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(54) **Imaging element comprising an improved electrically conductive layer containing acicular metalcontaining particles**

(57) The present invention is an imaging element which includes a support, an image-forming layer superposed on the support and an electrically-conductive layer superposed on the support. The electrically-conductive layer contains a film-forming binder and acicular, crystalline single-phase, electrically-conductive metal-containing particles. The acicular, crystalline single-phase, conductive metal-containing particles have a di-

ameter less than or equal to 0.02 μm and an aspect greater than or equal to 3:1. The electrically-conductive layer is formed by dispersing the acicular particles using polymeric milling media having a size less than 350 μm to form a colloidal dispersion, combining the colloidal dispersion with the film forming binder to form a mixture, coating the mixture onto the support and drying the mixture to form the electrically-conductive layer.

EP 0 947 878 A2

Description**FIELD OF THE INVENTION**

5 **[0001]** This invention relates generally to imaging elements comprising a support, one or more image-forming layers, and one or more transparent, electrically-conductive layers. More specifically, this invention relates to photographic and thermally-processable imaging elements comprising one or more sensitized silver halide emulsion layers and one or more electrically-conductive layers, the conductive layers comprising acicular metal-containing conductive nano-sized particles dispersed using polymeric milling media as a colloidal dispersion in one or more film-forming binders.

BACKGROUND OF THE INVENTION

10 **[0002]** Problems associated with the generation and discharge of electrostatic charge during the manufacture and use of photographic film and paper have been recognized for many years by the photographic industry. The accumulation of charge on film or paper surfaces can cause difficulties in support conveyance as well as lead to the attraction of dust, which can produce fog, desensitization, repellency spots during emulsion coating, and other physical defects. The discharge of accumulated static charge during or after the application of the sensitized emulsion layer(s) can produce irregular fog patterns or static marks in the emulsion. The severity of the static problems has been exacerbated greatly by increases in sensitivity of new emulsions, increases in coating machine speeds, and increases in post-coating drying efficiency. The charge generated during the coating process results primarily from the tendency of webs of high dielectric constant polymeric film base to undergo triboelectric charging during winding and unwinding operations, during conveyance through the coating machines, and during post-coating operations such as slitting, perforating, and spooling. Static charge can also be generated during the use of the finished photographic product. In an automatic camera, the repeated winding and unwinding of the photographic film in and out of the film cassette can result in the generation of electrostatic charge, especially in a low relative humidity environment. The accumulation of charge on the film surface results in the attraction and adhesion of dust to the film and can even produce static marking. Similarly, high-speed automated film processing equipment can generate static that produces marking. Sheet films are especially subject to static charging during use in automated high-speed film cassette loaders (e.g., x-ray films, graphic arts films, etc.).

20 **[0003]** In order to eliminate problems arising from electrostatic charging, there are various well known methods by which an electrically-conductive antistatic layer can be introduced into the photographic element to dissipate accumulated static charge, for example, as a subbing layer, an intermediate layer, and especially as an outermost layer overlying a silver halide emulsion layer, as a backing layer on the opposite side of the support from the silver halide emulsion layer(s) or on both sides of the support. A wide variety of conductive antistatic agents can be incorporated in antistatic layers to produce a broad range of surface electrical conductivities. Many of the traditional antistatic layers used in photographic elements employ materials which exhibit predominantly ionic conductivity. Antistatic layers containing simple inorganic salts, alkali metal salts of surfactants, alkali metal ion-stabilized colloidal metal oxide sols, ionic conductive polymers or polymeric electrolytes containing alkali metal salts and the like have been taught in prior art. The electrical conductivities of such ionic conductors are typically strongly dependent on the temperature and relative humidity of the surrounding environment. At low relative humidities and temperatures, the diffusional mobilities of the charge-carrying ions are greatly reduced and the bulk conductivity is substantially decreased. Further, at high relative humidities, an unprotected antistatic backing layer can absorb water, swell, and soften. Especially in the case of roll films, this can result in the adhesion (*viz.*, ferrotyping) and even physical transfer of portions of a backing layer to a surface layer on the emulsion side of the film (*viz.*, blocking).

