mean particle size.

The primary zinc oxide particles are preferably approximately spherical, preferably having a mean aspect ratio $d_1:d_2$ (where d_1 and d_2 , respectively, are the length and width of the particle (measured as described herein)) in the range from 0.6 to 1.4:1, more preferably 0.7 to 1.3:1, particularly 0.8 to 1.2:1, and especially 0.9 to 1.1:1. In a preferred embodiment of the invention, suitably at least 40%, preferably at least 55%,

more preferably at least 70%, particularly at least 80%, and especially at least 90% by number of particles have an aspect ratio within the above preferred ranges given for the mean aspect ratio.

5 In one embodiment of the invention, the primary zinc oxide particles aggregate to form clusters or agglomerates of secondary particles comprising a plurality of zinc oxide primary particles. The aggregation process of the primary zinc oxide particles may take place during the actual synthesis of the zinc oxide and/or during subsequent processing. The mean number of primary zinc oxide particles present in the
10 secondary particles according to the present invention is suitably less than 40, preferably in the range from 2 to 30, more preferably 4 to 20, particularly 6 to 15, and especially 7 to 11. The term "secondary" particle is partly used as a label to relate to particle size results obtained using a particular technique, as described herein.

15 The particulate zinc oxide according to the present invention suitably has a median volume particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value)) of the secondary particles (measured as described herein) of less than 150 nm, preferably
20 less than 100 nm, more preferably in the range from 60 to 95 nm, particularly 70 to 90 nm, and especially 75 to 85 nm.

The size distribution of the secondary zinc oxide particles can also be an important parameter in obtaining a masterbatch and UV absorbing polymeric composition having
25 the required properties. The zinc oxide particles suitably have less than 16% by volume of particles having a volume diameter of more than 55 nm, preferably more than 45 nm, more preferably more than 35 nm, particularly more than 25 nm, and especially more than 15 nm below the median volume particle diameter. In addition, the zinc oxide particles suitably have less than 30% by volume of particles having a
30 volume diameter of more than 35 nm, preferably more than 25 nm, more preferably more than 18 nm, particularly more than 12 nm, and especially more than 8 nm below the median volume particle diameter.

Further, the secondary zinc oxide particles suitably have more than 84% by volume of
35 particles having a volume diameter of less than 75 nm, preferably less than 60 nm,

more preferably less than 45 nm, particularly less than 35 nm, and especially less than 25 nm above the median volume particle diameter. Also, the zinc oxide particles suitably have more than 70% by volume of particles having a volume diameter of less than 35 nm, preferably less than 25 nm, more preferably less than 20 nm, particularly
5 less than 15 nm, and especially less than 10 nm above the median volume particle diameter.

It is preferred that none of the secondary zinc oxide particles should have an actual particle size exceeding 200 nm. Particles exceeding such a size may be removed by
10 milling processes which are known in the art. However, milling operations are not always totally successful in eliminating all particles greater than a chosen size. In practice, therefore, the size of 95%, preferably 99% by volume of the particles should not exceed 200 nm, preferably 150 nm.

15 The particulate zinc oxide used in the present invention may be formed by any suitable process. Typical processes are the French Method in which metallic zinc is melted and evaporated before being oxidized in the gas phase; the American method in which zinc ores are sintered and reduced with cokes and the zinc thus obtained is oxidised to zinc oxide; and wet methods in which a water soluble zinc salt such as zinc
20 chloride or zinc sulphate is crystallised and then converted to zinc oxide by sintering, gas phase oxidation of, for example, zinc salts, in which the salt is oxidized to form zinc oxide powder and grinding processes, in which larger particles of zinc oxide are mechanically ground to achieve the correct size and size distribution of zinc oxide powder. Fractionation techniques, as known in the art, may be employed in order to
25 obtain zinc oxide having the preferred particle size and size distribution as described herein.

The particles of zinc oxide may comprise substantially pure zinc oxide, but in one embodiment of the invention the particles have an inorganic and/or organic coating.
30 The inorganic coating is preferably one or more oxides or hydrous oxides of e.g. aluminium, silicon, titanium, zirconium, magnesium or zinc. The organic coating may be a fatty acid, an organic silicon compound, polyol, amine and/or alkanolamine. The coating is usually chosen to ensure compatibility with the particular medium that will be used with the zinc oxide particles. Thus, inorganic hydrophilic coatings are normally

preferred for incorporating the zinc oxide particles in polar media, and organic hydrophobic coatings for non-polar, particularly oil, media.

5 The level of purity of the zinc oxide particles can be an important requirement for use in certain applications. In a preferred embodiment, the lead content of the zinc oxide particles (uncoated and/or coated) is preferably less than 15 ppm, more preferably less than 13 ppm, particularly less than 10 ppm, and especially less than 6 ppm.

