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(54) Rutile resin formula for imaging supports

(57) The present invention is an imaging resin which includes a polyolefin having dispersed therein rutile TiO_2 having a particle size from 0.1 to 0.26 microns at a concentration of at least 10 weight percent, and a dispersing agent. The resin is applied to a support to create an imaging base. A imaging layer can be superposed on the imaging base to provide an imaging element. In a preferred embodiment the imaging element is a photographic element.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to imaging papers and, more particularly to imaging papers having high sharpness, whiteness and excellent manufacturability.

BACKGROUND OF THE INVENTION

[0002] Various methods are used to improve sharpness of the silver halide photographic photosensitive material on a reflective support. One such method is to increase the fill of the white pigment in the laminated resin on a paper support (JP-A-3156452 and JP-A-3156439). However, the manufacturing costs rise with increasing TiO_2 content. Another problem with loading more TiO_2 into the resin is poor extrusion quality which results in an inferior sheet. During extrusion coating of a polymer loaded with the TiO_2 pigment, an insoluble material builds up on the die land and interferes with the extrusion process. Eventually the build-up of material will cut into the extrudate and cause streaks (hereafter referred to as die-lines) in the machine direction. The die-lines get worse with time and cause poor quality. To alleviate the poor quality, the die must be cleaned on a frequent basis. This is a costly interruption to the extrusion operation and may be required as frequently as every hour depending on the pigment, pigment surface treatment and pigment loading.

[0003] A second method to improve sharpness is to use two or more layers of water-proof resin laminated on the imaging side of the paper having differing contents ofTiO_2 (US 5,429,916). The water-proof resin layer with the lowest level of TiO_2 is placed in the resin layer nearest to the paper base (US 5,573,898). US 5,573,898 teaches the use of either a rutile or anatase TiO_2 for the photographic support. However, US 5,573,898 teaches to use an anatase TiO_2 to achieve a white support and a rutile TiO_2 to achieve a sharp support. The anatase TiO_2 required to make a white support is costly and has poor filterability and runnability problems during extrusion coating. The high levels of anatase TiO_2 in the outer resin layer cause material to build-up on the lips of the extruder and make an inferior product. This method requires either multiple passes of a single extruder or the purchase of new extruder(s) and die to make a single pass of multiple resin layers.

[0004] The third method to improve sharpness is to change from the anatase to rutile TiO_2. The refractive index of anatase TiO_2 is 2.52, while rutile TiO_2 is 2.76. Rutile TiO_2's higher refractive index allows for a lower loading of TiO_2 to get the same sharpness as a highly loaded anatase support. However, previous to the present invention, rutile TiO_2 could not provide as white and as bright a support as one with anatase TiO_2.

[0005] Imaging supports require a very white support. TiO_2 increases the reflectivity or lightness of the support. Blue colorants are added to the resin coated support to increase the apparent whiteness. As you add blue colorant the support gets darker. Although, rutile TiO_2 is intrinsically lighter than the anatase structure, the large particle rutile (>0.26 micrometers) is yellower. Therefore, substantially more blue colorant is needed for the rutile than the anatase to get an equivalently blue support. The end result is that a support loaded with rutile TiO_2 looks darker than a support having anatase TiO_2.

[0006] A fourth method to improve sharpness but maintain a white support is to combine the rutile and anatase TiO_2 (US 5,569,577). Our studies show that imaging supports with more than 5 weight percent rutile TiO_2 in combination with anatase TiO_2 eliminates the whiteness advantage of the anatase TiO_2. Additionally, the manufacturability is poor and material costs high for the anatase/rutile blend.

[0007] Inkjet and thermal imaging sharpness is not determined by the TiO_2 type or level but by the quality of the original image and the printer. However, the problem for these type of imaging supports is obtaining a very white and opaque support. The hiding power and opacity of rutile TiO_2 is superior to anatase TiO_2 but the rutile TiO_2 is too yellow.

[0008] An additional problem with anatase TiO_2 is its thermal instability. Anatase TiO_2 yellows during extrusion processing unless large amounts of a metal soap, such as calcium stearate, is added to the resin layer. The calcium stearate prevents the anatase TiO_2 from yellowing during extrusion. However, the stearate produces by-products that build up on the external extruder parts and drips down onto the finished imaging sheet causing costly defects.

[0009] Finally, the environmental impact and cost to manufacture anatase TiO_2 is inferior to the manufacture of rutile TiO_2. Rutile TiO_2 can be made by the sulfate or chloride process while the anatase TiO_2 can only be made by the sulfate process. The chloride process is environmentally more friendly than the sulfate process. The sulfate process produces a large amount of acid waste and contaminated by products.

[0010] Despite all the problems associated with anatase TiO_2, manufacturers of photographic paper typically use the anatase rather than the rutile form of TiO_2 to obtain high whiteness and brightness. However, it would be desirable to use rutile TiO_2 rather than anatase TiO_2 due to the lower cost and improved manufacturability of rutile TiO_2. Furthermore, to obtain equivalent opacity and sharpness less rutile TiO_2 than anatase TiO_2 is required. The present invention provides an imaging support using rutile TiO_2 that has high sharpness, whiteness and excellent manufacturability.

