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(54) Title: PARTICULATE TITANIUM DIOXIDE

(57) Abstract: A particulate titanium dioxide contains a dopant metal having a median volume particle diameter in the range from 24 to 42 nm. The titanium dioxide can be used to form dispersions. The titanium dioxide and dispersions can be used to produce sunscreen products and organic resins, e.g. polymeric films, having effective UV absorption properties, improved transparency and/or reduced photoactivity.

Particulate Titanium Dioxide

Field of Invention

The present invention relates to doped titanium dioxide particles, a dispersion made therefrom, and in particular to the use thereof in an end-use product.

Background

Titanium dioxide has been employed as an attenuator of ultraviolet light in a wide range of applications such as sunscreens, organic resins, films and coatings.

Due to the increased awareness of the link between ultraviolet light and skin cancer, there has been a requirement for ultraviolet light protection in everyday skincare and cosmetics products. There is a need for titanium dioxide in a form which when incorporated into sunscreen products exhibits both effective UV absorption properties and be transparent in use. Titanium dioxide is often used in sunscreen products in combination with active materials such as vitamins, perfumes, and organic attenuators of ultraviolet light. Unfortunately, titanium dioxide may be photoactive which can lead to degradation of active materials, and for organic UV absorbers this can result in loss of UV absorption properties.

Many applications require organic resins such as films, coatings and varnishes to be used in exposed conditions, such as outdoors. In these environments, organic resins, e.g. plastic materials, 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) polymers where other protective materials (e.g. pigmentary titanium dioxide) cannot be employed. In applications where a thin cross section of plastic is used, 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. Titanium dioxide has been employed as an attenuator of ultraviolet light in applications such as films, resins and coatings, but existing materials either have insufficient UV absorption, and/or lack of transparency, and/or are sufficiently photoactive that degradation of the organic polymer will occur over time.

Thus, there is a need to provide a titanium dioxide which is transparent, exhibits effective UV absorption properties, and reduced photoactivity, enabling use thereof in a wide range of applications.

Summary of the Invention

We have now surprisingly discovered an improved titanium dioxide, which overcomes or significantly reduces at least one of the aforementioned problems.

Accordingly, the present invention provides a particulate titanium dioxide comprising a dopant metal having a median volume particle diameter of from 24 to 42 nm.

The invention also provides a particulate titanium dioxide comprising a dopant metal having an E_{308}/E_{524} ratio of greater than 20.

The invention further provides a dispersion comprising particulate titanium dioxide comprising a dopant metal having a median volume particle diameter of from 24 to 42 nm.

The invention yet further provides a sunscreen product comprising a particulate titanium dioxide comprising a dopant metal having a median volume particle diameter of from 24 to 42 nm.

The invention still further provides an organic resin comprising a particulate titanium dioxide comprising a dopant metal having a median volume particle diameter of from 24 to 42 nm.

The titanium dioxide particles preferably comprise anatase and/or rutile crystal form. The titanium dioxide in the particles suitably comprises a major portion of rutile, preferably greater than 70%, more preferably greater than 80%, particularly greater than 90%, and especially greater than 95% by weight of rutile.

The basic particles may be prepared by standard procedures, such as using the chloride process, or by the sulphate process, or by the hydrolysis of an appropriate titanium compound such as titanium oxydichloride or an organic or inorganic titanate, or by oxidation of an oxidisable titanium compound, e.g. in the vapour state. The titanium dioxide particles are preferably prepared by the hydrolysis of a titanium compound, particularly of titanium oxydichloride.

The process employed for making the titanium dioxide particles allows doping with a dopant metal selected from the group consisting of aluminium, chromium, cobalt, copper, gallium, iron, lead, manganese, nickel, silver, tin, vanadium, zinc, zirconium, and combinations thereof. The dopant is preferably selected from the group consisting of chromium, cobalt, copper, iron, manganese, nickel, silver, and vanadium, more preferably from chromium, manganese, and vanadium, and particularly manganese, and especially in the 3+ state.

Doping can be performed by normal methods known in the art. Doping is preferably achieved by co-precipitation of titanium dioxide and a soluble dopant complex such as manganese chloride or manganese acetate. Alternatively doping can be performed by a baking technique by heating a titanium complex in the presence of a dopant complex, e.g. manganese nitrate, at a temperature of greater than 500°C and normally up to 1,000°C. Dopants can also be added by oxidizing a mixture containing a titanium complex and dopant complex, e.g. manganese acetate, such as by spraying the mixture through a spray atomizer into an oxidation chamber.

