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(54) Ultraviolet ray absorbing polymer particle compositions

(57) The present invention discloses an ultraviolet ray absorbing polymer particle. The ultraviolet ray absorbing polymer particle includes an ultraviolet ray absorber and a polymer of the formula:

$$(A)_x(B)_y$$

where A is a polyfunctional ethylenically unsaturated monomer, B is a monofunctional ethylenically unsaturated monomer, x is 0.1 to 90 mole percent and y is (100-x) mole percent. The ultraviolet ray absorbing particle is particularly useful in an imaging element.

EP 0 825 484 A2

Description

FIELD OF THE INVENTION

This invention relates to image elements and particularly to photographic elements containing novel ultraviolet ray absorbing polymer particles.

BACKGROUND OF THE INVENTION

It is conventional to incorporate an absorbing compound or absorber, in particular, an ultraviolet ray absorber, in an image element to absorb light in a specific wavelength region. The ultraviolet ray absorbing light-insensitive layer is used, for example, in a silver halide photographic element to control the spectral composition of light incident upon a photographic emulsion layer, and to absorb or to remove ultraviolet light produced by static discharge, which occurs when the surfaces of the photographic element come into contact during production or treatment processes. Electric charges are generated by friction of separation. When accumulation of static electricity by charging reaches a certain limiting value, atmospheric discharge occurs at a particular moment and a discharge spark fires at the same time. When the photographic element is exposed to light by discharging, static marks appear after development.

Different methods for incorporating an ultraviolet ray absorber into a photographic element have been described in, for example, US Patent Nos. 2,739,888, 3,215,530, 3,352,681, and 3,707,375. Oil soluble ultraviolet absorbers are incorporated into photographic elements by dissolving the oil soluble absorber in a high boiling point organic solvent, and mixing under high shear or turbulence the organic solvent with an aqueous medium, which may also contain a surfactant, in order to break the organic phase into submicron particles dispersed in the continuous aqueous phase. However, when such dispersions are used in a light-insensitive layer, the layer becomes soft and the mechanical properties of the layer are lowered. Furthermore, even if no high boiling point solvent is used, many ultraviolet absorbers themselves are liquid, and they therefore can have a detrimental effect on the mechanical properties of the layer and adhesion with the adjacent layer. In order to prevent these problems, a large amount of gelatin is used in the layer containing ultraviolet ray absorbers. When the ultraviolet ray absorbers are incorporated in the outermost layer of a photographic element, they often migrate and crystallize at the surface of the layer. Therefore, an additional overcoat layer is used to minimize this undesirable blooming phenomenon.

US Patent No 5,110,717 describes a method of incorporating an ultraviolet ray absorbing compound or coupler by mechanically grinding a crystalline material to a desired particle size in a liquid that is not a solvent for the material, heating the crystalline particles to above their melting point, and cooling the melted particles to form amorphous particles.

Ultraviolet ray absorbing polymer particles obtained by polymerization of ultraviolet ray absorbing monomers are also known in the art. Different methods can be used to prepare such particles, for example, by emulsion polymerization or by dispersion of preformed ultraviolet ray absorbing polymers. Disadvantages of using such polymer particles are their high cost and poor light stability.

Another method of incorporating an ultraviolet ray absorber into a photographic element is by loading such an absorber into pre-formed latex particles as described in US Patent Nos. 4,199,363, 4,304,769, 4,247,627, and 4,368,258. In this process, a hydrophobe, such as an ultraviolet ray absorber, is first dissolved in a water miscible organic solvent and then blended with an aqueous latex. However, removing the water miscible solvent subsequent to loading requires large scale processing equipment and lengthy processing times, which increases the expenses of the incorporation procedure and cost of the resulting products.

US Patent No 5,536,628 describes a process for incorporating absorbers into a pre-formed latex polymer particle. In the process a polymer latex of known solids is heated with stirring to 70 to 80 °C. The absorbing compound is heated until it reaches its liquid state and is mixed with the polymer latex at high shear to generate an emulsion. The emulsion is then passed through a high energy homogenizer at least once to form an absorber impregnated latex polymer dispersion.

Processes described in US Patent Nos. 5,536,628, 4,199,363, 4,304,769, 4,247,627, and 4,368,258 can result in incomplete loading which leaves residual ultraviolet ray absorbers in the aqueous phase, which can then crystallize or form large oil droplets during storage and use. The ultraviolet ray absorbers can also diffuse out the polymer particles and crystallize or form oil droplets further shortening the shelf life of ultraviolet ray absorbing polymer particles. In addition, even smaller amounts of oil droplets or crystals can significantly degrade the physical and photographic properties of a photographic element by generating spots defects in the final coated layers.