25 **[0004]** Antistatic layers containing electronic conductors such as conjugated conductive polymers, conductive carbon particles, crystalline semiconductor particles, amorphous semiconductive fibrils, and continuous semiconductive thin films can be used more effectively than ionic conductors to dissipate static charge since their electrical conductivity is independent of relative humidity and only slightly influenced by ambient temperature. Of the various types of electronic conductors, electrically-conductive metal-containing particles, such as semiconductive metal oxides, are particularly effective when dispersed with suitable polymeric film-forming binders. Binary metal oxides doped with appropriate donor heteroatoms or containing oxygen deficiencies have been disclosed in prior art to be useful in antistatic layers for photographic elements, for example: U.S. Patent Nos. 4,275,103; 4,416,963; 4,495,276; 4,394,441; 4,418,141; 4,431,764; 4,495,276; 4,571,361; 4,999,276; 5,122,445; 5,294,525; 5,382,494; 5,459,021; and others. Suitable claimed conductive metal oxides include: zinc oxide, titania, tin oxide, alumina, indium oxide, silica, magnesia, zirconia, barium oxide, molybdenum trioxide, tungsten trioxide, and vanadium pentoxide. Preferred doped conductive metal oxide granular particles include Sb-doped tin oxide, Al-doped zinc oxide, and Nb-doped titania. Additional preferred conductive ternary metal oxides disclosed in US Patent No. 5,368,995 include zinc antimonate and indium antimonate. Other suitable conductive metal-containing granular particles including metal borides, carbides, nitrides, and silicides

have been disclosed in Japanese Kokai No. JP 04-055,492.

[0005] Antistatic backing or subbing layers containing colloidal amorphous vanadium pentoxide, especially silver-doped vanadium pentoxide, are described in U.S. Patent Nos. 4,203,769 and 5,439,785. Colloidal vanadium pentoxide is composed of highly entangled microscopic fibrils or ribbons 0.005-0.01 μm wide, 0.001 μm thick, and 0.1-1 μm in length. However, colloidal vanadium pentoxide is soluble at the high pH typical of developer solutions for wet photographic film processing and must be protected by a nonpermeable, overlying barrier layer as taught in U.S. Patent Nos. 5,006,451; 5,221,598; 5,284,714; and 5,366,855, for example. Alternatively, a film-forming sulfopolyester latex or polyesterionomer binder can be combined with colloidal vanadium pentoxide in the conductive layer to minimize degradation during processing as taught in U.S. Patent Nos. 5,360,706; 5,380,584; 5,427,835; 5,576,163; and others. While the use of a polyesterionomer binder provides improved coating solution stability and enhanced interlayer adhesion, a hydrophobic overcoat must be provided in order to ensure the degree of process-surviving capabilities desirable for photographic imaging elements. The need to overcoat the antistatic layer with such a hydrophobic barrier layer has several potential disadvantages including increased manufacturing cost and complexity; inability to use the antistatic layer as the outermost layer; and limited ability to overcoat the antistatic layer directly with a hydrophilic, water permeable layer such as a curl control layer or pelloid. Thus, it is desirable to avoid the use of a hydrophobic barrier layer overlying an antistatic layer in a photographic element.

[0006] Conductive backing and subbing layers for silver halide photographic films containing "short fibre", "needle-like" or "fibrous" conductive materials have been described in U.S. Patent Nos. 4,999,276; 5,122,445; European Patent Appln. No. 404,091; and Japanese Kokai Nos. JP 59-06235, 04-97339, 04-27937, 04-29134 and 04-97339. Examples of such fibrous conductive materials include acicular nonconductive metal oxide particles, such as TiO_2 or $\text{K}_2\text{Ti}_6\text{O}_{13}$ that have been coated with a thin conductive layer of antimony-doped SnO_2 fine particles. A photographic film having a conductive subbing or backing layer containing such acicular conductive TiO_2 particles and a transparent magnetic recording layer has been disclosed in U.S. Patent No. 5,459,021. The average size of the acicular conductive TiO_2 particles was 0.2 μm in diameter and 2.9 μm in length. The acicular conductive TiO_2 particles are commercially available from Ishihara Sangyo Kaisha under the tradename "FT-2000". However, because of their large size, conductive layers containing these acicular particles were described as exhibiting fine cracks which resulted in decreased electrical conductivity, increased haze, and decreased adhesion. Photographic films having conductive subbing, backing or surface protective layers containing acicular conductive $\text{K}_2\text{Ti}_6\text{O}_{13}$ particles at dry coverages of 0.1-10 g/m^2 are described in Japanese Kokai Nos. JP 63-98656 and 63-287849. Acicular conductive $\text{K}_2\text{Ti}_6\text{O}_{13}$ particles having an average size of 0.05-1 μm in diameter and 1-25 μm in length are commercially available from Otsuka Chemical Co. under the trade-name "Dentall WK-100S". The use of either acicular TiO_2 or $\text{K}_2\text{Ti}_6\text{O}_{13}$ conductive particles in conductive surface protective layers for photographic film is disclosed in U.S. Patent Nos. 5,122,445 and 5,582,959 and Japanese Kokai No. 63-098656 and in conductive backings for photographic paper in European Patent Application No. 616,252 and Japanese Kokai No. JP 01-262537.