The titanium dioxide particles preferably comprise in the range from 0.01 to 3%, more preferably 0.05 to 2%, particularly 0.1 to 1%, and especially 0.5 to 0.7% by weight of dopant metal, preferably manganese, calculated with respect to the weight of titanium dioxide.

In one embodiment of the present invention, the titanium dioxide particles are uncoated, i.e. consist essentially of titanium dioxide and dopant.

In another embodiment, the titanium dioxide particles are coated with an inorganic and/or organic coating.

The inorganic coating is preferably an oxide of aluminium, zirconium or silicon, or mixtures thereof such as alumina and silica. The amount of inorganic coating, suitably alumina and/or silica, is preferably in the range from 2 to 25%, more preferably 4 to 20%, particularly 6 to 15%, and especially 8 to 12% by weight, calculated with respect to the weight of titanium dioxide core particles.

In one embodiment of the invention, the titanium dioxide particles are hydrophobic. The hydrophobicity of the titanium dioxide can be determined by pressing a disc of titanium dioxide powder, and measuring the contact angle of a drop of water placed thereon, by standard techniques known in the art. The contact angle of a hydrophobic titanium dioxide is preferably greater than 50°.

The titanium dioxide particles can be coated in order to render them hydrophobic. Suitable coating materials are water-repellent, preferably organic, and include fatty acids, preferably fatty acids containing 10 to 20 carbon atoms, such as lauric acid, stearic acid and isostearic acid, salts of the above fatty acids such as sodium salts and aluminium salts, fatty alcohols, such as stearyl alcohol, and silicones such as polydimethylsiloxane and substituted polydimethylsiloxanes, and reactive silicones such as methylhydrosiloxane and polymers and copolymers thereof. Stearic acid and/or salt thereof is particularly preferred. Generally, the particles are treated with up to 25%, suitably in the range from 5 to 20%, more preferably 11 to 16%, particularly 12 to 15%, and especially 13 to 14% by weight of organic material, preferably fatty acid, calculated with respect to the titanium dioxide core particles.

In one embodiment of the invention, the doped titanium dioxide particles are coated with both an inorganic alumina and/or silica coating, and an organic coating, either sequentially or as a mixture. It is preferred that the alumina or silica is applied first followed by the organic coating, preferably fatty acid and/or salt thereof. Thus in one embodiment, titanium dioxide particles comprise (i) in the range from 70 to

94%, more preferably 75 to 87%, particularly 78 to 84%, and especially 80 to 82% by weight of titanium dioxide, (ii) in the range from 2 to 12%, more preferably 5 to 11%, particularly 7 to 10%, and especially 8 to 9% by weight of alumina or silica coating, (iii) in the range from 4 to 18%, more preferably 7 to 15%, particularly 9 to 12%, and especially 10 to 11% by weight of organic coating, preferably fatty acid and/or salt thereof, and (iv) in the range from 0.01 to 2.5%, more preferably 0.05 to 2%, particularly 0.1 to 0.8%, and especially 0.4 to 0.6% by weight of dopant metal, preferably manganese, all with respect to the total weight of the particles.

The individual or primary titanium dioxide particles are suitably acicular in shape and have a long axis (maximum dimension or length) and short axis (minimum dimension or width). The third axis of the particles (or depth) is preferably approximately the same dimensions as the width.

The mean length by number of the primary titanium dioxide particles is suitably in the range from 50 to 90 nm, preferably 55 to 77 nm, more preferably 55 to 73 nm, particularly 60 to 70 nm, and especially 60 to 65 nm. The mean width by number of the particles is suitably in the range from 5 to 20 nm, preferably 8 to 19 nm, more preferably 10 to 18 nm, particularly 12 to 17 nm, and especially 14 to 16 nm. The primary titanium dioxide particles preferably have a mean aspect ratio d_1:d_2 (where d_1 and d_2, respectively, are the length and width of the particle) in the range from 2.0 to 8.0:1, more preferably 3.0 to 6.5:1, particularly 4.0 to 6.0:1, and especially 4.5 to 5.5:1. The size of the primary particles can be suitably measured using electron microscopy. The size of a particle can be determined by measuring the length and width of a particle selected from a photographic image obtained by using a transmission electron microscope.

The titanium dioxide particles suitably have a mean crystal size (measured by X-ray diffraction as herein described) in the range from 5 to 20 nm, preferably 6 to 15 nm, more preferably 7 to 12 nm, particularly 8 to 11 nm, and especially 9 to 10 nm.

The size distribution of the crystal size of the titanium dioxide particles can be important, and suitably at least 30%, preferably at least 40%, more preferably at least 50%, particularly at least 60%, and especially at least 70% by weight of the

titanium dioxide particles have a crystal size within one or more of the above preferred ranges for the mean crystal size.