SUMMARY OF THE INVENTION

[0011] The present invention is an imaging resin which includes a polyolefin having dispersed therein rutile TiO_2 having a particle size from 0.1 to 0.26 microns at a concentration of at least 10 weight percent, and a dispersing agent. The resin is applied to a support to create an imaging base. A imaging layer can be superposed on the the imaging base to provide an imaging element. In a preferred embodiment the imaging element is a photographic element.

DETAILED DESCRIPTION OF THE INVENTION

[0012] As used herein the phrase "imaging element" is a material that may be used with the laminated support for the transfer of images to the support by techniques such as ink jet printing or thermal dye transfer as well as a support for silver halide images. As used herein, the phrase "photographic element" is a material that utilizes photosensitive silver halide in the formation of images. In the case of thermal dye transfer or inkjet, the image layer that is coated on the imaging element may be any material that is known in the art such as gelatin, pigmented latex, polyurethane, polyesters, (poly(vinyl chloride), poly(styrene-co-acrylonitrile) polycaprolactone, polyvinyl alcohol, polycarbonate, polyvinyl pyrrolidone, starch, methacrylate, polymers and co-polymers of acrylic acid, polyethylene oxide, cellulosics such as hydroxymethyl cellulose and porous receivers containing silica, sol-gels, alumina, calcium carbonate, clays, talc, zinc oxide, zeolites, barium sulfate, zinc sulfide, TiO_2or mixtures thereof. Mordants such as cationic polyester sulfonates may also be incorporated. The dye image-receiving layer may be present in any amount which is effective for the intended purpose. The photographic elements can be single color elements or multicolor elements. Multicolor elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

[0013] The reflective support of the present invention includes one or more resin coating layers on the support. One or more imaging layers may be superposed on the waterproof resin coating layers. The rutile TiO_2 is included in one or all of these resin coated layers. It is preferred to incorporate the resin layer with the lowest TiO_2 level next to the paper base.

[0014] The average pigment diameter of the rutile TiO_2 is most preferably in the range of 0.1 to 0.26 micrometers. Pigments that are greater than 0.26 micrometers are too yellow for an imaging element application and the pigments that are less than 0.1 micrometers are not sufficiently opaque when dispersed in polymers.

[0015] For a single layer structure, the rutile TiO_2 content of the resin coated layer is preferably greater than 10% and less than 50% by weight of the resin layer. If the rutile TiO_2 content is less than 10% the imaging element is inferior for sharpness and opacity. If the rutile TiO_2 content greater than 50% it will cause problems with melt fracture during extrusion. In the case of a multi-layer structure the rutile pigment may be present in one or all of the layers. The concentration of the small particle rutile in each layer preferably ranges from 0-50% by weight of the individual layer. In the layer with the highest concentration of TiO_2, the rutile concentration may be from 10 to 50 weight percent of the layer.

[0016] The surface of the rutile TiO_2 can be treated with inorganic compounds such as aluminum hydroxide, alumina or silica with a fluoride compound or fluorine ions, silicon hydroxide, silicon dioxide, boron oxide, barium modified silica as described in US Pat. 4,781,761, phosphates, zinc oxide, ZrO_2, etc. and with organic treatments such as polyhydric alcohol, polyhydric amine, metal soap, alkyl titanate, polysiloxanes, etc or with a combination of the inorganic and organic treating agents. The amount of the surface treating agents is preferably in the range of 0.2 to 2.0% for the inorganic treatment and 0.1 to 1% for the organic treatment, relative to the weight of the titanium dioxide.

[0017] Surprisingly, a sharp and white support is achieved when small particle rutile TiO_2 is incorporated in the resin layers of an imaging support. The small particle rutile TiO_2 resin layers provides an imaging support that is as white and as bright as the current anatase system.

[0018] Additionally, the small particle TiO_2 imparts high sharpness and opacity to the imaging supports. Small amounts of the small particle rutile TiO_2 can be added to an imaging support resin layer to get the same sharpness and opacity as a highly loaded anatase resin layer. The lower loading of the rutile pigment reduces cost and the propensity for die lines.

[0019] Furthermore, rutile TiO_2 does not thermally yellow during extrusion. The use of the small particle rutile TiO_2 eliminates the need to use large amounts of stearate slip agents. Reduction in stearate levels reduces the build-up of stearic acid on external extruder parts and consequently reduces imperfections and the need for cleaning of the extruder.

[0020] The use of small particle rutile in imaging resin layers produces a low cost support with high image sharpness, opacity, whiteness, and excellent manufacturability.

[0021] The polymer and the rutile TiO_2 are mixed with each other in the presence of a dispersing agent. Examples of dispersing agents are metal salts of higher fatty acids such as sodium palmitate, calcium palmitate, sodium laurate, calcium stearate, aluminum stearate, magnesium stearate, zirconium octylate, etc, higher fatty amides, and higher fatty acids. The preferred dispersing agent is sodium stearate and the most preferred dispersing agent is zinc stearate. Both of these dispersing agents give superior whiteness to the resin coated layer.