[0007] Thermal recording media having electrically-conductive layers containing fibrous conductive metal oxide particles 0.3 μm in diameter and 10 μm in length are described in Japanese Kokai JP 07-295146. Thermal recording media with an antistatic layer containing acicular, conductive ZnO , Si_3N_4 or $\text{K}_2\text{Ti}_6\text{O}_{13}$ particles are disclosed in WO 91-05668.

[0008] The use of crystalline, single-phase, acicular, conductive metal-containing particles in transparent conductive layers for various types of imaging elements has been disclosed in U.S. Patent Nos. 5,719,016 and 5,731,119. Suitable acicular, conductive metal-containing particles can have a cross-sectional diameter $\leq 0.02 \mu\text{m}$ and an aspect ratio (length to cross-sectional diameter) $\geq 5:1$. Preferred acicular, conductive metal-containing particles can have an aspect ratio $\geq 10:1$. Dispersion of nanosized crystalline particles with such high aspect ratios using conventional wet milling techniques and traditional milling media is well known to be very difficult to accomplish without shattering high aspect ratio particles into lower aspect ratio fragments. Fragile crystalline particles such as highly acicular, conductive metal-containing particles often cannot be dispersed effectively because of limitations on milling intensity or duration of milling dictated by the need to minimize degradation of both morphology and the electrical properties of the particles. The use of these poor quality dispersions to prepare conductive layers for imaging elements can result in decreased conductivity as well as increased optical losses due to scattering by agglomerates of particles.

[0009] The preparation of dispersions of submicron size particles of crystalline materials useful in imaging elements (e.g., filter dyes, sensitizing dyes, image-forming couplers, antifoggants, etc.) by comminution using conventional wet milling techniques well known in the pigment and paint industry, such as high-speed mixing, ball or roller milling or high energy media milling, has been disclosed in U.S. Patent Nos. 4,940,654; European Application No. 649,858 and Japanese Examined Application No. 02-601,887. This comminution process involves physical attrition of the material useful in imaging elements using milling media generally selected from a variety of dense, hard materials, such as steel, ceramic or glass. The action of such milling media on particulate materials useful in imaging elements results in particle size reduction as well as dispersion. The resulting fine particle dispersions can be stabilized using a variety of surfactants or dispersing aids to prevent re-agglomeration of the fine particles. It also may be necessary to adjust the pH during the milling process to stabilize the dispersion. The milling energy input levels required to produce dispersions

of very small size particles also typically result in the generation of excessive amounts of attrition-related contamination from erosion of the milling media and wear of components of the milling equipment. Such attrition-related contamination is usually present in the form of dissolved species or particulates of sizes comparable to or smaller than those of the dispersed particles and can lead to both physical and sensitometric defects in imaging elements containing these contaminated dispersions. Further, heat generated during high intensity milling operations may initiate chemical reactions, introduce surface defects or promote phase changes in the material being dispersed. Thus, the physical, chemical, electrical, optical, etc. properties of the dispersed particles may differ substantially from those of the particulate materials before milling. Such variations in properties can adversely affect the performance of imaging elements containing these materials.

[0010] A wet milling process using small milling media including a polymeric resin which results in reduced levels of attrition-related contamination in dispersions of fine particles of materials useful in imaging elements has been disclosed in U.S. Patent Nos. 5,478,705; 5,500,331; 5,513,803; and 5,662,279. Preferred milling media are composed of a polymeric resin and are nominally spherical in shape, chemically and physically inert, substantially free of metals, solvents or monomers, and are sufficiently hard and tough to avoid being chipped or crushed during the dispersion process. Alternatively, the milling media can be composite particles containing a core particle with a higher density than a polymeric resin overcoated with a layer of polymeric resin. The particle size of polymeric milling media suitable for preparing dispersions of materials useful in imaging elements can range from 5 μm to 1 mm. Further, in addition to polymeric milling media, the use of more dense ceramic or steel milling media of comparable size is disclosed in U.S. Patent Nos. 5,500,331 and 5,513,803. For some materials, fine ceramic or steel milling media (<100 μm) were found to be more efficient at size reduction than polymeric milling media and to produce lower levels of contamination than conventional size milling media (>350 μm) of the prior art.