When formed into a dispersion according to the present invention, the particulate titanium dioxide 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)), measured as herein described, in the range from 24 to 42 nm, preferably 27 to 39 nm, more preferably 29 to 37 nm, particularly 31 to 35 nm, and especially 32 to 34 nm.

The size distribution of the titanium dioxide particles in dispersion can also be an important parameter in obtaining a product having the required properties. In a preferred embodiment suitably less than 10% by volume of titanium dioxide particles have a volume diameter of more than 13 nm, preferably more than 11 nm, more preferably more than 10 nm, particularly more than 9 nm, and especially more than 8 nm below the median volume particle diameter. In addition, suitably less than 16% by volume of titanium dioxide particles have a volume diameter of more than 11 nm, preferably more than 9 nm, more preferably more than 8 nm, particularly more than 7 nm, and especially more than 6 nm below the median volume particle diameter. Further, suitably less than 30% by volume of titanium dioxide particles have a volume diameter of more than 7 nm, preferably more than 6 nm, more preferably more than 5 nm, particularly more than 4 nm, and especially more than 3 nm below the median volume particle diameter.

Also, suitably more than 90% by volume of titanium dioxide particles have a volume diameter of less than 30 nm, preferably less than 27 nm, more preferably less than 25 nm, particularly less than 23 nm, and especially less than 21 nm above the median volume particle diameter. In addition, suitably more than 84% by volume of titanium dioxide particles have a volume diameter of less than 19 nm, preferably less than 18 nm, more preferably less than 17 nm, particularly less than 16 nm, and especially less than 15 nm above the median volume particle diameter. Further, suitably more than 70% by volume of titanium dioxide particles have a volume diameter of less than 8 nm, preferably less than 7 nm, more preferably less than 6

nm, particularly less than 5 nm, and especially less than 4 nm above the median volume particle diameter.

Dispersion particle size of the titanium dioxide particles described herein may be measured by electron microscopy, coulter counter, sedimentation analysis 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 titanium dioxide particles in dispersion is suitably measured using a Brookhaven particle sizer, as described herein.

The titanium dioxide particles suitably have a BET specific surface area, measured as described herein, of greater than 40, preferably greater than 50, more preferably in the range from 55 to 150, particularly 60 to 90, and especially 65 to 75 m^2/g.

The titanium dioxide particles used in the present invention are transparent, suitably having an extinction coefficient at 524 nm (E_{524}), measured as herein described, of less than 2.0, preferably in the range from 0.4 to 1.5, more preferably 0.6 to 1.3, particularly 0.8 to 1.2, and especially 0.9 to 1.1 l/g/cm. In addition, the titanium dioxide particles suitably have an extinction coefficient at 450 nm (E_{450}), measured as herein described, in the range from 0.8 to 2.5, preferably 1.2 to 2.2, more preferably 1.4 to 2.0, particularly 1.5 to 1.9, and especially 1.6 to 1.8 l/g/cm.

The titanium dioxide particles exhibit effective UV absorption, suitably having an extinction coefficient at 360 nm (E_{360}), measured as herein described, of greater than 2, preferably in the range from 4 to 14, more preferably 5 to 11, particularly 6 to 9, and especially 7 to 8 l/g/cm. The titanium dioxide particles also suitably have an extinction coefficient at 308 nm (E_{308}), measured as herein described, of greater than 35, preferably in the range from 38 to 65, more preferably 41 to 60, particularly 43 to 57, and especially 45 to 55 l/g/cm.

The titanium dioxide particles suitably have a maximum extinction coefficient E(max), measured as herein described, in the range from 50 to 85, preferably 55 to 82, more preferably 60 to 80, particularly 62 to 78, and especially 64 to 76 l/g/cm.

The titanium dioxide particles suitably have a λ(max), measured as herein described, in the range from 260 to 285, preferably 265 to 280, more preferably 268 to 277, particularly 271 to 275, and especially 272 to 274 nm.

The titanium dioxide particles suitably have an E_{308}/E_{524} ratio of greater than 20, preferably in the range from 30 to 85, more preferably 35 to 70, particularly 40 to 60, and especially 45 to 55.

The titanium dioxide particles suitably have a photoactivity of less than 1×10^{-4}, preferably less than 5×10^{-5}, more preferably less than 1×10^{-5}, particularly in the range from 5×10^{-6} to 1×10^{-7}, and especially 1×10^{-6} to 5×10^{-7} mol dm^{-3} min^{-1} of acetone.