[0022] For photographic use, a white base with a slight bluish tint is preferred. The layers of the water-proof resin coating preferably contain colorants such as a bluing agent and magenta or red pigment. Applicable bluing agents include commonly know pigments, such as ultramarine blue, cobalt blue, oxide cobalt phosphate, quinacridone pigments, and a mixture thereof. Applicable red or magenta colorants are quinacridones and ultramarines.

[0023] The water-proof resin may also include a fluorescing agent which absorbs energy in the UV region and emits light largely in the blue region. Any one or a combination of the optical brighteners referred to in US patent 3,260,715 can be incorporated into the resin coating.

[0024] The water-proof resin coating may also contain an antioxidant(s) such as hindered phenol primary antioxidants used alone or in combination with a secondary antioxidants. Examples of hindered phenol primary antioxidants include pentaerythrityl tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl)proprionate] (such as Irganox 1010), octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)proprionate (such as Irganox 1076), benzenepropanoic acid 3,5-bis(1,1-dimethyl)-4-hydroxy-2[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropyl)hydrazide (such as Irganox MD1024), 2,2'-thiodiethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)proprionate] (such as Irganox 1035), 1,3,5-trimethyl-2,4,6-tri(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene (such as Irganox 1330), but are not limited to these examples. Secondary antioxidants include organic alkyl and aryl phosphites including examples such as triphenylphosphite (such as Irgastab TPP), tri(n-propylphenyl-phophite) (such as Irgastab SN-55), 2,4-bis(1,1-dimethylphenyl) phosphite (such as Irgafos 168).

[0025] Suitable polyolefins for the water-proof layer(s) include polyethylene, polypropylene, polymethylpentene, polystyrene, polybutylene and mixtures thereof. Polyolefin copolymers, including copolymers of polyethylene, propylene and ethylene such as hexene, butene, and octene are also useful. Polyethylene is preferred, as it is low in cost and has desirable coating properties. As polyethylene, usable are high-density polyethylene, low-density polyethylene, linear low density polyethylene, and polyethylene blends.

[0026] Other suitable polymers that can be included in the polyolefin include polyesters produced from aromatic, aliphatic or cycloaliphatic dicarboxylic acids of 4-20 carbon atoms and aliphatic or alicyclic glycols having from 2-24 carbon atoms. Examples of suitable dicarboxylic acids include terephthalic, isophthalic, phthalic, naphthalene dicarboxylic acid, succinic, glutaric, adipic, azelaic, sebacic, fumaric, maleic, itaconic, 1,4-cyclohexanedicarboxylic, sodiosulfoisophthalic and mixtures thereof. Examples of suitable glycols include ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, other polyethylene glycols and mixtures thereof. Preferred continuous matrix polyesters are those having repeat units from terephthalic acid or naphthalene dicarboxylic acid and at least one glycol selected from ethylene glycol, 1,4-butanediol and 1,4-cyclohexanedimethanol. Poly(ethylene terephthalate), which may be modified by small amounts of other monomers, is especially preferred. Other suitable polyesters include liquid crystal copolyesters formed by the inclusion of suitable amount of a co-acid component such as stilbene dicarboxylic acid. Examples of such liquid crystal copolyesters are those disclosed in U.S. Pat. Nos. 4,420,607, 4,459,402 and 4,468,510.

[0027] Useful polyamides include nylon 6, nylon 66, and mixtures thereof Copolymers of polyamides are also suitable continuous phase polymers. An example of a useful polycarbonate is bisphenol-A polycarbonate. Cellulosic esters suitable for use as the continuous phase polymer of the composite sheets include cellulose nitrate, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate, and mixtures or copolymers thereof. Useful polyvinyl resins include polyvinyl chloride, poly(vinyl acetal), and mixtures thereof. Copolymers of vinyl resins can also be utilized.

[0028] The small particle rutile TiO_2, colorants, slip agents, optical brightener, antioxidant are incorporated either together or separately with the polymer using a mixer. A concentrate of the additives in the form of a pellet is typically made. The concentration of the rutile pigment can be from 20% to 80% by weight of the masterbatch. The master batch is then adequately diluted for use with the waterproof resin.

[0029] The support to which the water-proof resin layer is laminated may be a polymeric, a synthetic paper, cloth, woven polymer fibers, or a cellulose fiber paper support, or laminates thereof. The base also may be a microvoided polyethylene terephthalate such as disclosed in U.S. Patent Nos. 4,912,333; 4,994,312 and 5,055,371. The preferred support is a photographic grade cellulose fiber paper.