[0011] Compounds useful in imaging elements that can be dispersed by milling with polymeric milling media claimed in U.S. Patent No. 5,478,705 include dye-forming couplers, development inhibitor release couplers, development inhibitor anchimeric release couplers, masking couplers, filter dyes, thermal transfer dyes, optical brighteners, nucleators, development accelerators, oxidized development scavengers, ultraviolet radiation absorbing compounds, sensitizing dyes, development inhibitors, antifoggants, bleach accelerators, magnetic particles, lubricants, and matting agents. However, the utility of polymeric milling media to disperse electrically-conductive metal-containing particles, especially acicular, conductive metal-containing particles which can be incorporated in transparent, conductive layers useful as antistatic layers or electrodes for a variety of imaging elements as described in U.S. Patent No. 5,719,016 was neither anticipated nor disclosed.

[0012] The enhanced efficiency of conductive network formation by acicular conductive metal-containing particles relative to granular, nominally spherical conductive particles permits the preparation of conductive layers for use in imaging elements using a lower volume fraction of conductive particles relative to the film-forming binder as described in U.S. Patent Nos. 5,719,016 and 5,731,119. An increase in aspect ratio of the conductive particles results in even further improvement in efficiency of conductive network formation. However, the dispersion of very high aspect ratio crystalline particles without degrading particle morphology or electrical properties or introducing attrition-related contamination is very difficult using conventional dispersion techniques which rely on comminution and typically use ceramic or steel milling media.

[0013] Because the requirements for an electrically-conductive layer to be useful in an imaging element are extremely demanding, the art has long sought to develop improved conductive layers exhibiting a balance of the necessary chemical, physical, optical, and electrical properties. As indicated hereinabove, the prior art for providing electrically-conductive layers useful for imaging elements is extensive and a wide variety of suitable electroconductive materials have been disclosed. However, there is still a critical need in the art for improved conductive layers which can be used in a wide variety of imaging elements, which can be manufactured at a reasonable cost, which are resistant to the effects of humidity change, which are durable and abrasion-resistant, which do not exhibit adverse sensitometric or photographic effects, which exhibit acceptable adhesion to overlying or underlying layers, which exhibit suitable cohesion, and which are substantially insoluble in solutions with which the imaging element comes into contact, such as processing solutions used for photographic elements.

[0014] It is toward the objective of providing electrically-conductive layers with improved transparency and conductivity containing acicular conductive metal-containing particles that more effectively meet the diverse needs of imaging elements, especially those of silver halide-based photographic elements, but also of a wide variety of other types of imaging elements than those of the prior art that the present invention is directed.

SUMMARY OF THE INVENTION

[0015] The present invention is an imaging element which includes a support, an image-forming layer superposed on the support and an electrically-conductive layer superposed on the support. The electrically-conductive layer contains a film-forming binder and acicular, crystalline single-phase, electrically-conductive metal-containing particles. The

acicular, crystalline single-phase, conductive metal-containing particles have a diameter less than or equal to $0.02\text{ }\mu\text{m}$ and an aspect greater than or equal to 3:1. The electrically-conductive layer is formed by dispersing the acicular particles using polymeric milling media having a size less than $350\text{ }\mu\text{m}$ to form a colloidal dispersion, combining the colloidal dispersion with the film forming binder to form a mixture, coating the mixture onto the support and drying the mixture to form the electrically-conductive layer.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The present invention provides an imaging element for use in an image-forming process including a support, at least one imaging layer, and at least one electrically-conductive layer, wherein the electrically-conductive layer contains acicular, crystalline, single-phase, electrically-conductive, metal-containing particles having an average cross-sectional diameter $\leq 0.02\text{ }\mu\text{m}$ and an aspect ratio (length to cross-sectional diameter) $\geq 3:1$ dispersed in a film-forming binder. Dispersion of the acicular metal-containing conductive particles is accomplished by means of a wet milling process using fine polymeric milling media. The use of fine polymeric milling media to disperse the fragile acicular metal-containing particles minimizes degradation of the aspect ratio and preserves the required electrical properties. Conductive layers in accordance with this invention can be used to dissipate electrostatic charge as antistatic layers. In addition to providing antistatic protection, such layers also can serve as transparent electrodes for use in an image-forming process, such as in electrostatographic or dielectric imaging. One consequence of the higher effective aspect ratio of acicular metal-containing conductive particles dispersed using fine polymeric milling media, is that conductive layers of this invention typically exhibit higher levels of conductivity for a specific volume percentage of conductive particles than such layers containing acicular conductive particles dispersed using conventional ceramic milling media. The volume percent loading of acicular conductive particles in the conductive layer of this invention ranges from 1 to 70 percent. The lower volume percentage of acicular conductive particles in the conductive layer of this invention results in decreased light scattering and haze and improved adhesion of the conductive layer to the support and to underlying or overlying layers as well as improved cohesion of the conductive layer compared to conductive layers of prior art containing higher percentages of either acicular or granular conductive particles. Further, conductive layers prepared in accordance with this invention exhibit substantially lower levels of metallic, ceramic, ionic, and other types of contamination resulting from attrition of the milling media and wear of components of the milling equipment.