The titanium dioxide particles suitably exhibit reduced whiteness, having a change in whiteness ΔL of a sunscreen product containing the particles, measured as herein described, of less than 3, preferably in the range from 0.05 to 0.5, more preferably 0.1 to 0.3, and particularly 0.15 to 0.25. In addition, a sunscreen product containing the particles suitably has a whiteness index, measured as herein described, of less than 50%, preferably less than 20%, more preferably in the range from 0.1 to 10%, particularly 0.5 to 5%, and especially 1 to 2%.

The particulate titanium dioxide according to the present invention may be in the form of a free-flowing powder. A powder having the required particle size may be produced by milling processes known in the art. The final milling stage of the titanium dioxide is suitably carried out in dry, gas-borne conditions to reduce aggregation. A fluid energy mill can be used in which the aggregated titanium dioxide powder is continuously injected into highly turbulent conditions in a confined chamber where multiple, high energy collisions occur with the walls of the chamber and/or between the aggregates. The milled powder is then carried into a cyclone and/or bag filter for recovery. The fluid used in the energy mill may be any gas, cold or heated, or superheated dry steam.

The particulate titanium dioxide may be formed into a slurry, or preferably a liquid dispersion, in any suitable aqueous or organic liquid medium. 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.

For use in a sunscreen product, cosmetically acceptable materials are preferred as the liquid medium. A useful organic medium is a liquid oil such as vegetable oils, e.g. fatty acid glycerides, fatty acid esters and fatty alcohols. A preferred organic medium is a siloxane fluid, especially a cyclic oligomeric dialkylsiloxane, such as the cyclic pentamer of dimethylsiloxane known as cyclomethicone. Alternative fluids include dimethylsiloxane linear oligomers or polymers having a suitable fluidity and phenyltris(trimethylsiloxy)silane (also known as phenyltrimethicone).

Examples of suitable organic media include non-polar materials such as C13-C14 isoparaffin, isohexadecane, paraffinum liquidum (mineral oil), squalane, squalene, hydrogenated polyisobutene, and polydecene; and polar materials such as C12-C15 alkyl benzoate, caprylic/capric triglyceride, cetearyl isononanoate, ethylhexyl isostearate, ethylhexyl palmitate, isononyl isononanoate, isopropyl isostearate, isopropyl myristate, isostearyl isostearate, isostearyl neopentanoate, octyldodecanol, pentaerythrityl tetraisostearate, PPG-15 stearyl ether, triethylhexyl triglyceride, dicaprylyl carbonate, ethylhexyl stearate, helianthus annus (sunflower) seed oil, isopropyl palmitate, and octyldodecyl neopentanoate.

The dispersion according to the present invention 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 9 to 20%, particularly 11 to 17%, and especially 13 to 15% by weight based on the total weight of titanium dioxide particles.

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.

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.

An advantage of the present invention is that dispersions can be produced which preferably contain at least 30%, more preferably at least 35%, particularly at least 40%, especially at least 45%, and generally up to 55% by weight of the total weight of the dispersion, of titanium dioxide particles.

A composition, preferably a sunscreen product, containing the titanium dioxide particles according to the present invention preferably has a Sun Protection Factor (SPF), measured as herein described, of greater than 10, more preferably greater than 15, particularly greater than 20, and especially up to 40.

The titanium dioxide particles and dispersions of the present invention are useful as ingredients for preparing sunscreen compositions, especially in the form of oil-in-water or water-in-oil emulsions. The compositions may further contain conventional additives suitable for use in the intended application, such as conventional cosmetic ingredients used in sunscreens. The particulate titanium dioxide as defined herein, may provide the only ultraviolet light attenuators in a sunscreen product according to the invention, but other sunscreening agents, such as other titanium dioxides and/or other organic materials may also be added. For example, the preferred

titanium dioxide particles defined herein may be used in combination with other existing commercially available titanium dioxide and/or zinc oxide sunscreens. The titanium dioxide particles and dispersions of the present invention are particularly suitable for use in combination with organic UV absorbers such as butyl methoxydibenzoylmethane (avobenzone), benzophenone-3 (oxybenzone), 4-methylbenzylidene camphor (enzacamene), benzophenone-4 (sulisobenzone), bis-ethylhexyloxyphenol methoxyphenyl triazine (bemotrizinol), diethylamino hydroxybenzoyl hexyl benzoate, diethylhexyl butamido triazone, disodium phenyl dibenzimidazole tetrasulfonate, drometrizole trisiloxane, ethylhexyl dimethyl PABA (padimate O), ethylhexyl methoxycinnamate (octinoxate), ethylhexyl salicylate (octisalate), ethylhexyl triazone, homosalate, isoamyl *p*-methoxycinnamate (amiloxate), isopropyl methoxycinnamate, menthyl anthranilate (meradimate), methylene bis-benzotriazolyl tetramethylbutylphenol (bisoctrizole), octocrylene, PABA (aminobenzoic acid), phenylbenzimidazole sulfonic acid (ensulizole), terephthalylidene dicamphor sulfonic acid, and mixtures thereof.