[0030] Chemical sensitization of the emulsion typically employs sensitizers such as: sulfur-containing compounds, e.g., allyl isothiocyanate, sodium thiosulfate and allyl thiourea; reducing agents, e.g., polyamines and stannous salts; noble metal compounds, e.g., gold, platinum; and polymeric agents, e.g., polyalkylene oxides. As described, heat treatment is employed to complete chemical sensitization. Spectral sensitization is effected with a combination of dyes, which are designed for the wavelength range of interest within the visible or infrared spectrum. It is known to add such dyes both before and after heat treatment.

[0031] After spectral sensitization, the emulsion is coated on a support. Various coating techniques include dip coating, air knife coating, curtain coating and extrusion coating.

[0032] The silver halide emulsions utilized in this invention may be comprised of any halide distribution. Thus, they may be comprised of silver chloride, silver chloroiodide, silver bromide, silver bromochloride, silver chlorobromide, silver iodochloride, silver iodobromide, silver bromoiodochloride, silver chloroiodobromide, silver iodobromochloride, and silver iodochlorobromide emulsions. It is preferred, however, that the emulsions be predominantly silver chloride emulsions. By predominantly silver chloride, it is meant that the grains of the emulsion are greater than 50 mole percent silver chloride. Preferably, they are greater than 90 mole percent silver chloride; and optimally greater than 95 mole percent silver chloride.

[0033] The silver halide emulsions can contain grains of any size and morphology. Thus, the grains may take the form of cubes, octahedrons, cubooctahedrons, or any of the other naturally occurring morphologies of cubic lattice type silver halide grains. Further, the grains may be irregular such as spherical grains or tabular grains. Grains having a tabular or cubic morphology are preferred.

[0034] The photographic elements of the invention may utilize emulsions as described in *The Theory of the Photographic Process*, Fourth Edition, T.H. James, Macmillan Publishing Company, Inc., 1977, pages 151-152. Reduction sensitization has been known to improve the photographic sensitivity of silver halide emulsions. While reduction sensitized silver halide emulsions generally exhibit good photographic speed, they often suffer from undesirable fog and poor storage stability.

[0035] Reduction sensitization can be performed intentionally by adding reduction sensitizers, chemicals which reduce silver ions to form metallic silver atoms, or by providing a reducing environment such as high pH (excess hydroxide ion) and/or low pAg (excess silver ion). During precipitation of a silver halide emulsion, unintentional reduction sensitization can occur when, for example, silver nitrate or alkali solutions are added rapidly or with poor mixing to form emulsion grains. Also, precipitation of silver halide emulsions in the presence of ripeners (grain growth modifiers) such as thioethers, selenoethers, thioureas, or ammonia tends to facilitate reduction sensitization.

[0036] Examples of reduction sensitizers and environments which may be used during precipitation or spectral/chemical sensitization to reduction sensitize an emulsion include ascorbic acid derivatives; tin compounds; polyamine compounds; and thiourea dioxide-based compounds described in U.S. Patents 2,487,850; 2,512,925; and British Patent 789,823. Specific examples of reduction sensitizers or conditions, such as dimethylamineborane, stannous chloride, hydrazine, high pH (pH 8-11) and low pAg (pAg 1-7) ripening are discussed by S.Collier in Photographic Science and Engineering, 23,113 (1979). Examples of processes for preparing intentionally reduction sensitized silver halide emulsions are described in EP 0 348934 A1 (Yamashita), EP 0 369491 (Yamashita), EP 0 371388 (Ohashi), EP 0 396424 A1 (Takada), EP 0 404142 A1 (Yamada), and EP 0 435355 A1 (Makino).

[0037] The photographic elements of this invention may use emulsions doped with Group VIII metals such as iridium, rhodium, osmium, and iron as described in Research Disclosure, September 1996, Item 38957, Section I, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12*a* North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND. Additionally, a general summary of the use of iridium in the sensitization of silver halide emulsions is contained in Carroll, "Iridium Sensitization: A Literature Review," Photographic Science and Engineering, Vol. 24, No. 6, 1980. A method of manufacturing a silver halide emulsion by chemically sensitizing the emulsion in the presence of an iridium salt and a photographic spectral sensitizing dye is described in U.S. Patent 4,693,965. In some cases, when such dopants are incorporated, emulsions show an increased fresh fog and a lower contrast sensitometric curve when processed in the color reversal E-6 process as described in The British Journal of Photography Annual, 1982, pages 201-203.

[0038] A typical multicolor photographic element of the invention comprises the invention laminated support bearing a cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler; a magenta image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler; and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element may contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. The support of the invention may also be utilized for black and white photographic print elements.

[0039] The photographic elements may also contain a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support, as in U.S. Patents 4,279,945 and 4,302,523. Typically, the element will have a total thickness (excluding the support) of from 5 to 30 μm.

[0040] In the following Table, reference will be made to (1) Research Disclosure, December 1978, Item 17643, (2) Research Disclosure, December 1989, Item 308119, and (3) Research Disclosure, September 1996, Item 38957, all published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND. The Table and the references cited in the Table are to be read as describing particular components suitable for use in the elements of the invention. The Table and its cited references also describe suitable ways of preparing, exposing, processing and manipulating the elements, and the images contained therein.