10 The preferred zinc oxide particles used in the present invention are transparent in use, suitably having an extinction coefficient at 524 nm (E_{524}) (measured as described herein) of less than 4.5, preferably less than 3.0, more preferably in the range from 0.1 to 2.0, particularly 0.3 to 1.5, and especially 0.5 to 1.0 l/g/cm. In addition, the zinc oxide particles suitably have an extinction coefficient at 450 nm (E_{450}) (measured as described herein) of less than 7, preferably less than 5, more preferably in the range
15 from 0.5 to 3, particularly 1.0 to 2.5, and especially 1.5 to 2.0 l/g/cm.

The zinc oxide particles exhibit effective UV absorption, suitably having an extinction coefficient at 360 nm (E_{360}) (measured as described herein) of greater than 10, preferably in the range from 12 to 20, more preferably 13 to 18, particularly 14 to 17,
20 and especially 15 to 16 l/g/cm. The zinc oxide particles also suitably have an extinction coefficient at 308 nm (E_{308}) (measured as described herein) of greater than 10, preferably in the range from 12 to 20, more preferably 13 to 18, particularly 14 to 16, and especially 14.5 to 15.5 l/g/cm.

25 The zinc oxide particles suitably have a maximum extinction coefficient $E(\max)$ (measured as described herein) in the range from 10 to 25, preferably 12 to 20, more preferably 13 to 18, particularly 14 to 17, and especially 15 to 16 l/g/cm. The zinc oxide particles suitably have a $\lambda(\max)$ (measured as described herein) in the range from 350 to 380, preferably 355 to 375, more preferably 360 to 372, particularly 364 to
30 370, and especially 366 to 368 nm.

The zinc oxide particles suitably have an E_{308}/E_{524} ratio of greater than 4, preferably greater than 10, more preferably in the range from 12 to 30, particularly 14 to 25, and especially 16 to 20.

In addition, the zinc oxide particles suitably have an E_{360}/E_{524} ratio of greater than 4, preferably greater than 10, more preferably in the range from 13 to 35, particularly 15 to 27 and especially 17 to 22.

- 5 The zinc oxide particles can exhibit reduced whiteness, suitably having a change in whiteness ΔL of a dispersion containing the particles (measured as described herein) of less than 10, preferably in the range from 1 to 7, more preferably 2 to 6, particularly 3.5 to 5, and especially 3 to 4. In addition, a dispersion containing the zinc oxide particles suitably has a whiteness index (measured as described herein) of less than
10 100%, preferably less than 70%, more preferably in the range from 5 to 45%, particularly 10 to 35%, and especially 15 to 25%.

- The secondary (or dispersion) particle size of the zinc oxide particles described herein may be measured by electron microscopy, coulter counter, sedimentation analysis
15 and static or dynamic light scattering. Techniques based on sedimentation analysis are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile. The median particle volume diameter and particle size distribution of the zinc oxide particles in dispersion is
20 suitably measured using a Brookhaven particle sizer, as described herein.

- In a preferred embodiment of the invention, the zinc oxide particles suitably have a BET specific surface area (measured as described herein) in the range from 10 to 40, preferably 15 to 35, more preferably 20 to 30, particularly 23 to 27, and especially 24
25 to 26 m^2g^{-1} .

- The concentration of zinc oxide particles in a masterbatch composition according to the present invention is preferably in the range from 1 to 50%, more preferably 5 to 40%, particularly 10 to 35%, and especially 20 to 30% by weight, based upon the total
30 weight of the masterbatch composition.

- The zinc oxide particles are preferably dispersed in the organic dispersing medium. The organic dispersing medium preferably has a melting point lower than the melting point, more preferably lower than the glass transition temperature (T_g), of the organic
35 resin in the masterbatch composition.

The organic dispersing medium preferably has a melting point of less than 400°C, more preferably less than 300°C, particularly less than 270°C, and especially less than 250°C. The dispersing medium is preferably liquid at ambient temperature (25°C).

5 Suitable dispersing media include non-polar materials such as C13-14 isoparaffin, isohexadecane, paraffinum liquidum (mineral oil), squalane, squalene, hydrogenated polyisobutene, polydecene; silicone oils and polar materials such as C12-15 alkyl benzoate, cetearyl isononanoate, ethylhexyl isostearate, ethylhexyl palmitate, isononyl isononanoate, isopropyl isostearate, isopropyl myristate, isostearyl isostearate,
10 isostearyl neopentanoate, octyldodecanol, pentaerythrityl tetraistearate, PPG-15 stearyl ether, triethylhexyl triglyceride, dicaprylyl carbonate, ethylhexyl stearate, helianthus annuus (sunflower) seed oil, isopropyl palmitate, octyldodecyl neopentanoate, glycerol monoester (C4 to C24 fatty acid, e.g. glycerol monostearate, glycerol monoisostearate), glycerol diester (C4 to C24 fatty acid), glycerol triester or
15 triglyceride (C4 to C24 fatty acid, e.g. caprylic/capric triglyceride or Estol 1527), ethylene bis-amide (C4 to C24 fatty acid, e.g. ethylene bis-stearamide), C4 to C24 fatty acid amide (e.g. erucamide), polyglycerol ester (C4 to C24 fatty acid) and organosilicones. Preferably the dispersing medium is selected from the group consisting of glycerol esters, glycerol ethers, glycol esters, glycerol ethers, alkyl
20 amides, alkanolamines, and mixtures thereof. More preferably, the dispersing medium is glycerol monostearate, glycerol monoisostearate, diethanolamine, stearamide, oleamide, erucamide, behenamide, ethylene bis-stearamide, ethylene bis-isostearamide, polyglycerol stearate, polyglycerol isostearate, polyglycol ether, triglyceride, or mixtures thereof.