Organic UVA absorbers are preferred, such as those selected from the group consisting of butyl methoxydibenzoylmethane (avobenzone), benzophenone-3 (oxybenzone), benzophenone-4 (sulisobenzone), diethylamino hydroxybenzoyl hexyl benzoate, disodium phenyl dibenzimidazole tetrasulfonate, octocrylene, PABA (aminobenzoic acid), phenylbenzimidazole sulfonic acid (ensulizole), and mixtures thereof. Particularly preferred organic UV absorbers are butyl methoxydibenzoylmethane and benzophenone-3, and particularly butyl methoxydibenzoylmethane.

In addition, broad spectrum organic UV absorbers, which have good efficacy against both UVA and UVB, may be employed such as bis-ethylhexyloxyphenol methoxyphenyl triazine (bemotrizinol) and drometrizole trisiloxane, and mixtures thereof.

In an alternative embodiment of the present invention, the particulate titanium dioxide and dispersions described herein can be incorporated into an organic resin, which 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 or coatings 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 polyvinyldiene chloride, proteins e.g. 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 (Tg) in the range from -200 to 500°C, more preferably -150 to 400°C, and particularly -125 to 300°C.

The titanium dioxide particles are suitably dispersed in an organic dispersing medium which preferably has a melting point lower than the melting point, more preferably lower that the glass transition temperature (Tg), of the organic resin.

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).

Suitable dispersing media, for use in incorporating into an organic resin, include non-polar materials such as C13-C14 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, isostearyl neopentanoate, octyldodecanol, pentaerythrityl tetraisostearate, PPG-15 stearyl ether, triethylhexyl triglyceride, dicaprylyl carbonate, ethylhexyl stearate, helianthus annus (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 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), polyglyercol 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 amides, alkanolamines, or 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.

In one embodiment of the present invention, the particulate titanium dioxide is formed into a slurry, more preferably a liquid dispersion, at the concentrations described herein, in the aforementioned suitable liquid organic dispersing medium

prior to mixing with the aforementioned organic resin. A dispersing agent as described herein may also be employed.

In an alternative embodiment, the titanium dioxide is dispersed in a semi-solid or solid carrier prior to incorporating into an organic resin. Suitable solid or semi-solid dispersions may contain, for example, in the range from 50 to 90%, preferably 60 to 85% by weight of particulate titanium dioxide, and a high molecular polymeric material, such as a wax, e.g. glycerol monostearate.

The concentration of titanium dioxide particles in the organic resin composition is preferably in the range from 0.05 to 20%, more preferably 0.1 to 5%, particularly 0.2 to 2%, and especially 0.25 to 1% by weight, based upon the total weight of the composition.

The organic resin composition may contain the titanium dioxide particles described herein as the sole UV absorbing agent, or the titanium dioxide 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 titanium dioxide particles may be used in combination with other existing commercially available titanium dioxide and/or zinc oxide particles.

The titanium dioxide particles and dispersions described herein may be used in an organic resin in binary, tertiary or further multiple combinations with organic UV absorbers such as benzophenones, benzotriazoles, triazines, hindered benzoates, hindered amines (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.

The concentration of organic UV absorber in the organic resin composition is preferably in the range from 0.1 to 10%, more preferably 1 to 8%, particularly 2 to 6%, and especially 3 to 5% by weight, based upon the total weight of the composition.

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

The organic resin composition (or end-use product, preferably 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 2.0, preferably in the range from 0.3 to 1.5, more preferably 0.4 to 1.2, particularly 0.5 to 1.0, and especially 0.6 to 0.9 l/g/cm.

The organic resin composition (or end-use product, preferably a polymeric film) exhibits effective UV absorption, suitably having an extinction coefficient at 308 nm (E_{308}), measured as described herein, of greater than 20, preferably in the range from 25 to 55, more preferably 30 to 50, particularly 35 to 45, and especially 37 to 43 l/g/cm.

A particularly preferred embodiment of the present invention is that the organic resin composition (or end-use product, preferably a polymeric film) suitably has an E_{308}/E_{524} ratio of greater than 10, preferably greater than 20, more preferably greater than 30, particularly greater than 40, and especially in the range from 50 to 70.

One feature of the present invention is that an organic resin composition (or end-use product, preferably a polymeric film) containing titanium dioxide particles can be produced having an E_{308}/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 titanium dioxide particles (measured as described herein (in dispersion)).