Reference	Section	Subject Matter
1 2 3	I,II I, II, IX, X, XI, XII, XIV, XV I, II, III, IX A & B	Grain composition, morphology and preparation. Emulsion preparation including hardeners, coating aids, addenda, etc.
1 2 3	III, IV III, IV IV, V	Chemical sensitization and spectral sensitization/desensitization
1 2 3	V V VI	UV dyes, optical brighteners, luminescent dyes
1 2 3	VI VI VII	Antifoggants and stabilizers
1 2 3	VIII VIII, XIII, XVI VIII, IX C & D	Absorbing and scattering materials; Antistatic layers; matting agents
1 2 3	VII VII X	Image-couplers and image-modifying couplers; Dye stabilizers and hue modifiers
1 2 3	XVII XVII XV	Supports
3	XI	Specific layer arrangements
3	XII, XIII	Negative working emulsions; Direct positive emulsions
2 3	XVIII XVI	Exposure
1 2 3	XIX, XX XIX, XX, XXII XVIII, XIX, XX	Chemical processing; Developing agents
3	XIV	Scanning and digital processing procedures

[0041] The photographic elements can be exposed with various forms of energy which encompass the ultraviolet, visible, and infrared regions of the electromagnetic spectrum as well as with electron beam, beta radiation, gamma radiation, x-ray, alpha particle, neutron radiation, and other forms of corpuscular and wave-like radiant energy in either noncoherent (random phase) forms or coherent (in phase) forms, as produced by lasers. When the photographic elements are intended to be exposed by x-rays, they can include features found in conventional radiographic elements.

[0042] The photographic elements are preferably exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image, and then processed to form a visible image, preferably by other than heat treatment. Processing is preferably carried out in the known RA-4™ (Eastman Kodak Company) Process or other processing systems suitable for developing high chloride emulsions.

[0043] To form the water-proof resin coating according to the present invention, the pellet containing the pigment and other additives is subjected to hot-melt coating onto a running support of paper or synthetic paper. If desired, the pellet is diluted with a polymer prior to hot melt coating. In the case of a single layer coating the resin layer may be formed by lamination. In the case of a multi-layer coating, the layers may be formed through either successive lamination or other laminations using a multi-layer extrusion die such as a die employing a feed block, a die of a multi-slot type or a multi-manifold. The die is not limited to any specific type and may be any one of the common dies such as a T-slot or coat hanger die. An exit orifice temperature in heat melt extrusion of the water-proof resin ranges from 500-660°F. Further, before coating the support with resin, the support may be treated with a activating treatment such as corona discharge, flame, ozone, plasma, or glow discharge.

[0044] The total thickness of the single layer or multi-layerwater-proof resin, which are applied to a base paper of the reflective support used in the present invention at a side for imaging, is preferably in the range of 5 to 100 micrometers and most preferably in the range of 10 to 50 micrometers.

[0045] If the waterproof layer is a multi-layer structure, then the thickness of each layer is preferably in a range from 0.5 to 50 micrometers. For example, with two layer structure of water-proofresin coating, it is preferable that a thickness of each layer ranges from 0.5 to 50 micrometers and the total thickness is in the range of 5 to 100 micrometers and most preferably in the range of 10 to 50 micrometers.

[0046] The thickness of the resin layer applied to a base paper on the side opposite the imaging element is preferably in a range from 5 to 100 micrometers and more preferably from 10 to 50 micrometers.

[0047] The surface of the water-proofresin coating at the imaging side may be a glossy, fine, silk, grain, or matte surface. On the surface of the waterproof coating on the side which is not coated with an imaging layer may also be glossy, fine, silk, or matte surface. The preferred waterproof surface for the side away from the imaging element is matte.

EXAMPLES

[0048] A photographic paper support was produced by refining a pulp furnish of 100% bleached hardwood Kraft through a double disk refiner, then a Jordan conical refiner. To the resulting pulp furnish was added 0.8% sodium stearate, 0.5% aluminum chloride, 0.15% stilbene triazine FWA, 0.2% polyamideepichlorohydrin, 0.7% anionic polyacrylamide, and 0.6% TiO2 on a dry weight basis. An about 31.5 lbs. per 1000 sq. ft. (ksf) bone dry weight base paper was made on a fourdrinier paper machine, wet pressed to a solid of 42%, and dried to a moisture of 3% using steam-heated dryers achieving an apparent density of 0.70 g/cc. The paper base was then surface sized using a vertical size press with a 16% hydroxyethylated cornstarch solution to achieve a loading of 4.2 wt. % starch. The surface sized support was dried to a moisture of 8.8% using steam-heated dryers and calendered to an apparent density of 1.08 gm/cc.