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The concentration of organic dispersing medium in a masterbatch composition according to the present invention is preferably in the range from 1 to 50%, more preferably 5 to 40%, particularly 12 to 30%, and especially 15 to 25% by weight, based upon the total weight of the masterbatch composition.

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In a preferred embodiment of the present invention, the particulate zinc oxide is formed into a slurry, more preferably a liquid dispersion, in the aforementioned suitable organic dispersing medium prior to mixing with the aforementioned organic resin.

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By liquid dispersion is meant a true dispersion, i.e. where the solid particles are stable to aggregation. The particles in the dispersion are relatively uniformly dispersed and resistant to settling out on standing, but if some settling out does occur, the particles can be easily redispersed by simple agitation.

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The dispersion may also contain a dispersing agent in order to improve the properties thereof. The dispersing agent is suitably present in the range from 1 to 30%, preferably 2 to 20%, more preferably 3 to 150%, particularly 4 to 9%, and especially 5 to 7% by weight based on the total weight of zinc oxide particles.

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Suitable dispersing agents include substituted carboxylic acids, soap bases and polyhydroxy acids. Typically the dispersing agent can be one having a formula X.CO.AR in which A is a divalent bridging group, R is a primary secondary or tertiary amino group or a salt thereof with an acid or a quaternary ammonium salt group and X is the residue of a polyester chain which together with the -CO- group is derived from a hydroxy carboxylic acid of the formula HO-R'-COOH. As examples of typical dispersing agents are those based on ricinoleic acid, hydroxystearic acid, hydrogenated castor oil fatty acid which contains in addition to 12-hydroxystearic acid small amounts of stearic acid and palmitic acid. Dispersing agents based on one or more polyesters or salts of a hydroxycarboxylic acid and a carboxylic acid free of hydroxy groups can also be used. Compounds of various molecular weights can be used.

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Other suitable dispersing agents are those monoesters of fatty acid alkanolamides and carboxylic acids and their salts. Alkanolamides are based on ethanolamine, propanolamine or aminoethyl ethanolamine for example. Alternative dispersing agents are those based on polymers or copolymers of acrylic or methacrylic acids, e.g. block copolymers of such monomers. Other dispersing agents of similar general form are those having epoxy groups in the constituent radicals such as those based on the ethoxylated phosphate esters. The dispersing agent can be one of those commercially referred to as a hyper dispersant. Polyhydroxystearic acid is a particularly preferred dispersing agent.

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The dispersions used in the present invention suitably contain at least 40%, preferably at least 45%, more preferably at least 50%, particularly at least 55%, especially at

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least 60%, and generally up to 70% by weight of the total weight of the dispersion, of zinc oxide particles.

5 The concentration of zinc oxide dispersion in a masterbatch composition according to the present invention is preferably in the range from 5 to 80%, more preferably 10 to 70%, particularly 20 to 60%, and especially 30 to 50% by weight, based upon the total weight of the masterbatch composition.

10 The masterbatch and UV absorbing polymeric composition according to the present invention may further contain other additional components often used in such compositions, such as pigments, dyes, catalysts and curing accelerators, flow control additives, antifoaming, matting agents, antioxidants, antislip, and in particular other UV absorbing agents.

15 The masterbatch and UV absorbing polymeric composition may contain zinc oxide particles described herein as the sole UV absorbing agent, or the zinc oxide particles may be used together with other UV absorbing agents such as other metal oxides and/or organics and/or organometallic complexes. For example, the zinc oxide particles may be used in combination with other existing commercially available
20 titanium dioxide and/or zinc oxide particles.

The zinc oxide particles and dispersions described herein may be used in binary, tertiary or further multiple combinations with organic UV absorbers such as benzophenones, benzotriazoles, triazines, hindered benzoates, hindered amines
25 (HALS) or co-ordinated organo-nickel complexes. Examples of such organic UV absorbing materials include 2-hydroxy-4-n-butyloctylbenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-(2'-hydroxy-3',5'-di-*t*-amylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di(1,1-dimethylbenzyl))-2H-benzotriazole, bis(2,2,6,6-tetramethyl-4-piperidenyl) sebacate and [2,2'-thiobis(4-*t*-octylphenolate)] N-butylamine-nickel.