In one embodiment of the invention, masterbatch technology may be employed such that the organic resin composition is a masterbatch which is suitable for let down into a substrate using any method normally used for pigmenting substrates with masterbatches. Where the organic resin composition is to be used as a masterbatch, the concentration of (i) titanium dioxide particles in the masterbatch

composition is preferably in the range from 1 to 50%, more preferably 5 to 40%, particularly 10 to 30%, and especially 12 to 20% by weight, based upon the total weight of the composition, and/or (ii) organic UV absorber in the 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 composition.

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 or resins used, and is readily determined by a person skilled in the art. The second organic resin may be a thermoplastic or thermoset resin. Suitable second organic resins in which masterbatches are used 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, 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 polyvinyldiene chloride, proteins, soy protein, triglycerides and variants or co-polymers thereof.

When formed using a masterbatch, the final (or end use) UV absorbing organic resin 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 0.25 to 2% by weight of titanium dioxide.

Data obtained by analysis of an organic resin containing the titanium dioxide particles described herein 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 can be sufficiently similar to the polymer not containing the titanium dioxide particles described herein or of sufficient value in their own right as to be commercially applicable.

The UV absorbing organic resin composition of the present invention can be used in many applications, such as coatings, varnishes, plastic films used in agriculture to cover and protect crops, in food packaging and medical applications. The compositions can also be used in 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) Crystal Size Measurement of Titanium Dioxide Particles

Crystal size was measured by X-ray diffraction (XRD) line broadening. Diffraction patterns were measured with Cu Kα radiation in a Siemens D5000 diffractometer equipped with an energy dispersive detector acting as a monochromator. Programmable slits were used to measure diffraction from a 12 mm length of specimen with a step size of 0.02°. The data was analysed by fitting the diffraction pattern between 22 and 48° 2θ with a set of peaks corresponding to the reflection positions for rutile and, where anatase was present, an additional set of peaks corresponding to those reflections. The fitting process allowed for removal of the

effects of instrument broadening on the diffraction line shapes. The value of mean crystal size was determined for the rutile 110 reflection (at approximately 27.4 °2θ) based on its full width at half maximum height (FWHM) using the Scherrer equation, described e.g. in B. E. Warren, "X-Ray Diffraction", Addison-Wesley, Reading, Massachusetts, 1969, pp 251-254.

2) Median Particle Volume Diameter and Particle Size Distribution of Titanium Dioxide Particles in Dispersion

A dispersion of titanium dioxide particles was produced by mixing 6.3 g of polyhydroxystearic acid with 48.7 g of C12-C15 alkylbenzoate, and then adding 45 g of titanium dioxide into the solution. The mixture was passed through a horizontal bead mill, operating at approximately 2100 r.p.m. and containing zirconia beads as grinding media for 15 minutes. The dispersion of titanium dioxide 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 distribution measured.

3) BET Specific Surface Area of Titanium Dioxide Particles

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

4) Change in Whiteness and Whiteness Index

A sunscreen formulation (e.g. as in Example 2) 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 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 change in whiteness ΔL compared to a standard doped titanium dioxide (= 100% value) (Optisol TM (ex Oxonica)).

5) Photoactivity of Titanium Dioxide Particles

Photocatalytic oxidation activity was measured at 30°C by monitoring the photo-generation of acetone by a dispersion of 0.4 g of titanium dioxide in 50 ml of

isopropanol. The reaction was carried out in a cylindrical glass vessel illuminated, from the base, by two UV lamps with a maximum output at approx. 365 nm (Philips PL-L 36W 09). The reaction mixture was sampled by a hypodermic syringe through a port fitted with a septum cap and filtered to remove titanium dioxide. Samples were analysed for acetone by gas chromatography (Cambridge GC94, Chromosorb wax 60/80 mesh at 70°C) calibrated with mixtures of acetone and propan-2-ol using a diethyl ether internal standard. Straight-line calibration plots (R^2 0.997) were obtained and results expressed as mol dm^{-3} min^{-1} of acetone.

6) Sun Protection Factor

The Sun Protection Factor (SPF) of a sunscreen formulation (e.g. as in Example 2) was determined using the *in vitro* method of Diffey and Robson, J. Soc. Cosmet. Chem. Vol. 40, pp 127-133,1989.

7) Extinction Coefficients

(a) Titanium Dioxide Particles in Dispersion

0.1 g sample of a titanium dioxide disperson 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 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.c.l, where A=absorbance, E=extinction coefficient in litres per gram per cm, c=concentration in grams per litre, and l=path length in cm.