EXAMPLE 1

[0049] A blend of high and low density polyethylene was melt extruded at 600°F and a coverage of 6.0 lbs/1000ft^2 onto one side of the paper described above. On the opposite side of the paper, 5.5 lb./1000ft^2 of a low density polyethylene resin containing 12% of a 0.22μm rutile TiO_2, available from Dupont, 0.3% zinc stearate, 0.05% optical brightener, 0.1% antioxidant, 0.6% blue colorant, and 0.002% red colorant were extrusion coated at 600 °F and 30 micrometers thickness. The resulting resin coated support was sensitized as described below.

[0050] Blue sensitive emulsion (Blue EM-1) was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. Cesium pentachloronitrosylosmate was added from during the making process and potassium iodide was added towards the end of the making process to form a band of silver iodide in the grain. The resultant emulsion contained cubic shaped grains of 0.6 mm in edgelength size. This emulsion was optimally sensitized by the addition of glutaryldiaminophenyldisulfide followed by the addition of a colloidal suspension of aurous sulfide and heat ramped to 60°C during which time blue sensitizing dye, BSD-4, potassium hexachloroiridate, Lippmann bromide and 1-(3-acetamidophenyl)-5-mercaptotetrazole were added.

[0051] Green sensitive emulsion (Green EM-1) was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. Cesium pentachloronitrosylosmate was added during most of the making process. The resultant emulsion contained cubic shaped grains of 0.3 mm in edgelength size. This emulsion was optimally sensitized by the addition of a colloidal suspension of aurous sulfide and heated to 55°C. The following were then added, potassium hexachloroiridate, Lippmannbromide and green sensitizing dye, GSD-1. The finished emulsion was then allowed to cool and 1-(3-acetamidophenyl)-5-mercaptotetrazole was added a few seconds after the cool down began.

[0052] Green sensitive emulsion (Green EM-2) was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. Cesium pentachloronitrosylosmate was added during most of the making process and potassium iodide was added at towards the end of the making process to form a band of silver iodide in the grain. Further, pentachlorothiazoleiridate (III) potassium salt was added towards the end of the making process. The resultant emulsion contained cubic shaped grains of 0.22 mm in edgelength size. This emulsion was optimally sensitized by the addition of glutaryldiaminophenyldisulfide, followed by the addition of a colloidal suspension of aurous sulfide and heat ramped to 60°C during which time green sensitizing dye, GSD-1, potassium hexachloroiridate, Lippmann bromide and 1-(3-acetamidophenyl)-5-mercaptotetrazole were added.

[0053] Red sensitive emulsion (Red EM-1) was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. The resultant emulsion contained cubic shaped grains of 0.4 mm in edgelength size. This emulsion was optimally sensitized by the addition of Bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate)gold(I)fluoroborate and sodium thiosulfate followed by heat digestion at 65°C. The following were then added, 1-(3-acetamidophenyl)-5-mercaptotetrazole, potassium hexachloroiridate and potassium bromide. The emulsion was cooled to 40°C and the red sensitizing dye, RSD-1, was added.

[0054] Coupler dispersions were emulsified by methods well known to the art, and the following layers were coated on a polyethylene resin coated paper support, that was sized as described in U.S. Patent 4,994,147 and pH adjusted as described in U.S. Patent 4,917,994. The polyethylene layer coated on the emulsion side of the support contained a mixture of 0.1 % (4,4'-bis(5-methyl-2-benzoxazolyl) stilbene and 4,4'-bis(2-benzoxazolyl) stilbene, 12.5 % TiO2, and 3 % ZnO white pigment. The layers were hardened with bis(vinylsulfonyl methyl) ether at 1.95 % of the total gelatin weight.

Layer 1: Blue Sensitive Layer

[0055]

Gelatin	1.133 g/m^2
Blue Sensitive Silver (Blue EM-1)	0.186g Ag/m^2
Y-4	0.420 g/m^2
ST-23	0.420 g/m^2
Dibutyl phthalate	0.186 g/m^2
ST-16	0.010 g/m^2

Layer 2: Interlayer

[0056]

Gelatin	0.650 g/m^2
Di-*t*-octyl hydroquinone	0.056 g/m^2
Dibutyl phthalate	0.163 g/m^2

Layer 3: Green Sensitive Layer

[0057]

Gelatin	1.087 g/m^2
Green Sensitive Silver (Green EM-1)	0.067g Ag/m^2
M-7	0.280 g/m^2
Dibutyl phthalate	0.076 g/m^2

(continued)

Diundecyl phthalate	0.033 g/m^2
ST-8	0.019 g/m^2
ST-21	0.167 g/m^2
ST-22	0.530 g/m^2

Layer 4: UV Interlayer

[0058]

Gelatin	0.630 g/m^2
UV-1	0.028 g/m^2
UV-2	0.158 g/m^2
Di-*t*-octyl hydroquinone	0.046 g/m^2
1,4-Cyclohexylenedimethylene bis(2-ethylhexanoate)	0.032 g/m^2
Dibutyl phthalate	0.032 g/m^2

Layer 5: Red Sensitive Layer

[0059]