PROBLEM TO BE SOLVED BY INVENTION

Therefore, an objective of the present invention is to provide an improved ultraviolet ray absorbing polymer particle having excellent stability against diffusion of the ultraviolet absorber out of the polymer particle during storage and use of such particles.

SUMMARY OF THE INVENTION

This invention provides an ultraviolet ray absorbing polymer particle comprising an ultraviolet ray absorber and a polymer of the formula:

$$(A)_x(B)_y \tag{I}$$

where A is a polyfunctional ethylenically unsaturated monomer, B is a monofunctional ethylenically unsaturated monomer, x is 0.1 to 90 mole %, and y is (100-x) mole %.

In a particular embodiment, the invention is directed to an imaging element comprising a support and a layer and is characterized in that the layer includes a binder and the ultraviolet ray absorbing polymer particle wherein the polymer is represented by Formula I.

DETAILED DESCRIPTION OF THE INVENTION

The imaging elements of this invention can be of many different types depending on the particular use for which they are intended. Such elements include, for example, photographic, electrophotographic, electrostatographic, photothermographic, migration, electrothermographic, dielectric recording and thermal-dye-transfer imaging elements. Photographic elements can comprise various polymeric films, papers, glass, and the like, but both acetate and polyester supports well known in the art are preferred. The thickness of the support is not critical. Support thickness of 2 to 10 mil (0.002 to 0.010 inches) can be used. The supports typically employ an undercoat or subbing layer well known in the art that comprises, for example, for polyester support a vinylidene chloride/methyl acrylate/itaconic acid terpolymer or vinylidene chloride/acrylonitrile/acrylic acid terpolymer.

In accordance with the present invention, the polymer contained in the ultraviolet ray absorbing polymer particles has a composition given by Formula I, in which A is a polyfunctional ethylenically unsaturated monomer and B is a monofunctional ethylenically unsaturated monomer. x is 0.1 to 90 mole %, more preferably 1 to 50 mole %, and most preferably 1 to 25 mol %, and y = (100 - x) mole %. The ultraviolet ray absorbing polymer particles have a mean size from 0.01 µm to 50 µm, preferably from 0.02 µm to 10 µm and most preferably from 0.03 µm to 5 µm.

Suitable polyfunctional ethylenically unsaturated monomers which can be used as component A of the present invention are monomers which are polyfunctional with respect to the polymerization reaction, and may include, for example, the following monomers and their mixtures: esters of unsaturated monohydric alcohols with unsaturated monocarboxylic acids, such as allyl methacrylate, allyl acrylate, butenyl acrylate, undecenyl acrylate, undecenyl methacrylate, vinyl acrylate, and vinyl methacrylate; dienes such as butadiene and isoprene; esters of saturated glycols or diols with unsaturated monocarboxylic acids, such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,3-butanediol dimethacrylate; and polyfunctional aromatic compounds such as divinyl benzene. Preferably, monomer A is ethylene glycol dimethacrylate, ethylene glycol diacrylate, or divinylbenzene.

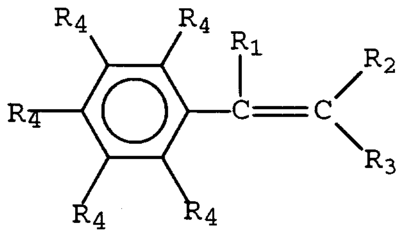
As to divinylbenzene, although available as pure monomer for laboratory use, it is most commonly sold commercially as a mixture of divinylbenzene and ethylvinylbenzene. Available, for instance, from Dow Chemical Company as DVB-55 (typical assay 55.8% divinylbenzene and 43.0% ethylvinylbenzene) or DVB-HP (typical assay 80.5% divinylbenzene and 18.3% ethylvinylbenzene).

Suitable monofunctional ethylenically unsaturated monomers which can be used as component B of the present invention may include, for example, the following monomers and their mixtures: acrylic monomers, such as acrylic acid, or methacrylic acid, and their alkyl esters such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, n-octyl acrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, nonyl acrylate, benzyl methacrylate; hydroxyalkyl esters of the same acids such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate; nitriles and amides of the same acids such as acrylonitrile, methacrylonitrile, acrylamide and methacrylamide, vinyl acetate, vinyl propionate, vinylidene chloride, vinyl chloride; and vinyl aromatic compounds such as styrene, t-butyl styrene, ethyl vinyl benzene, vinyl toluene, dialkyl maleates, dialkyl itaconates, dialkyl methylene-malonates, isoprene, and butadiene.

In general, the amount of ultraviolet absorbers present in the polymer particles can be anywhere within the range of 1:40 to 3:1 in terms of a weight ratio of ultraviolet ray absorber to polymer. It is preferred that the weight ratio is in the range of from 1:10 to 2:1, and most preferably from 1:5 to 1:1.