(b) Organic Resin Composition

A 1 x 5 cm section of 65 µm film formed using an organic resin composition containing titanium dioxide particles was placed in a spectrophotometer (Perkin-Elmer Lambda 2 UV/VIS Spectrophotometer), previously calibrated with a control or comparative film not containing titanium dioxide particles, and held in 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.

Examples

Example 1

1 mole of titanium oxydichloride in acidic solution and manganese chloride, equivalent to 0.7% by weight of Mn on TiO_2 weight, were reacted with 3 moles of NaOH in aqueous solution. After the initial reaction period, the temperature was increased to above 70°C, and stirring continued. The reaction mixture was neutralised by the addition of aqueous NaOH, and allowed to cool below 70°C. To the resultant slurry, an alkaline solution of sodium aluminate was added, equivalent to 10.5% by weight Al_2O_3 on TiO_2 weight. The temperature was maintained below 70°C during the addition. 13.5% by weight of sodium stearate on TiO_2 dissolved in hot water was added into the 75°C solution. The slurry was equilibrated for 15 minutes and neutralized by adding 20% hydrochloric acid dropwise over 30 minutes before the slurry was allowed to cool to less than 50°C. The slurry was filtered using a Buchner filter until the cake conductivity at 100 gdm^{-3} in water was <150 µS. The filter cake was oven-dried for 16 hours at 110°C and ground into a fine powder by an IKA Werke dry powder mill operating at 3,250 rpm.

The titanium dioxide powder was subjected to the photoactivity test described herein, and gave a value of 2×10^{-6} mol dm^{-3} min^{-1} of acetone.

A dispersion was produced by mixing 6.3 g of polyhydroxystearic acid with 48.7 g of C12-C15 alkylbenzoate, and then adding 45 g of pre-dried titanium dioxide powder produced above into 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 titanium dioxide dispersion was subjected to the test procedures described herein, and exhibited the extinction coefficients;

E_{524}	E_{450}	E_{308}	E_{360}	E(max)	λ (max)	E_{308}/E_{524}
1.0	1.7	45.0	7.3	64.0	273	45.0

Example 2

The titanium dioxide dispersion produced in Example 1 was used to prepare a sunscreen product having the following composition.

Trade Name	INCI Name	% w/w
Phase A.		
Arlacel™ 165 VP (ex Croda)	Glyceryl Stearate (and) PEG-100 Stearate	6.0
Span™ 60 (ex Croda)	Sorbitan Stearate	0.5
Tween™ 60 (ex Croda)	Polysorbate 60	2.7
Crodamol™ TN (ex Croda)	Isotridecyl Isononanoate	6.0
Crodamol™ AB (ex Croda)	C12-C15 Alkyl Benzoate	4.0
Cromollient™ DP3A (ex Croda)	Di-PPG-3 Myristyl Ether Adipate	3.0
Stearyl Alcohol	Stearyl Alcohol	1.0
Antaron V-220	PVP/Eicosene Copolymer	1.0
Parsol 1789	Butylmethoxy Dibenzoylmethane	3.0
Parsol MCX	Ethylhexyl Methoxycinnamate	5.0
TiO_2 Dispersion (Produced in Ex.1)		11.1
Phase B.		
Water	Water	60.0
Keltrol RD (E)	Xanthan Gum	0.2
Veegum Ultra	Magnesium Aluminum Silicate	0.8
Propylene Glycol	Propylene Glycol	4.0
Phase C.		
Nipaguard MPA	Benzyl Alcohol & Methylparaben & Propylparaben	0.7

Procedure

1. Keltrol RD was dispersed into phase B water, and the remaining phase B ingredients were added and the mixture was heated to 80°C.
2. All of the phase A ingredients except for Crodamol™ TN, Crodamol™ AB and the TiO_2, were mixed together and heated to 80°C.
3. Crodamol™ TN, Crodamol™ AB and the TiO_2 were premixed with homogenisation (1,000 rpm) and added to phase A. The temperature was maintained at 80°C
4. Phase A was added to phase B with stirring and homogenised for 1 minute at 1,000 rpm.

5. The mixture was cooled to 40°C, phase C was added and the mixture stirred and cooled to room temp.

The sunscreen product was subjected to the test procedures described herein, and exhibited the following properties:

i) Change in whiteness $\Delta L = 0.2$, and

ii) Whiteness index = 1.7% (ΔL value for Optisol TM (ex Oxonica) was 12).

Example 3

A dispersion was produced by mixing 7.2 g of polyhydroxystearic acid with 47.8 g of caprylic/capric triglyceride, and then adding 45 g of pre-dried titanium dioxide powder produced in Example 1 into 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.