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The concentration of organic UV absorber in a masterbatch composition is preferably in the range from 0.1 to 50%, more preferably 1 to 40%, particularly 5 to 30%, and especially 10 to 20% by weight, based upon the total weight of the masterbatch composition.

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It is generally necessary to intimately mix the ingredients of the masterbatch composition of the invention in order to achieve a satisfactorily homogeneous finished concentrate. Commonly used methods of producing an intimate mixture include melt-mixing and dry blending.

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In the melt-mixing process, dry ingredients (e.g. organic resin, and other additives) are weighed into a batch mixer such as a high intensity impeller mixer, a medium intensity plough-share mixer or a tumble mixer. Mixing times depend upon the equipment used. For high intensity mixers, the mixing time is usually in the range 1 to 5 minutes and the mixing time in a tumble mixer is frequently in the range 30 to 60 minutes. The premix thus formed is then compounded together with liquid ingredients (e.g. zinc oxide dispersion) in a high shear extruder such as a single screw extruder (e.g. Buss Ko-kneader [RTM]) or a twin screw extruder. It is particularly important to ensure that the combination of temperature of the mixture and residence time for thermosetting compositions is such that little or no curing takes place in the extruder, although the temperature is usually slightly above the melting point of the organic resin. The appropriate processing temperature is chosen to suit the resin present in the composition, but is usually in the range 60 to 300°C.

Residence time in the extruder is usually in the range from 0.5 to 2 minutes. The resultant mixture is then typically extruded through a strand die. The extruded material is usually cooled rapidly by water cooling, such as in a water trough, and broken into pellets or chips with a size of about 5 to 10 mm. These pellets or chips can then be dried and ground further to an appropriate particle size using conventional techniques as necessary. Frequently, thermoplastic resins need to be ground using cryogenic techniques.

Masterbatch compositions can also be prepared by dry blending, and this technique is particularly suitable where the organic resin is plasticised poly(vinyl chloride). All of the ingredients are agitated in a high speed mixer at an elevated temperature in order to achieve intimate mixing.

It is desirable that the masterbatch produced according to the invention is free of holes or voids resulting from incorporation of moisture or volatiles in the masterbatch during

compounding. Methods of prevention of such (venting of compounding extruder barrels via vacuum etc) are well known in the art.

5 The masterbatch composition according to the present invention suitably has an extinction coefficient at 524 nm (E_{524}), measured as described herein, of less than 4.5, preferably less than 3.0, more preferably in the range from 0.1 to 2.0, particularly 0.3 to 1.5, and especially 0.5 to 1.0 l/g/cm.

10 The masterbatch composition exhibits effective UV absorption, suitably having (i) an extinction coefficient at 360 nm (E_{360}) (measured as described herein) of greater than 10, preferably in the range from 12 to 20, more preferably 13 to 18, particularly 14 to 17, and especially 15 to 16 l/g/cm, and/or (ii) an extinction coefficient at 308 nm (E_{308}) (measured as described herein) of greater than 10, preferably in the range from 12 to 20, more preferably 13 to 18, particularly 14 to 16, and especially 14.5 to 15.5 l/g/cm.

15 In a particularly preferred embodiment of the present invention, the masterbatch composition suitably has (i) an E_{308}/E_{524} ratio of greater than 4, preferably greater than 10, more preferably in the range from 12 to 30, particularly 14 to 25, and especially 16 to 20, and/or (ii) an E_{360}/E_{524} ratio of greater than 4, preferably greater than 10, more preferably in the range from 13 to 35, particularly 15 to 27 and especially 17 to 22.

20 A surprising feature of the present invention is that a masterbatch composition containing zinc oxide particles can be produced having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio suitably at least 45%, preferably at least 55%, more preferably at least 65%, particularly at least 75%, and especially at least 85% of the original value for the zinc oxide particles (measured as described herein (in dispersion)).

25 The masterbatch composition according to the invention is suitable for let down into a substrate resin using any method normally used for pigmenting substrates with masterbatches. The precise nature of the substrate or second organic resin will often determine the optimum conditions for application. The appropriate temperature for let down and application depends principally upon the actual resin(s) used, and is readily determined by a person skilled in the art. The substrate organic resin may be a thermoplastic or thermoset resin. Suitable substrate resins in which masterbatches are used include poly(vinyl chloride) and co-polymers thereof, polyamides and co-

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polymers thereof, polyolefins and co- polymers thereof, polystyrenes and co-polymers thereof, poly(vinylidene fluoride) and co- polymers thereof, acrylonitrile-butadiene-styrene, polyoxymethylene and acetal derivatives, polybutylene terephthalate and glycolised derivatives, polyethylene terephthalate and glycolised derivatives, polyacrylamide nylon (preferable nylon 11 or 12), polyacrylonitrile and co-polymers thereof, polycarbonate and co-polymers thereof. Polyethylene and polypropylene, which may be modified by grafting a carboxylic acid or anhydride groups onto the polymer backbone, are suitable polyolefins. Low density polyethylene may be used. A poly(vinyl chloride) may be plasticised, and preferably is a homopolymer of vinyl chloride.