[0017] Conductive layers in accordance with this invention are broadly applicable to photographic, thermographic, electrothermographic, photothermographic, dielectric recording, dye migration, laser dye-ablation, thermal dye transfer, electrostatographic, electrophotographic imaging elements, and others. Details with respect to the composition and function of this wide variety of imaging elements are provided in U.S. Patent Nos. 5,719,016 and 5,731,119. Conductive layers of this invention may be present as a backing, subbing, intermediate or protective overcoat layer on either or both sides of the support. For silver halide imaging elements, the function of the conductive layer can be incorporated directly into the sensitized emulsion layer(s). Further, the conductive properties are essentially independent of relative humidity and persist even after exposure to aqueous solutions having a wide range of pH values (e.g., $2 \leq \text{pH} \leq 13$) encountered in the wet-processing of silver halide photographic films. Thus, it is not generally necessary to provide a protective overcoat overlying the conductive layer of this invention, although optional protective layers may be present in the imaging element.

[0018] As described hereinabove, the conductive layer of this invention includes acicular conductive metal-containing fine particles dispersed in a film-forming polymeric binder. It is an objective of this invention to disperse these fragile acicular conductive metal-containing particles with minimal diminution of their aspect ratio and limited degradation of their electrical properties as well as to avoid contamination of the dispersion during the dispersion process. In accordance with the preferred embodiment of this invention, dispersion of the acicular conductive metal-containing particles is accomplished by means of a wet milling process using fine polymeric milling media. The acicular, conductive metal-containing particles are single-phase, crystalline, and have nanometer-size dimensions. Suitable dimensions for the acicular conductive particles are less than $0.05\text{ }\mu\text{m}$ in cross-sectional diameter (minor axis) and less than $1\text{ }\mu\text{m}$ in length (major axis), preferably less than $0.02\text{ }\mu\text{m}$ in cross-sectional diameter and less than $0.5\text{ }\mu\text{m}$ in length, and more preferably less than $0.01\text{ }\mu\text{m}$ in cross-sectional diameter and less than $0.15\text{ }\mu\text{m}$ in length. These dimensions tend to minimize optical losses of coated layers containing such particles due to Mie-type scattering by the particles. A mean aspect ratio (major/minor axes) of at least 3:1 is suitable; a mean aspect ratio of greater than or equal to 5:1 is preferred; and a mean aspect ratio of greater than or equal to 10:1 is more preferred. An increase in mean aspect ratio of the acicular conductive particles is well known to result in an improvement in the volumetric efficiency of conductive network formation.

[0019] One particularly useful class of acicular, electrically-conductive, metal-containing particles comprises acicular, semiconductive metal oxide particles. Acicular, semiconductive metal oxide particles suitable for use in the conductive layers of this invention exhibit a specific (volume) resistivity of less than $1 \times 10^4\text{ ohm-cm}$, more preferably less than $1 \times 10^2\text{ ohm-cm}$, and most preferably, less than $1 \times 10^1\text{ ohm-cm}$. One example of such a preferred acicular semiconductive

metal oxide is the acicular electroconductive tin oxide described in U.S. Patent No. 5,575,957 which is available under the tradename "FS-10P" from Ishihara Techno Corporation. This electroconductive tin oxide are composed of acicular particles of single-phase, crystalline tin oxide doped with 0.3-5 atom percent antimony in a solid solution. The specific (volume) resistivity of the acicular tin oxide is 10-100 ohm-cm when measured as a packed powder by a method similar to that described in U.S. Patent No. 5,236,737 using a DC two-probe test cell. The mean dimensions of the acicular tin oxide particles determined by image analysis of transmission electron micrographs are approximately 0.01 μm in cross-sectional diameter and 0.1 μm in length with a mean aspect ratio of 10:1. An x-ray powder diffraction analysis of this acicular tin oxide has confirmed that it is single-phase and highly crystalline. The mean value for the x-ray crystallite size of these acicular tin oxide particles determined in the manner described in U.S. Patent No. 5,484,694 is 19-21 nm for the as-supplied dry powder. Other suitable acicular electroconductive metal oxides include, for example, a tin-doped indium sesquioxide similar to that described in U.S. Patent No. 5,580,496, but with a smaller mean cross-sectional diameter, aluminum-doped zinc oxide, niobium-doped titanium dioxide, an oxygen-deficient titanium suboxide, TiO_x , where $x < 2$ and a titanium oxynitride, TiO_xN_y , where $(x+y) \leq 2$, similar to those phases described in U.S. Patent No. 5,320,782. Additional examples of other non-oxide, acicular, electrically-conductive, metal-containing particles include selected fine particle metal carbides, nitrides, silicides, and borides.