A masterbatch composition was produced by mixing 308 g EVA (Evatene 2020, ex Arkema (MFI = 20, vinyl acetate content = 20%)) with 132 g of the titanium dioxide 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 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 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 70% EVA and 30% titanium dioxide dispersion (12% TiO_2).

Example 4

To prepare a LDPE blown film sample of 65 µm thickness, a homogenous let down mixture of 25 g of the masterbatch composition produced in Example 3 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 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	
B1	169°C
B2	180°C
B3	190°C
Die 1	190°C
Die 2	191°C
Die 3	185°C
Polymer residence	5 mins
Screw rpm	36
Motor Current	13 A
Output rate	3.42 m/min
Output rate	52 g/min

Physical characteristics of film

Single film	65 microns
Film width	130 mm

The film was subjected to the test procedures described herein, and the extinction coefficient ratio E_{308}/E_{524} was 46.6.

The above examples illustrate the improved properties of a particulate titanium dioxide, dispersion, sunscreen product, organic resin composition and/or polymeric film according to the present invention.

CLAIMS

1. A particulate titanium dioxide comprising a dopant metal having a median volume particle diameter of from 24 to 42 nm.

2. A titanium dioxide according to claim 1 wherein the dopant metal is selected from the group consisting of aluminium, chromium, cobalt, copper, gallium, iron, lead, manganese, nickel, silver, tin, vanadium, zinc, zirconium, and combinations thereof.

3. A titanium dioxide according to either one of claims 1 and 2 comprising 0.01 to 3% by weight of dopant metal.

4. A titanium dioxide according to any one of the preceding claims wherein the particles have a mean crystal size of 5 to 20 nm.

5. A titanium dioxide according to any one of the preceding claims having a median volume particle diameter of from 29 to 37 nm.

6. A titanium dioxide according to any one of the preceding claims having an extinction coefficient at 524 nm of less than 2.0 l/g/cm.

7. A titanium dioxide according to any one of the preceding claims having an E_{308}/E_{524} ratio of greater than 20.

8. A titanium dioxide according to any one of the preceding claims having a photoactivity of less than 1×10^{-4} mol dm^{-3} min^{-1} of acetone.

9. A titanium dioxide according to claim 8 having a photoactivity of 5×10^{-6} to 1×10^{-7} mol dm^{-3} min^{-1} of acetone.

10. A particulate titanium dioxide comprising a dopant metal having an E_{308}/E_{524} ratio of greater than 20.

11. A dispersion comprising titanium dioxide particles as defined any one of the preceding claims.

12. A dispersion according to claim 11 comprising at least 30% by weight of titanium dioxide particles.

13. A sunscreen product comprising titanium dioxide particles as defined in any one of claims 1 to 10, and/or a dispersion as defined in either one of claims 11 and 12.

14. A sunscreen product according to claim 13 additionally comprising an organic UVA absorber.

15. A sunscreen product according to claim 14 wherein the organic UVA absorber is selected from the group consisting of butyl methoxydibenzoylmethane (avobenzone), benzophenone-3 (oxybenzone), benzophenone-4 (sulisobenzone), diethylamino hydroxybenzoyl hexyl benzoate, disodium phenyl dibenzimidazole tetrasulfonate, octocrylene, PABA (aminobenzoic acid), phenylbenzimidazole sulfonic acid (ensulizole), and mixtures thereof.

16. An organic resin comprising titanium dioxide particles as defined in any one of claims 1 to 10, and/or a dispersion as defined in either one of claims 11 to 12.

17. An organic resin according to claim 16 having an extinction coefficient at 524 nm of less than 2.0 l/g/cm.

18. An organic resin according to either one of claims 16 and 17 having an E_{308}/E_{524} ratio of greater than 10.

19. An organic resin according to any one of claims 16 to 18 having an E_{308}/E_{524} ratio at least 45% of the original value for the titanium dioxide particles.

20. An organic resin according to any one of claims 16 to 19 in the form of a polymeric film.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2008/000924

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/36 C01G23/047 A61K8/29 A61Q17/04 C09D7/12
C08K3/22

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)
C01G C09C

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	page 1, line 3 - line 7 page 3, line 19 - line 24 page 5, line 1 - line 29 page 8, line 16 - line 22 example 3 claim 1	6-20

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

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 June 2008	12/06/2008

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2008/000924

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	examples 1,2 page 1, line 10 - line 11 page 1, line 35 - page 2, line 28 page 3, line 33 - line 37 page 5, line 8 - line 20 page 6, line 19 - page 7, line 26 page 9, line 31 - page 10, line 32	1-5
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International application No
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