Gelatin	1.170 g/m^2
Red sensitive silver (Red EM-1)	0.160g Ag/m^2
C-3	0.365 g/m^2
Dibutyl phthalate	0.362 g/m^2
UV-2	0.230 g/m^2
2-(2-butoxyethoxy)ethyl acetate	0.028 g/m^2
Di-*t*-octyl hydroquinone	0.003 g/m^2
Potassium tolylthiosulfonate	0.0023 g/m^2
Potassium tolylsulfinate	0.0002 g/m^2

Layer 6: UV Overcoat

[0060]

Gelatin	0.446 g/m^2
UV-1	0.019 g/m^2
UV-2	0.111 g/m^2
Di-*t*-octyl hydroquinone	0.033 g/m^2

(continued)

1,4-Cyclohexylenedimethylene bis(2-ethylhexanoate)	0.022 g/m^2
Dibutyl phthalate	0.022 g/m^2

Layer 7: SOC

[0061]

Gelatin	0.557 g/m^2
Di-*t*-octyl hydroquinone	0.019 g/m^2
Silica	0.204 g/m^2
Polydimethylsiloxane	0.017 g/m^2
SF-2	0.002 g/m^2
Tergitol 15-S-5	0.002 g/m^2

EXAMPLE 2

[0062] A blend of high and low density polyethylene was melt extruded at 600°F and a coverage of 6.0 lbs/1000ft^2 onto one side of the paper described above. On the opposite side of the bleached Kraft paper, 5.5 lb/1000ft^2 of a polyethylene resin containing 12 weight % of a 0.22μ rutile TiO_2, 0.3 weight % sodium stearate, 0.05 weight % optical brightener, 0.1 weight % antioxidant, 0.6 weight % blue colorant, and 0.002 weight % red colorant are extrusion coated at 600F onto photographic paper. The resulting resin coated support was sensitized as described in Example 1.

EXAMPLE 3

[0063] A blend of high and low density polyethylene was melt extruded at 600°F and a coverage of 6.0 lbs/1000ft^2 onto one side of the paper described above. On the opposite side of the bleached Kraft paper, 5.5 lb./1000ft^2 of a polyethylene resin containing 12 weight % of a 0.22μ rutile TiO_2, 0.3 weight % Kemamide w40 fatty bisamide , 0.05 weight % optical brightener, 0.1 weight % antioxidant, 0.6 weight % blue colorant, and 0.002 weight % red colorant are extrusion coated at 600 °F onto photographic paper. The resulting resin coated support was sensitized as described in Example 1.

COMPARATIVE EXAMPLE 1

[0064] A blend of high and low density polyethylene was melt extruded at 600 °F and a coverage of 6.0 lbs/1000ft^2 onto one side of the paper described above. On the opposite side of the bleached Kraft paper, 5.5 lb./1000ft^2 of a polyethylene resin containing 14.5 weight % of a 0.18μm anatase TiO_2, 0.5 weight % calcium stearate, 0.05 weight % optical brightener, 0.1 weight % antioxidant, 0.6 weight % blue colorant, and 0.002 weight % red colorant are extrusion coated at 600 °F onto photographic paper. The resulting resin coated support was sensitized as described in Example 1.

EXAMPLE 4

[0065] The polyethylene resin containing 12% of a 0.22μm rutile TiO_2, 0.5 weight % zinc stearate, 0.05 weight % optical brightener, 0.1 weight % antioxidant, 0.6 weight % blue colorant, and 0.002 weight % red colorant from example 1 was tested for die line propensity by extruding the resin on a 1.5" Egan extruder. The resin was dried for 17 hours in a desiccant (-7.5°F dew point) hot air (180°F) drier. The resins were extruded are 587°F at a rate of about 50-60 lb/hour with a die gap of 30 mils. The resins were extruded in the drool mode (no coating just running into a cool water bath) at 130 RPM's. Six pounds of resin blend per 1000 square feet was coated onto standard photographic grade paper every 30 minutes. The metric used to determine the time to die-lines was the time it took for the first die-line to show up on the resin coated sheet.

EXAMPLE 5

[0066] The polyethylene resin containing 12 weight % of the 0.22μm rutile TiO_2, 0.3 weight % Kemamide w40 fatty bisamide , 0.05 weight % optical brightener, 0.1 weight % antioxidant, 0.6 weight % blue colorant, and 0.002 weight % red colorant from example 3 was tested for die line propensity by extruding the resin on a 1.5" Egan extruder. The resin was dried for 17 hours in a desiccant (-7.5 °F dew point) hot air (180 °F) drier. The resins were extruded are 587 °F at a rate of about 50-60 lb./hour with a die gap of 30 mils. The resins were extruded in the drool mode at 130 RPM's (no coating just running into a cool water bath). Six pounds of resin blend per 1000 square feet was coated onto standard photographic grade paper every 30 minutes. The metric used to determine the time to die-lines was the time it took for the first die-line to show up on the resin coated sheet.