The types of ultraviolet ray absorbers which can be used for the practice of the present invention are not particularly limited provided their absorption maximum wavelengths fall within the range of 300 to 400 nm, and they have no harmful effect on the imaging properties of the element. Such UV compounds include ultraviolet absorbers of the thiazolidone type, the benzotriazole type, the cinnamic acid ester type, the benzophenone type, and the aminobutadiene type and have been described in detail in, for example, US patent Nos. 1.023,859, 2,685,512, 2,739,888, 2,748,021, 3,004,896, 3,052,636, 3,215,530, 3,253,921, 3,533,794, 3,692,525, 3,705,805, 3,707,375, 3,738,837, 3,754,919, and British Patent No 1,321,355.

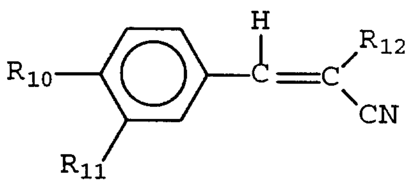
A preferred ultraviolet ray absorber useful for the practice of the present invention is represented by formula II.



(II)

wherein R_4 may be the same or different, and each represents a hydrogen atom, or a halogen atom, an alkyl, an aryl group having from 6 to 20 carbon atoms, an alkoxy group, an aryloxy, an alkylthio group, an arylthio group, an amine group, an alkylamino group, an arylamino group, an hydroxyl group, a cyano group, a nitro group, an acylamino group, a sulfonyl group, a sulfoamido group, an acyloxy group, or an oxycarbonyl group, or two neighboring R_4 groups may form a 5- or 6-member ring by ring closure. R_1 represents a hydrogen atom, or an alkyl group. R_2 or R_3 each represents a cyano group, $-COOR_9$, $-CO-NHR_9$, $-SO_2R_9$, $CO-R_9$, where R_9 represents an alkyl group, and an aryl group.

Most preferred ultraviolet ray absorbers represented by formula II are given by formula III.

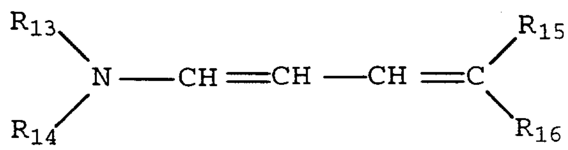


(III)

The following represents limited examples of compounds given by formula III.

Compound No.	R_{10}	R_{11}	R_{12}
UV-1	H	H	$CO_2C_{16}H_{33}$
UV-2	CH_3	H	$CO_2C_{16}H_{33}$
UV-3	CH_3	H	$CO_2C_3H_7$
UV-4	CH_3	H	$CO_2C_{12}H_{25}$
UV-5	CH_3	H	$SO_2C_{12}H_{25}$
UV-6	OCH_3	H	$CO_2C_3H_7$
UV-7	OCH_3	H	$CO_2C_5H_{11}$
UV-8	OCH_3	H	2-ethylhexyl
UV-9	OCH_3	H	$CO_2C_8H_{17}$
UV-10	OCH_3	H	$CO_2C_9H_{19}$
UV-11	OCH_3	H	$CO_2C_{10}H_{21}$
UV-12	OCH_3	H	$CO_2C_{12}H_{25}$
UV-13	OCH_3	H	$CO_2C_{16}H_{33}$
UV-14	OCH_3	H	$CO_2C_{18}H_{37}$
UV-15	OCH_3	H	$SO_2C_{12}H_{25}$
UV-16	OCH_3	H	$SO_2C_{10}H_{21}$
UV-17	OCH_3	H	$SO_2C_8H_{17}$
UV-18	OCH_3	H	$SO_2C_6H_{13}$
UV-19	OCH_3	H	$SO_2C_4H_9$
UV-20	OCH_3	H	$SO_2C_3H_7$
UV-21	OCH_3	H	SO_2CH_3
UV-22	OC_3H_7	H	$CO_2C_3H_7$
UV-22	OC_3H_7	H	$CO_2C_5H_{11}$
UV-23	OC_3H_7	H	2-ethylhexyl
UV-24	OC_3H_7	H	$CO_2C_8H_{17}$
UV-25	OC_3H_7	H	$CO_2C_9H_{19}$
UV-26	OC_3H_7	H	$CO_2C_{10}H_{21}$
UV-27	OC_3H_7	H	$CO_2C_{12}H_{25}$
UV-28	OC_3H_7	H	$CO_2C_{16}H_{33}$
UV-29	OC_3H_7	H	$CO_2C_{18}H_{37}$
UV-30	OC_3H_7	H	$SO_2C_{12}H_{25}$
UV-31	OC_3H_7	H	$SO_2C_{10}H_{21}$
UV-32	OC_3H_7	H	$SO_2C_8H_{17}$
UV-33	OC_3H_7	H	$SO_2C_6H_{13}$
UV-34	OC_3H_7	H	$SO_2C_4H_9$
UV-35	OC_3H_7	H	$SO_2C_3H_7$
UV-36	OC_3H_7	H	SO_2CH_3
UV-37	OC_2H_5	OCH_3	$CO_2C_2H_5$
UV-38	OC_4H_9	OCH_3	$CO_2C_2H_5$
UV-39	OC_6H_5	OCH_3	$CO_2C_2H_52OH$
UV-40	$OCH_2C_6H_5$	OH	$CO_2C_2H_5$
UV-41	OC_4H_9	OCH_3	$CO_2C_2H_5$
UV-42	$OCH_2OCO_2C_2H_5$	OCH_3	$CONHC_6H_5$
UV-43	$OC_2H_4OCOCH_3$	OCH_3	$CONHCH_2C_6H_5$