The substrate or second organic resin is preferably a resin selected or polymerized from the following polymers or monomers that are frequently used for polymeric films either with or without biodegradable qualities; alkyl vinyl alcohols, alkyl vinyl acetates, carbohydrates, casein, collagen, cellulose, cellulose acetate, glycerol, lignin, low density polyethylene, linear low density polyethylene, nylon, polyalkylene esters, polyamides, polyanhydrides, polybutylene adipate/terephthalate, polybutylene succinate, polybutylene succinate/adipate, polycaprolactone, polyesters, polyester carbonate, polyethylene succinate, polyethylene terephthalate, polyglycerol, polyhydroxyalkanoates, polyhydroxy butyrate, polypropylene, polylactates, polysaccharides, polytetramethylene adipate/terephthalate, polyvinyl alcohol polyvinylidene chloride, proteins, soy protein, triglycerides and variants or co-polymers thereof.

Let down of the masterbatch composition to give the desired zinc oxide concentration in the final application may be achieved by tumble mixing the masterbatch composition with a quantity of a compatible diluent substrate resin. The mixture is then fed to a single or twin-screw compounding extruder and processed as described earlier (in the context of the preparation of a masterbatch composition) to produce a fully compounded resin with additives present at the concentrations required in the final application or is fed to a profile or sheet extrusion, blown or cast polymer foil or film unit for conversion into the desired product form.

Alternatively the masterbatch and compatible diluent substrate resin can be fed by an automatic metering system of a type common within the industry to a single or twin-

screw compounding extruder and processed as described earlier to produce a fully compounded resin with additives present at the concentrations required in the final application; or is fed to a profile or sheet extrusion, blown or cast polymer foil or film unit for conversion into the desired product form.

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Generally, the first organic resin (used in the masterbatch) is the same as the substrate resin (let down). However, this is not necessarily the case, and it is possible that the first organic resin may be different to the substrate or second organic resin.

10 Data obtained by an analysis of a successfully let down masterbatch containing the zinc oxide particles described here show values for transmittance, haze, clarity, L^* , a^* , b^* as well as other physical (e.g. gloss 60° and 20°), mechanical and toxicological characteristics that are either sufficiently similar to the polymer not containing the masterbatches described here or of sufficient value in their own right as to be
15 commercially applicable. Typical masterbatch formulations are developed so as to be manufactured by an economical route, thus it is desirable that the use of additives provided by the present invention affects such processes as little as possible. This is typically assessed by measuring the power consumption of blender/extruder unit and production rate.

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The application of the masterbatch in the let-down of a plastic needs to produce material that is neither economically deleterious to processing efficiency or quality of the final product. The quality of the let down product is measured as for the masterbatch itself (opacity, L^* , a^* , b^* , gloss (60 and 20) and other mechanical data).

25 The efficiency of the manufacture of the let down product is measured as per masterbatch formulation (power consumption and rate).

In an alternative embodiment of the present invention, the UV absorbing polymeric composition may be produced using a zinc oxide dispersion as defined herein as a
30 liquid carrier system. Liquid carrier systems are normally used in injection and blow moulding, but they can also be applied to the manufacture of polymeric film and fibre. The pre-dispersion can be pumped using a peristaltic, gear or other suitable pump into the extruder section of the process, where it is directly injected into the polymeric resin. Suitable polymeric resins include any one or more of the substrate or second
35 organic resins described herein.

The final or end-use UV absorbing polymeric composition, for example in the form of a polymeric film, according to the present invention suitably has an extinction coefficient at 524 nm (E_{524}), measured as described herein, of less than 4.5, preferably less than 3.0, more preferably in the range from 0.1 to 2.0, particularly 0.3 to 1.5, and especially 0.5 to 1.0 l/g/cm.

The UV absorbing polymeric composition, for example in the form of a polymeric film, exhibits effective UV absorption, suitably having (i) an extinction coefficient at 360 nm (E_{360}) (measured as described herein) of greater than 10, preferably in the range from 12 to 20, more preferably 13 to 18, particularly 14 to 17, and especially 15 to 16 l/g/cm, and/or (ii) an extinction coefficient at 308 nm (E_{308}) (measured as described herein) of greater than 10, preferably in the range from 12 to 20, more preferably 13 to 18, particularly 14 to 16, and especially 14.5 to 15.5 l/g/cm.