COMPARATIVE EXAMPLE 2

[0067] The resin formulation from comparative example 1 was tested for die line propensity by extruding the resin on a 1.5" Egan extruder. The resin was dried for 17 hours in a desiccant (-7.5 °F dew point) hot air (180 °F) drier. The resins were extruded are 587 °F at a rate of about 50-60 lb./hour with a die gap of 30 mils. The resins were extruded in the drool mode at 130 RPM's (no coating just running into a cool water bath). Six pounds of resin blend per 1000 square feet was coated onto standard photographic grade paper every 30 minutes. The metric used to determine the time to die-lines was the time it took for the first die-line to show up on the resin coated sheet.

[0068] Samples of example 1-3 and comparative example 1 were chemically photo processed (with no exposure) to yield a sample of minimum dye density. The samples minimum dye samples were tested for color using a spectrogard colorimeter (Table 1).

Table 1

Colorimetry						
Resin	UVO L*	UVO a*	UVO b*	UVI L*	UVI a*	UVI b*
Example 1	91.61	-0.21	-2.17	91.76	0.12	-3.54
Example 2	91.73	-0.10	-2.10	91.86	0.25	-3.60
Example 3	91.70	-0.65	-2.05	91.87	-0.35	-3.48
Comparative Example 1	91.65	-0.57	-1.33	91.84	0.05	-3.51
L* is the lightness, a* the redness, and b* the blueness of the support. Higher L* values are lighter, higher a* are redder, lower b*'s are bluer. The lighter and bluer the support the more white the support appears. For the photographic system, L* is a function of b*. To make a support more blue, one can add more blue colorant, but the lightness will be reduced. UVO measurements are equivalent to tungsten lighting, UVI is equivalent to fluorescent lighting. UVO measurements at equivalent L* values, the rutile support is ~0.7 b* units bluer while UVI, the support are essentially equivalent in b*. A value of 0.4 b* is noticeably bluer to the average person. Therefore, in typical room light the rutile support will appear whiter than the anatase support and in florescent lighting the rutile and anatase support will appear to be equally white.						

[0069] The samples were assessed visually in various types of lighting (D5500, fluorescent and tungsten). A visual assessment correlated well with the spectrogard data, the invention was equivalent to or superior to the comparative example.

Table 2

Sharpness		
Resin	TiO_2 concentration (wt%)	13" DMT's
Example 1	12	42.81
Example 2	12	42.75

Table 2 (continued)

Sharpness		
Resin	TiO_2 concentration (wt%)	13" DMT's
Example 3	12	42.83
Comparative Example 1	14.5	42.20
DMT Sharpness is a directly proportional to the anatase or rutile TiO_2 concentration. Although the rutile TiO_2 examples contain 17% less TiO_2, the sharpness of the invention is superior to the comparative example.		

Table 3

Die line results		
Resin	TiO_2	Time to die lines (hrs)
Example 4	small particle rutile	22
Example 5	small particle rutile	24
Comparative Example 2	Anatase	8

[0070] Both examples of the invention ran over 2X longer than the anatase comparison sample.

Claims

1. An imaging resin comprising:

    a polyolefin having dispersed therein rutile TiO_2 having a particle size of from 0.1 to 0.26 microns at a concentration of at least 10 weight percent, and a dispersing agent.

2. The imaging resin of claim 1 wherein the polyolefin is selected from the group consisting of polyethylene, polypropylene, polymethylpentene, polystyrene and polybutylene.

3. The imaging resin of claim 1 wherein the rutile TiO_2 has a surface treated with aluminum hydroxide, silicon hydroxide, phosphates, zinc oxide, ZrO_2, polyhydric alcohol, polyhydric amine, metal soap, alkyl titanate or polysiloxanes.

4. The imaging resin of claim 1 further comprising colorants, slip agents, optical brighteners or antioxidants.

5. An imaging base comprising;

    a support having a front side and a back side;
    a polyolefin resin superposed on at least one side of the support, having dispersed therein rutile TiO_2 having a particle size of from 0.1 to 0.26 microns at a concentration of at least 10 weight percent, and a dispersing agent.

6. The imaging base of claim 5 wherein the polyolefin is selected from the group consisting of polyethylene, polypropylene, polymethylpentene, polystyrene and polybutylene.

7. The imaging base of claim 5 wherein the rutile TiO_2 has a surface treated with aluminum hydroxide, silicon hydroxide, phosphates, zinc oxide, ZrO_2, polyhydric alcohol, polyhydric amine, metal soap, alkyl titanate or polysiloxanes.

8. The imaging base of claim 5 wherein the resin further comprises colorants, slip agents, optical brighteners or antioxidants.

9. The imaging base of claim 5 wherein the support comprises paper, cloth, woven polymeric fibers or laminates thereof.

10. An imaging element comprising;

a support having a front side and a back side;
a polyolefin resin superposed on at least one side of the support, having dispersed therein rutile TiO_2 having a particle size of from 0.1 to 0.26 microns at a concentration of at least 10 weight percent, and a dispersing agent; and
an imaging layer superposed on the polyolefin resin..

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 1617

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 September 1999	Buscha, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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