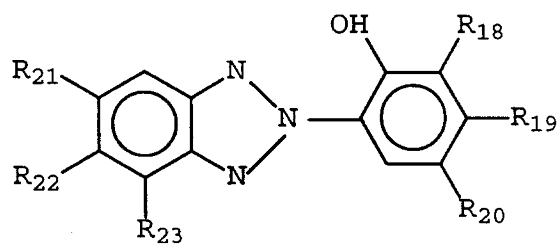
A second preferred ultraviolet ray absorber for the practice of the present invention has structures given by Formula IV:



(IV)

where R_{13}, and R_{14}, which may be the same or different, each represents a hydrogen atom, an alkyl group, an aryl group, R_{15} and R_{16} each represents a cyano group, -$COOR_{17}$, COR_{17}, SO_2R_{17}, where R_{17} represents an alkyl group, or an aryl group.

A third preferred ultraviolet absorber for the practice of the present invention has structures given by Formula V:



(V)

where R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, and R_{23} may be the same or different, and each represents a hydrogen atom, a halogen atom, a nitro group, a hydroxyl group, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an aralkylthio group, an akoxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, a mono or dialkylamino group, etc.

The ultraviolet ray absorbing polymer particles of this invention can be made by various well-known techniques in the art, such as, for example, emulsion polymerization, dispersion polymerization, suspension polymerization, and the like (see, for example, Padget, J. C. in Journal of Coating Technology, Vol 66, No. 839, pages 89-105, 1994; El-Aasser, M. S. and Fitch, R. M. Ed. Future Directions in Polymer Colloids, NATO ASI Series, No 138, Martinus Nijhoff Publishers, 1987; Arshady, R. Colloid & Polymer Science, 1992, No 270, pages 717-732; Odian, G. Principles of Polymerization, 2nd Ed. Wiley(1981); and Sorenson, W. P. and Campbell, T. W. Preparation Method of Polymer Chemistry, 2nd Ed, Wiley (1968)).

A preferred method of preparing ultraviolet ray absorbing polymer particles in accordance with this invention is by a limited coalescence technique where a mixture of polymerizable monomers and ultraviolet ray absorbers is added to an aqueous medium containing a particlulate suspending agent to form a discontinuous (oil droplet) phase in continuous (water) phase. The mixture is subjected to shearing forces, by agitation, homogenization and the like to reduce the size of the droplets. After shearing is stopped an equilibrium is reached with respect to the size of the droplets as a result of the stabilizing action of the particulate suspending agent in coating the surface of the droplets and then polymerization is completed to form an aqueous suspension of polymer particles. This process is described in U.S. Pat. Nos. 2,932,629; 5,279,934; and 5,378,577 incorporated herein by reference.

A second preferred method of preparing ultraviolet ray absorbing polymer particles in accordance with this invention is by an emulsion polymerization process where an ultraviolet ray absorber is mixed with an ethylenically unsaturated monomer together with a water soluble initiator and a surfactant. The polymerization process is initiated in general with free radical initiators. Free radicals of any sort may be used. Preferred initiators include persulfates (such as ammonium persulfate, potassium persulfate, etc., peroxides (such as hydrogen), azo compounds (such asazobiscyanovaleric acid), and redox initiators (such as hydrogen peroxide-iron(II) salt, potassium persulfate-sodium hydrogen sulfate, etc.). Surfactants which can be used include, for example, a sulfate, a sulfonate, a cationic compound, an amphoteric compound, and a polymeric protective colloid. Specific examples are described in "McCUTCHEON'S Volume 1: Emulsifiers & Detergents, 1995, North American Edition". Chain transfer agents may also be used to control the properties of the polymer particles formed.