[0020] The small average dimensions of the preferred acicular conductive metal-containing particles minimize the amount of light scattering and result in increased optical transparency and decreased haze for the conductive layers in accordance with this invention. In addition to maintaining transparency, the small average dimensions of the acicular particles also promote the formation of numerous interconnected chains of particles linked into an extended network which in turn provides a multiplicity of electrically-conductive pathways, even in thin coated layers. The higher effective aspect ratio of acicular metal-containing conductive particles dispersed using fine polymeric milling media results in greater efficiency of conductive network formation. This increased efficiency of conductive network formation results in higher levels of conductivity for a specific volume percentage of conductive particles relative to the polymeric film-forming binder in conductive layers of this invention than for such layers containing acicular conductive particles dispersed using standard ceramic or steel milling media. It is an especially important feature of this invention that it results in conductive layers which exhibit relatively high levels of electrical conductivity using relatively low volume percentages of acicular conductive metal-containing particles. Further, the resulting increase in the volume percentage of polymeric binder improves various binder-related properties of the conductive layer such as adhesion to an underlying or overlying layer as well as cohesion of the conductive layer. Also, at the lower conductive particle to binder ratios possible with acicular conductive metal-containing particles dispersed in accordance with this invention, transparency of the conductive layer is increased and surface scattering (i.e., haze) decreased.

[0021] The acicular conductive metal-containing particles can constitute 1 to 70 volume percent of the conductive layer of this invention. The amount of acicular conductive metal-containing particles contained in the conductive layer is defined in terms of volume percent rather than weight percent since the densities of the various suitable conductive acicular particles vary widely. For the preferred acicular antimony-doped tin oxide particles described hereinabove, this corresponds to tin oxide particle to polymeric binder weight ratios of from approximately 1:19 to 19:1. The optimum ratio of conductive particles to binder varies depending on particle size, binder type, and conductivity requirements of the particular imaging element. Use of significantly less than 1 volume percent of acicular conductive metal-containing particles will not provide a useful level of surface electrical conductivity. Use of significantly more than 70 volume percent of acicular conductive metal-containing particles defeats several of the objectives of this invention in that it results in reduced transparency and increased haze due to scattering losses, diminished adhesion between the conductive layer and underlying or overlying layer(s) and decreased cohesion of the conductive layer. When the conductive layers of this invention are to be used as electrodes in imaging elements, the acicular conductive metal oxide particles preferably should constitute 40 to 70 volume percent of the layer in order to obtain a suitable level of conductivity. When used as antistatic layers, it is especially preferred to incorporate the acicular conductive metal oxide particles in an amount from 1 to 50 volume percent of the electrically-conductive layer. The use of less than 50 volume percent of acicular conductive metal oxide particles results in increased transparency, decreased haze, and improved adhesion to underlying and overlying layers as well as cohesion of the conductive layer. Further, lower volume percentages of metal oxide particles results in decreased tool wear and decreased dirt generation in finishing operations. Thus, antistatic layers of this invention contain acicular, conductive, metal-containing particles in the amount of 70 volume percent or less, preferably 50 volume percent or less, more preferably 25 volume percent or less, and most preferably 10 volume percent or less.

[0022] Polymeric film-forming binders useful in conductive layers prepared by the method of this invention include: water-soluble, hydrophilic polymers such as gelatin, gelatin derivatives, maleic acid anhydride copolymers; cellulose derivatives such as carboxymethyl cellulose, hydroxyethyl cellulose, cellulose acetate butyrate, diacetyl cellulose or triacetyl cellulose; synthetic hydrophilic polymers such as polyvinyl alcohol, poly-N-vinylpyrrolidone, acrylic acid copolymers, polyacrylamide, their derivatives and partially hydrolyzed products, vinyl polymers and copolymers such as polyvinyl acetate and polyacrylate acid ester; derivatives of the above polymers; and other synthetic resins. Other

suitable binders include aqueous emulsions of addition-type polymers and interpolymers prepared from ethylenically unsaturated monomers such as acrylates including acrylic acid, methacrylates including methacrylic acid, acrylamides and methacrylamides, itaconic acid and its half-esters and diesters, styrenes including substituted styrenes, acrylonitrile and methacrylonitrile, vinyl acetates, vinyl ethers, vinyl and vinylidene halides, and olefins and aqueous dispersions of polyurethanes or polyesterionomers. Gelatin and gelatin derivatives, polyurethanes, polyesterionomers, and aqueous emulsions of vinylidene halide interpolymers are the preferred binders.