In a particularly preferred embodiment of the present invention, the UV absorbing polymeric composition, for example in the form of a polymeric film, suitably has (i) an E_{308}/E_{524} ratio of greater than 4, preferably greater than 10, more preferably in the range from 12 to 30, particularly 14 to 25, and especially 16 to 20, and/or (ii) an E_{360}/E_{524} ratio of greater than 4, preferably greater than 10, more preferably in the range from 13 to 35, particularly 15 to 27 and especially 17 to 22.

A surprising feature of the present invention is that a UV absorbing polymeric composition, for example in the form of a polymeric film, containing zinc oxide particles can be produced having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio suitably at least 45%, preferably at least 55%, more preferably at least 65%, particularly at least 75%, and especially at least 85% of the original value for the zinc oxide particles (measured as described herein (in dispersion)).

In one preferred embodiment of the present invention, the UV absorbing polymeric composition containing zinc oxide particles exhibits antimicrobial properties, preferably against at least bacteria, fungi and yeasts, more preferably against bacteria and fungi, and particularly against bacteria.

In one embodiment, the final or end use UV absorbing polymeric composition, preferably in the form of a film, suitably comprises (i) 60 to 99.9%, preferably 80 to

99.7%, more preferably 90 to 99.6%, and particularly 98 to 99.5% by weight of organic resin; (ii) 0.05 to 20%, preferably 0.1 to 10%, more preferably 0.2 to 5%, and particularly 0.3 to 2% by weight of organic dispersing medium; and (iii) 0.05 to 20%, preferably 0.1 to 10%, more preferably 0.2 to 5%, and particularly 0.3 to 2% by weight of zinc oxide.

The UV absorbing polymeric composition of the present invention can be used in many applications, such as plastic films used in agriculture to cover and protect crops, in food packaging and medical applications. The compositions can also be used as containers such as drinks bottles, and for fibre spinning for clothes or other fabric manufacture such as carpets and curtain materials.

In this specification the following test methods have been used:

1) Particle Size Measurement of Primary Zinc Oxide Particles

A small amount of zinc oxide, typically 2 mg, was worked into approximately 2 drops of an oil, for one or two minutes on a flat surface using the tip of a steel spatula. The resultant suspension was diluted with solvent and a carbon-coated grid suitable for transmission electron microscopy was wetted with the suspension and dried on a hot-plate. Approximately 18 cm x 21 cm photographs were produced at an appropriate, accurate magnification. Generally about 300-500 particles were displayed at about 2 diameters spacing. A minimum number of 300 primary particles were manually sized using a transparent size grid consisting of a row of circles of gradually increasing diameter, representing spherical particles. Each circle had ellipses of gradually increasing aspect ratio but equal volume beneath it. The outline of each particle was then fitted to the appropriate sphere or ellipse and logged against its equivalent spherical diameter. The mean particle diameter, and particle size distribution, of the particles were calculated from the above measurements. In addition, the aspect ratio of the particles was determined from the maximum and minimum dimensions of at least 100 particles. Alternatively, the measurements could be performed by computerised image analysis.

The basic method assumes log normal distribution standard deviations in the 1.2-1.6 range (wider crystal size distributions would require many more crystals to be counted, for example of the order of 1000). The suspension method described above has been

found to be suitable for producing almost totally dispersed distributions of primary zinc oxide particles whilst introducing minimal crystal fracture. Any residual aggregates (or secondary particles) are sufficiently well defined that they, and any small debris, can be ignored, and effectively only primary particles included in the count.

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2) Median Particle Volume Diameter and Particle Size Distribution of the Secondary Zinc Oxide Particles

A dispersion was produced by mixing 3.6 g of polyhydroxystearic acid with 36.4 g of caprylic/capric triglyceride, and then adding 60 g of zinc oxide powder to the mixture.

10 The mixture was passed through a horizontal bead mill, operating at 1500 r.p.m. and containing zirconia beads as grinding media for 15 minutes. The dispersion of zinc oxide particles was diluted to between 30 and 40 g/l by mixing with isopropyl myristate. The diluted sample was analysed on the Brookhaven BI-XDC particle sizer in centrifugation mode, and the median particle volume diameter and particle size
15 distribution measured.

3) BET Specific Surface Area of Zinc Oxide Particles

The single point BET specific surface area was measured using a Micromeritics Flowsorb II 2300.

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4) Change in Whiteness and Whiteness Index

A zinc oxide dispersion, e.g. produced in 2) above, was coated on to the surface of a glossy black card and drawn down using a No 2 K bar to form a film of 12 microns wet thickness. The film was allowed to dry at room temperature for 10 minutes and the
25 whiteness of the coating on the black surface (L_F) measured using a Minolta CR300 colourimeter. The change in whiteness ΔL was calculated by subtracting the whiteness of the substrate (L_S) from the whiteness of the coating (L_F). The whiteness index is the percentage whiteness ΔL compared to a standard zinc oxide (=100% value) (Z-Cote (ex BASF)).