The surface of the ultraviolet ray absorbing polymer particles may include reactive functional groups which form covalent bonds with binders by intermolecular crosslinking or by reaction with a crosslinking agent (i. e. a hardener). Suitable reactive functional groups include: hydroxyl, carboxyl, carbodiimide, epoxide, aziridine, vinyl sulfone, sulfinic acid, active methylene, amino, amide, allyl, and the like. There is no particular restriction on the amount of reactive groups present, but their concentrations are preferably in the range of from 0.5 to 10 weight percent. The particle surface may also be surrounded with a layer of gelatin as described in US Patent No. 4,855,219.

Any suitable binders can be used in practice of the present invention. They include hydrophilic colloids such as gelatin as well as hydrophobic polymer resin binders. The actual amount of binder and ultraviolet ray absorbing particle will vary depending on the types of applications. It is preferred that the binder is coated at a weight ratio to the ultraviolet ray absorbing particle from 1:100 to 100:1, and more preferably from 20:80 to 95:5.

Useful resin binders include polyurethane (e.g. Neorez R960 sold by ICI), cellulose acetates (e.g. cellulose diacetate, cellulose acetate butyrate, cellulose acetate propionate), poly(methyl methacrylate), polyesters (e.g. Vitel R sold by Goodyear Tire & Rubber Co.), polyamides (e.g. Unirez sold by Union Camp, Vesamide sold by General Electric Co.), polycarbonates (e.g. Makrolon sold by Mobay Chemical Co., Lexan sold by General Electric Co.), polyvinyl acetate, and the like.

Any suitable hydrophilic binder can be used in practice of this invention, such as naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g. cellulose esters), polysaccharides, casein, and the like, and synthetic water permeable colloids such as poly(vinyl lactams), acrylamide polymers, poly(vinyl alcohol) and its derivatives, hydrolyzed polyvinyl acetates, polymers of alkyl and sulfoalkyl acrylates and methacrylates, polyamides, polyvinyl pyridine, acrylic acid polymers, maleic anhydride copolymers, polyalkylene oxide, methacrylamide copolymers, polyvinyl oxazolidinones, maleic acid copolymers, vinyl amine copolymers, methacrylic acid copolymers, acryloyloxyalkyl sulfonic acid copolymers, vinyl imidazole copolymers, vinyl sulfide copolymers, homopolymer or copolymers containing styrene sulfonic acid, and the like. Gelatin is the most preferred hydrophilic binder.

Gelatin can be used together with other water dispersible polymers as binders in the practice of the present invention. The water dispersible polymers can be incorporated into either light sensitive or light-insensitive layers. Suitable water dispersible polymers include both synthetic and natural water dispersible polymers. Synthetic water dispersible polymers may contain a nonionic group, an anionic group, or a nonionic group and an anionic group in the molecular structure. The nonionic group may be, for example, an ether group, an ethylene oxide group, an amide group, or a hydroxyl group. The anionic group may be, for example, a sulfonic acid group or the salt thereof, a carboxylic acid group or the salt thereof, or a phosphoric acid group or the salt thereof. The natural water soluble polymer may include a nonionic group, an anionic group, or a nonionic group and an anionic group in the molecular structure. The water dispersible polymers may be incorporated into the photographic materials of the present invention in an amount of preferably at least 0.5 percent, preferably from 1 to 50 percent, and most preferably from 2 to 30 percent based on the amount of the whole coated amount of gelatin.

The image element of the present invention can contain at least one electrically conductive layer, which can be either surface protective layer or a sub layer. The surface resistivity of at least one side of the support is preferably less than 1×10^{12} Ω/square, more preferably less than 1×10^{11} Ω/square at 25°C and 20 percent relative humidity. To lower the surface resistivity, a preferred method is to incorporate at least one type of electrically conductive material in the electrically conductive layer. Such materials include both conductive metal oxides and conductive polymers or oligomeric compounds. Such materials have been described in detail in, for example, U.S. Patent Nos. 4,203,769; 4,237,194; 4,272,616; 4,542,095; 4,582,781; 4,610,955; 4,916,011; and 5,340,676.

The coating composition of the invention can be applied by any of a number of well-know techniques, such as dip coating, rod coating, blade coating, air knife coating, gravure coating and reverse roll coating, extrusion coating, slide coating, curtain coating, and the like. The ultraviolet ray absorbing particles and the binder are mixed together in a liquid medium to form a coating composition. After coating, the layer is generally dried by simple evaporation, which may be accelerated by known techniques such as convection heating. Known coating and drying methods are described in further detail in Research Disclosure No. 308, Published Dec. 1989, pages 1007 to 1008.

The present invention will now be described in detail with reference to examples; however, the present invention should not limited by these examples.