[0023] Solvents useful for preparing dispersions and coatings of conductive acicular metal-containing particles by the method of this invention include: water; alcohols such as methanol, ethanol, propanol, isopropanol; ketones such as acetone, methylethyl ketone, and methylisobutyl ketone; esters such as methyl acetate, and ethyl acetate; glycol ethers such as methyl cellusolve, ethyl cellusolve; ethylene glycol, and mixtures thereof. Preferred solvents include water, alcohols, and acetone.

[0024] In addition to binders and solvents, other components that are well known in the photographic art also can be included in the conductive layer of this invention. Other addenda, such as matting agents, surfactants or coating aids, polymer lattices to improve dimensional stability, thickeners or viscosity modifiers, hardeners or cross-linking agents, soluble antistatic agents, soluble and/or solid particle dyes, antifoggants, lubricating agents, and various other conventional additives optionally can be present in any or all of the layers of the multilayer imaging element.

[0025] Dispersions of acicular conductive metal-containing particles in a suitable liquid vehicle can be prepared in the presence of appropriate levels of optional dispersing aids, colloidal stabilizing agents or polymeric binders by any of various wet milling processes well-known in the art of pigment dispersion and paint making. Liquid vehicles useful for preparing dispersions of acicular metal-containing particles of this invention include water; aqueous salt solutions; alcohols such as methanol, ethanol, propanol, butanol; ethylene glycol; and other solvents described hereinabove. The dispersing aid can be chosen from a wide variety of surfactants and surface modifiers such as those described in U.S. Patent No. 5,145,684, for example. The dispersing aid can be present in an amount ranging from 0.1 to 20% of the dry weight of the acicular conductive particles.

[0026] Typically, the milling media can be particles, preferably nominally spherical in shape, such as polymeric resin beads. Polymeric resins which are suitable for use as polymeric milling media are chemically and physically inert, substantially free from metals, solvents, and monomers, and of sufficient hardness and toughness to enable them to avoid being fractured, chipped or crushed during the dispersion process. Suitable polymeric resins include cross-linked polystyrenes, such as polystyrene cross-linked with divinyl benzene, styrene copolymers, polycarbonates, polyacetals, such as Delrin™, vinyl chloride polymers and copolymers, polyurethanes, polyaramides, poly(tetrafluoroethylenes), e. g., Teflon™, and other fluoropolymers, high density polyethylenes, polypropylenes, cellulose ethers and esters, such as cellulose acetate, polyacrylates, such as poly(methylmethacrylate), poly(hydroxymethacrylate), and poly(hydroxyethylacrylate) silicone-containing polymers such as polysiloxanes and the like. The polymer can also be biodegradable including poly(lactides), poly(glycolide), copolymers of lactides and glycolides, polyanhydrides, poly(hydroxyethylmethacrylate), poly(iminocarbonates), poly(N-acylhydroxyproline) esters, poly(N-palmitoyl hydroxyproline) esters, ethylene-vinylacetate copolymers, poly(orthoesters), poly(caprolactones), and poly(phosphazenes). Preferred polymers for polymeric milling media in accordance with this invention are polystyrene cross-linked with divinyl benzene, polymethylmethacrylate, and polycarbonate.

[0027] The polymeric media can have a density ranging from 0.8 to 3 g/cm³. For dispersion of acicular conductive particles of this invention, a low density is preferred in order to minimize attrition and degradation of the particle aspect ratio. Higher density milling media more efficiently provide size reduction as well as dispersion. Additional size reduction is especially disadvantageous for the acicular conductive metal-containing particles useful for this invention.

[0028] Alternatively, the polymeric milling media can be particles having a core and a coating of polymeric resin thereon as disclosed in U.S. Patent No. 5,478,705. The core material can be selected from those materials known to be useful for milling media. Suitable core materials include zirconium oxides stabilized with either magnesia or yttria, zirconium silicate and related phases, glass, stainless steel, titania, alumina, beria, and other ceramic materials. However, the use of core materials with a density greater than 2.5 g/cm³, can produce milling media which cause attrition and degradation of the aspect ratio of the acicular conductive particles. The core particles can be coated with various polymer resins, such as those described hereinabove, by various techniques well-known in the art such as spray coating, fluidized bed coating, and melt coating. Adhesion of the polymer resin to the core particle can be improved by providing optional adhesion promoting or tie layers, roughening the surface of the core particle, or by corona discharge treatment, and the like. The thickness of the polymer coating preferably is less than the diameter of the core particle.