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5) Determination of Transmittance, Haze and Clarity

Transmittance, haze and clarity of the, preferably 65 μm thick, polymeric film were measured using a Byk Haze-gard PLUS meter (Cat. No.4725). Transmittance is defined as the ratio of total transmitted light to incident light. Clarity is defined as
35 narrow angle scattering. More specifically, clarity is the percentage of transmitted light

that deviates from the incident by less than 2.5 degrees on average. Haze is defined as wide angle scattering. More specifically, haze is the percentage of transmitted light that deviates from the incident by greater than 2.5 degrees.

5 6) Extinction Coefficients

(a) Zinc Oxide Particles in Dispersion

0.1 g sample of a zinc oxide dispersion, e.g. produced in 2) above, was diluted with 100 ml of cyclohexane. This diluted sample was then further diluted with cyclohexane in the ratio sample:cyclohexane of 1:19. The total dilution was 1:20,000. The diluted
10 sample was then placed in a spectrophotometer (Perkin-Elmer Lambda 2 UV/VIS Spectrophotometer) with a 1 cm path length and the absorbance, of UV and visible light measured. Extinction coefficients were calculated from the equation $A = E \cdot c \cdot l$, where A = absorbance, E = extinction coefficient in litres per gram per cm, c = concentration of zinc oxide particles in grams per litre, and l = path length in cm.

15 (b) Masterbatch Composition and UV Absorbing Polymeric Composition

A 1 x 5 cm section of 65 μm film, e.g. formed using a zinc oxide masterbatch composition (produced as described in the Examples) was placed in a spectrophotometer (Perkin-Elmer Lambda 2 UV/VIS Spectrophotometer), previously calibrated with a blank or control film not containing zinc oxide particles, and held in
20 place by a specially designed sample holder. Absorbance measurements were taken at 10 random positions on the film sample, and mean extinction coefficient values calculated.

The invention is illustrated by the following non-limiting examples.

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Examples

Example 1

A dispersion was produced by mixing 3.6 g of polyhydroxystearic acid with 36.4 g of
30 caprylic/capric triglyceride, and then adding 60 g of zinc oxide powder to the mixture. The mixture was passed through a horizontal bead mill, operating at 1500 r.p.m. and containing zirconia beads as grinding media for 15 minutes.

The dispersion was subjected to the test procedures described herein, and the zinc
35 oxide exhibited the following extinction coefficient values:

E_{524}	E_{450}	E_{308}	E_{360}	$E(\text{max})$	$\lambda(\text{max})$	E_{308}/E_{524}	E_{360}/E_{524}
0.8	1.7	15.0	15.5	16.0	367	18.8	19.4

Example 2

5 The zinc oxide dispersion produced in Example 1 was used to prepare an ethylene vinyl acetate (EVA) masterbatch composition. 198 g EVA (Evatene 2020, ex Arkema (MFI = 20, vinyl acetate content = 20%)) was combined with 118 g zinc oxide dispersion in a plastic sack, followed by agitation (by hand) to give a homogenous mixture. This mixture was then added to a Thermo Prism 16 mm twin screw extruder
 10 operated in the temperature range of 85 to 100°C (feed zone 85°C, compression zone 90°C, metering zone 100°C). The extruded masterbatch was continuously produced at a rate of 3 kg per hour, and the 16 mm diameter masterbatch extrudate was immediately cooled in a water trough at a temperature of 6 to 10°C. A screw torque value of 35 to 40% was maintained throughout extrusion. The extruded masterbatch
 15 sample was then processed (chopped up) further to reduce the average extrudate length to around 5 mm. The resulting pellets were collected and placed in a drying oven for 30 minutes at approximately 40°C. This gave a final masterbatch sample of composition 62.5% EVA and 37.5% zinc oxide dispersion (22.5% zinc oxide).

20 Example 3

The procedure of Example 2 was repeated except that low density polyethylene (LDPE) (Exxon PLX6101RQP, MFI = 26) was used instead of EVA. The only change in the process conditions was that the Thermo Prism 16 mm twin screw extruder was
 25 operated in the temperature range of 105 to 125°C (feed zone 105°C, compression zone 115°C, metering zone 125°C).

Example 4

The masterbatch composition produced in Example 2 was used to make a LDPE blown film sample of 65 µm thickness.

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To prepare the film, a homogenous let down mixture of 25 g of the masterbatch composition prepared in Example 2 and 975 g of LDPE (Exxon LD165BW1) was hand blended in a plastic sack. The intimate mixture was then added into a Secor 25 mm single screw extruder fitted with three phase pre-die heating (B1, B2 and B3, with B1
 35 closest to the film die), and three phase die heating (Die 1, Die 2 and Die 3) with

adjustable film die 50 mm outside diameter and 49.5 mm internal diameter.

Processing was carried out using the conditions given below to give a blown polyethylene film of 65 microns thickness. The film was collected via a conventional film tower with collapsing boards and nip rolls. The film samples were collected on cardboard spools by hand and immediately stored in polythene bags, to avoid static dust contamination. Extrusion temperatures and screw speed were kept constant.