Examples

Preparation of ultraviolet ray absorbing polymer particles by free radical emulsion polymerization

Example 1 (Invention): Polymer particles impregnated with propyl I, 2-cyano-3-(4-methoxyphenyl) -2-propenoate ultraviolet ray absorber.

A stirred reactor containing 559.45 g of deionized water is heated to 80 °C and purged with N_2 for 1 hour followed by addition in sequence of 20 g of 10% Rhodapex CO-436 (Rhone-Poulenc) in deionized water, 0.2 g of $NaHCO_3$, 0.3 g of potassium persulfate, 0.05 g of sodium metabisulfate, and 20 g of ethyl acrylate. The reaction is allowed to continue for an additional 2 hours. 0.2 g of 4,4-azobis(4-cyanovaleric acid) in 20 g of deionized water is then added to the reactor. An emulsion containing 189 g of deionized water, 30 g of 10% Rhodapex CO-436 in deionized water, 10 g of methacrylamide, 4 g of ethylene glycol dimethacrylate, 100 g of ethyl acrylate, 0.8 g of 4,4-azobis(4-cyanovaleric acid), and 66 g of propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate is added continuously for 1 hour. The reaction is allowed to continue for 3 more hours before the reactor is cooled down to room temperature. The latex prepared is filtered through an ultrafine filter (5 µm cut-off) to remove any coagulum. The resultant polymer particles contain the polyfunctional monomer ethylene glycol dimethacrylate, have a polymer to ultraviolet ray absorber ratio of 2:1, and are stable against crystallization of UV absorber in the water phase outside of the polymer particles for more than 5 weeks when stored at 4 °C.

Example 2 (Comparison): Polymer particles impregnated with propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate ultraviolet ray absorber

A stirred reactor containing 559.45 g of deionized water is heated to 80 °C and purged with N_2 for 1 hour followed by addition in sequence of 15 g of 10% Rhodapex CO-436 (Rhone-Poulenc) in deionized water, 0.75 g of potassium persulfate, 0.05 g of sodium metabisulfate. An emulsion containing 10 g of ethyl acrylate, 5 g of 10% Rhodapex CO-436, 40 g of deionized water is added. The reaction is allowed to continue for 2 hour. An emulsion containing 149.5 g of deionized water, 30 g of 10% Rhodapex CO-436 in deionized water, 6.7 g of methacrylamide, 117.3 g of ethyl acrylate, 0.25 g of potassium persulfate, and 66 g of propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate is added continuously for 1 hour. The reaction is allowed to continue for 3 more hours before the reactor is cooled down to room temperature. The latex prepared is filtered through an ultrafine filter (5 µm cut-off) to remove any coagulum. The resultant polymer particles contain no polyfunctional ethylenically unsaturated monomer, have a polymer to ultraviolet ray absorber ratio of 2:1, and show massive crystallization of propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate in the aqueous phase, outside of the polymer particles after storage at 4 °C for 2 days.

Example 3 (Invention): Polymer particles impregnated with both propyl I, 2-cyano-3-(4-methoxy-phenyl)-2-propenoate and 3-di-n-hexylaminoallylidene-malononitrile ultraviolet ray absorbers

A stirred reactor containing 559.45 g of deionized water is heated to 80 °C and purged with N_2 for 1 hour followed by addition in sequence of 15 g of 10% Triton 770 (Union Carbide) in deionized water, 0.2 g of $NaHCO_3$, 0.3 g of potassium persulfate, and 0.05 g of sodium metabisulfate. An emulsion containing 5 g of 10% Triton 770 aqueous solution, 40 g of deionized water, and 10 g of ethyl methacrylate is added to the reactor. The reaction is allowed to continue for an additional 2 hours. 0.2 g of 4,4-azobis(4-cyanovaleric acid) in 20 g of deionized water is then added to the reactor. An emulsion containing 149 g of deionized water, 30 g of 10% Triton 770 in deionized water, 6 g of 2-acrylamido-2-methylpropane sufonic acid, 2.4 g of ethylene glycol dimethacrylate, and 101.6 g of ethyl methacrylate, 0.8 g of 4,4-azobis(4-cyanovaleric acid), 40 g of propyl I, 2-cyano-3-(4-methoxyphenyl)-2-propenoate, and 40 g of 3-di-n-hexylaminoallylidene-malononitrile is added continuously for 1 hour. The reaction is allowed to continue for 3 more hours before the reactor is cooled down to room temperature. The latex prepared is filtered through an ultrafine filter (5 µm cut-off) to remove any coagulum. The resultant polymer particles contain the polyfunctional monomer ethylene glycol dimethacrylate, have a polymer to ultraviolet ray absorber ratio of 1.5:1, and are stable against crystallization or leaching of UV absorbers into the water phase outside of the polymer particles for more than 4 months when stored at 4 °C.

Example 4 (Comparison): Polymer particles impregnated with propyl I, 2-cyano-3-(4-methoxyphenyl)-2-propenoate ultraviolet ray absorber

A stirred reactor containing 559.39 g of deionized water is heated to 80 °C and purged with N_2 for 1 hour followed by addition in sequence of 15 g of 10% Rhodapex CO-436 (Rhone-Poulenc) in deionized water, 0.22 g of $NaHCO_3$, 0.34 g of potassium persulfate, 0.06 g of sodium metabisulfate. An emulsion containing 10 g of methyl methacrylate, 5 g of 10% Rhodapex CO-436, 40 g of deionized water is added. The reaction is allowed to continue for 2 hour. 0.2 g of 4,4-azobis(4-cyanovaleric acid) in 20 g of deionized water is then added to the reactor. An emulsion containing 148.9 g of deionized water, 30 g of 10% Rhodapex CO-436 in deionized water, 140 g of methy methacrylate, 0.9 g of 4,4-azobis(4-cyanovaleric acid), and 50 g of propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate is added continuously for 1 hour. The reaction is allowed to continue for 3 more hours before the reactor is cooled down to room temperature. The latex prepared is filtered through an ultrafine filter (5 µm cut-off) to remove any coagulum. The resultant polymer particles contain no polyfunctional ethyleneically unsaturated monomer, have a polymer to ultraviolet ray absorber ratio of 3:1, and show crystallization of propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate in the aqueous phase after storage at room temperature for 6 days.

Example 5 (Invention): Polymer particles impregnated with propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate ultraviolet ray absorber

A stirred reactor containing 559.39 g of deionized water is heated to 80 °C and purged with N_2 for 1 hour followed by addition in sequence of 15 g of 10% Rhodapex CO-436 (Rhone-Poulenc) in deionized water, 0.22 g of $NaHCO_3$, 0.34 g of potassium persulfate, 0.06 g of sodium metabisulfate. An emulsion containing 10 g of methyl methacrylate, 5 g of 10% Rhodapex CO-436, 40 g of deionized water is added. The reaction is allowed to continue for 2 hours. 0.2 g of 4,4-azobis(4-cyanovaleric acid) in 20 g of deionized water is then added to the reactor. An emulsion containing 148.9 g of deionized water, 30 g of 10% Rhodapex CO-436 in deionized water, 110 g of methy methacrylate, 30 g of ethylene glycol dimethacrylate, 0.9 g of 4,4-azobis(4-cyanovaleric acid), and 50 g of propyl I, 2-cyano-3-(4-methoxyphenyl)-2-propenoate is added continuously for 1 hour. The reaction is allowed to continue for 3 more hours before the reactor is cooled down to room temperature. The latex prepared is filtered through an ultrafine filter (5 µm cut-off) to remove any coagulum. The resultant polymer particles contain the polyfunctional monomer ethylene glycol dimethacrylate, have a polymer to ultraviolet ray absorber ratio of 3:1, and are stable against crystallization of UV absorber in the water phase outside of the polymer particles for more than 10 weeks when stored at room temperature.

Preparation of ultraviolet ray absorbing polymer particles by limited coalescence polymerization

Example 6 (Invention): Polymer particles impregnated with propyl I,2-cyano-3-(4-methoxyphenyl) -2-propenoate ultraviolet ray absorber.

An aqueous phase consisting of 1000 g deionized water, 117 g Ludox TM and 7.7 g poly(methylaminoethanol adipate) is prepared. A monomer phase consisting of 100 g methyl methacrylate, 25 g ethylene glycol dimethacrylate, 58.3 g propyl I,2-cyano-3-(4-methoxyphenyl)-2-propenoate and 4 g lauroyl peroxide is prepared. The phases are combined and the resulting mixture passed three times through a Gaulin homogenizer. The mixture is then placed in a 3 liter flask and heated at 74 °C overnight with stirring. The mixture is dialyzed to remove water miscible residuals and impurities. The resultant polymer particles contain the polyfunctional monomer ethylene glycol dimethacrylate, have a polymer to ultraviolet ray absorber ratio of 2:1, and are stable against crystallization of UV absorber in the water phase outside of the polymer particles for more than 2 months when stored at room temperature.

The above examples show that the ultraviolet ray absorbing particles of the present invention prevent diffusion and/or crystallization of the ultraviolet ray absorber out of the polymer particle during storage. This improves manufacturabililty of photographic elements employing such ultraviolet ray absorbing polymer particles.