Processing Conditions

Screw Extruder

10	B1	169°C
	B2	180°C
	B3	190°C
	Die 1	190°C
	Die 2	191°C
15	Die 3	185°C
	Polymer residence	5 mins
	Screw rpm	36
	Motor Current	13 A
	Output rate	3.42 m/min
20	Output rate	52 g/min

Physical characteristics of film

Single film	65 microns
Film width	130 mm

25 Example 5

The procedure of Example 4 was repeated except that 25 g of the masterbatch composition produced in Example 3 was used instead to make a LDPE blown film sample of 65 µm thickness.

30 Example 6

As a comparative example, the procedure of Example 4 was repeated except that 1000 g of LDPE (Exxon LD165BW1) was used with no masterbatch composition to make a LDPE blown film sample of 65 µm thickness.

The films were subjected to the test procedures described herein, and exhibited the following properties:

		<u>E₅₂₄</u>	<u>E₃₀₈</u>	<u>E₃₆₀</u>	<u>E(max)</u>	<u>λ (max)</u>	<u>E₃₀₈/E₅₂₄</u>	<u>E₃₆₀/E₅₂₄</u>
5	Example 4	0.7	12.2	12.7	13.0	364	17.4	18.1
	Example 5	0.8	11.0	11.9	12.4	366	13.8	14.9

	Example 4	Example 5	Example 6 (Comparative)
Transmittance	92.2	90.2	92.7
Haze	36.6	40.2	40.2
Clarity	36.6	35.3	32.0

- 10 The above examples illustrate the improved properties of a masterbatch and UV absorbing polymeric composition according to the present invention.

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CLAIMS

1. A UV absorbing polymeric composition having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4 which comprises an organic resin and zinc oxide particles.
2. A composition according to claim 1 having an extinction coefficient at 524 nm (E_{524}) of less than 4.5 l/g/cm.
3. A composition according to either one of claims 1 and 2 having an extinction coefficient at 308 nm (E_{308}) and/or 360 nm (E_{360}) of greater than 10 l/g/cm.
4. A composition according to any one of the preceding claims having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 10.
5. A composition according to any one of the preceding claims having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio at least 55% of the original value for the zinc oxide particles.
6. A composition according to any one of the preceding claims comprising (i) 60 to 99.9% by weight of organic resin; (ii) 0.05 to 20% by weight of organic dispersing medium; and (iii) 0.05 to 20% by weight of zinc oxide particles.
7. A composition according to claim 6 wherein the dispersing medium is selected from the group consisting of glycerol esters, glycerol ethers, glycol esters, glycerol ethers, alkyl amides, alkanolamines, and mixtures thereof.
8. A composition according to any one of the preceding claims wherein the secondary zinc oxide particles have a median volume particle diameter of 60 to 95 nm.
9. A masterbatch composition comprising an organic resin, an organic dispersing medium and zinc oxide particles.
10. A masterbatch according to claim 9 wherein the organic resin has a melting point of 75 to 400°C.

11. A masterbatch according to either one of claims 9 and 10 wherein the organic dispersing medium is selected from the group consisting of glycerol monostearate, glycerol monoisostearate, diethanolamine, stearamide, oleamide, erucamide, behenamide, ethylene bis-stearamide, ethylene bis-isostearamide polyglycerol stearate, polyglycerol isostearate, polyglycol ether, triglyceride, and mixtures thereof.
12. A masterbatch according to any one of claims 9 to 11 formed from zinc oxide particles having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4.
13. A masterbatch according to any one of claims 9 to 12 having an extinction coefficient at 524 nm (E_{524}) of less than 3.0 l/g/cm and/or an extinction coefficient at 308 nm (E_{308}) and/or 360 nm (E_{360}) of greater than 10 l/g/cm.
14. A masterbatch according to any one of claims 9 to 13 having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 10.
15. A masterbatch according to any one of claims 9 to 14 having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio at least 55% of the original value for the zinc oxide particles.
16. A method of producing a masterbatch composition as defined in any one of claims 9 to 15 which comprises mixing a dispersion of zinc oxide particles in an organic dispersing medium, with an organic resin.
17. A method of producing a UV absorbing polymeric composition having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4 which comprises an organic resin and zinc oxide particles, comprising the steps of providing (i) a masterbatch composition comprising an organic resin, an organic dispersing medium and zinc oxide particles, and mixing the masterbatch composition with a substrate organic resin, or (ii) a dispersion of zinc oxide particles in an organic dispersing medium, and incorporating the dispersion directly into a substrate organic resin.
18. The use of a UV absorbing polymeric composition having an E_{308}/E_{524} and/or E_{360}/E_{524} ratio of greater than 4, which comprises an organic resin and zinc oxide particles, as an antimicrobial agent.