Claims

1. An ultraviolet ray absorbing polymer particle comprising:

   a ultraviolet ray absorbing compound
   a polymer of the formula

$$(A)_x(B)_y$$

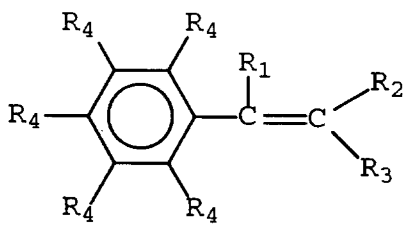
   where A is a polyfunctional ethylenically usaturated monomer,
   B is a monofunctional ethylenically unsaturated monomer,
   x is 0.1 to 90 mole %,
   y is (100-x) mole %.

2. The polymer particle according to claim 1, wherein the polyfunctional ethylenically unsaturated monomer is selected from the group consisting of esters of unsaturated monohydric alcohols with unsaturated monocarboxylic acids, dienes, esters of saturated glycols or diols with unsaturated monocarboxylic acids, and polyfunctional aromatic compounds.

3. The polymer particle according to claim 1, wherein the monofunctional ethylenically unsaturated monomer is selected from the group consisting of alkyl esters of acrylic acids, hydroxy alkyl esters of acrylic acids, nitrites of acrylic acids, amides of acrylic acids and vinyl aromatic compounds.

4. The polymer particle according to claim 1, wherein the ultraviolet ray absorbing compound is selected from the group consisting of thiazolidones, benzotriazoles, cinnamic acid esters, benzophenones, and aminobutadienes.

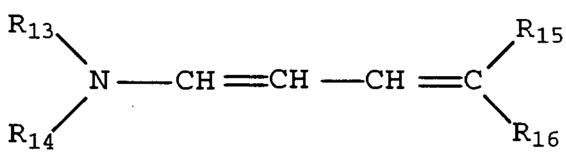
5. The polymer particle according to claim 1, wherein the ultraviolet ray absorbing compound has the general formula:



wherein R_4 is independently selected from the group consisting of hydrogen, halogen, alkyl, aryl having from 6-20 carbon atoms, alkoxy, aryloxy, alkylthio, arylthio, amine, alkylamino, arylamino, hydroxyl, cyano, nitro, acylamino, sulfonyl, sulfamido, acyloxy, and oxycarbonyl;

R_1 is a hydrogen or alkyl;
R_2 and R_3 are independently selected from the group consisting of cyano, $-COOR_9$, $CONHR_9$, SO_2R_9 where R_9 is an alkyl or aryl group.

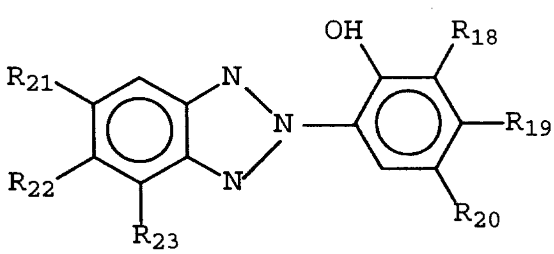
6. The polymer particle according to claim 1, wherein the ultraviolet ray absorbing compound has the general formula:



(IV)

where R_{13}, and R_{14}, is independently selected from the group consisting of hydrogen, alkyl, and aryl, R_{15} and R_{16} is independently selected from the group consisting of cyano, $-COOR_{17}$, COR_{17}, and SO_2R_{17}, where R_{17} is selected from the group consisting of alkyl, and aryl.

7. The polymer particle according to claim 1, wherein the ultraviolet ray absorbing compound has the general formula:



(V)

where R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, and R_{23} are independently selected from the group consisting of hydrogen, halogen, nitro, hydroxyl, alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, aralkylthio, akoxycarbonyl, carbamoyl, alkylsulfonyl, and mono or dialkylamino.

8. An imaging element comprising a support, at least one light-sensitive layer and at least one layer containing ultraviolet ray absorber particles comprising:

an ultraviolet ray absorbing compound
a polymer of the formula

$$(A)_x(B)_y$$

where A is a polyfunctional ethylenically usaturated monomer,
B is a monofunctional ethylenically unsaturated monomer,
x is 0.1 to 90 mole %,
y is (100-x) mole %.

9. The imaging element according to claim 8, wherein the polyfunctional ethylenically unsaturated monomer is selected from the group consisting of esters of unsaturated monohydric alcohols with unsaturated monocarboxylic acids, dienes, esters of saturated glycols or diols with unsaturated monocarboxylic acids, and polyfuntional aromatic compounds.

10. The imaging element according to claim 8, wherein the monofunctional ethylenically unsaturated monomer is selected from the group consisting of alkyl esters of acrylic acids, hydroxy alkyl esters of acrylic acids, nitrites of acrylic acids, amides of acrylic acids and vinyl aromatic compounds.