[0029] Preferred polymeric milling media for use in accordance with this invention comprise poly(styrene-co-divinylbenzene)-20/80 beads prepared as described in U.S. Patent No. 5,478,705 and European Application No. 649,858. Polymeric milling media suitable for this invention can range in size up to 350 μm. However, to ensure production of high quality dispersions and to minimize attrition and degradation of the aspect ratio of the acicular conductive particles, media with a mean particle size of less than 250 μm are preferred, less than 100 μm are more preferred, and less than

50 μm are most preferred. Use of milling media with a particle size less than 5 μm is also contemplated.

[0030] The wet milling dispersion process can be performed using any suitable type of high speed disperser or media milling apparatus. High speed dispersers can consist of a simple vessel containing a high speed mixing blade, for example, a Cowles-type sawtooth impeller, rotor-stator mixers or other conventional mixers which can produce high fluid velocity and high shear. The media milling equipment can include conventional mill designs such as a roller mill, a ball mill, a stirred ball mill, an attritor, a horizontal media mill, a vertical media mill, a sand mill, a pebble mill, a vibratory mill, a planetary mill, a shaker mill, and a bead mill. The processing time can range from 1 hour to over 100 hours depending on the particular wet milling process and apparatus chosen, the surface properties of the particular particles being dispersed, the average particle aggregate/agglomerate size, the milling media, the type and level of dispersing aid(s), and other processing conditions. For ball mills, processing times from several days to weeks may be required. The use of high energy media mills can produce comparable or superior quality dispersions at substantially shorter residence times. However, use of a simple vessel with a high-speed disperser is preferred for preparing dispersions of acicular conductive metal-containing particles using polymeric milling media in accordance with this invention because of the simplicity of design, low cost, and ease of use. Preferred vessel geometries include diameter to depth ratios of 1:1 to 1:10. Vessel volumes can range from less than 1 ml to greater than 4000 liters. A vessel cover can be used to minimize contamination during processing and maintain pressure, vacuum or inert atmosphere. Jacketed vessels which permit temperature control during processing are preferred. Processing temperatures can span the range between the freezing and boiling temperature of the liquid vehicle. Elevated pressure can be applied to control boiling at high temperatures. Suitable impeller designs include axial or radial flow impellers, pegs, disks, saw-tooth disperser impellers, etc. High-speed mixers employing radial flow are preferred because they produce both high media velocity and high shear with minimal pumping action. Mixer speeds of 1 to 50 m/sec can be used, but speeds of 20 to 40 m/sec are preferred for simple vessels. The preferred proportions of milling media, acicular conductive particles, liquid vehicle, and optional dispersing aids and colloid stabilizers can vary within wide limits and depend upon the particular acicular particles selected, the size and relative density of the polymeric milling media, the type of high-speed disperser or mill selected, as well as other process-related parameters.

[0031] Colloidal dispersions of conductive, metal-containing, acicular particles in suitable liquid vehicles can be formulated with a polymeric film-forming binder and various addenda and applied to a variety of supports to form electrically-conductive layers of this invention. Typical photographic film supports include: cellulose nitrate, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, poly(vinyl acetal), poly(carbonate), poly(styrene), poly(ethylene terephthalate), poly(ethylene naphthalate), poly(ethylene terephthalate) or poly(ethylene naphthalate) having included therein a portion of isophthalic acid, 1,4-cyclohexane dicarboxylic acid or 4,4-biphenyl dicarboxylic acid used in the preparation of the film support; polyesters wherein other glycols are employed such as, for example, cyclohexanedimethanol, 1,4-butanediol, diethylene glycol, polyethylene glycol; ionomers as described in U.S. Patent No. 5,138,024, such as polyester ionomers prepared using a portion of the diacid in the form of 5-sodiumsulfo-1,3-isophthalic acid or like ion containing monomers, polycarbonates, and the like; blends or laminates of the above polymers. Supports can be either transparent or opaque depending upon the application. Transparent film supports can be either colorless or colored by the addition of a dye or pigment. Film supports can be surface-treated by various processes including corona discharge, glow discharge, UV exposure, flame treatment, electron-beam treatment, as described in U.S. Patent No. 5,718,995; or treatment with adhesion-promoting agents including dichloro- and trichloroacetic acid, phenol derivatives such as resorcinol, 4-chloro-3-methyl-phenol and p-chloro-m-cresol; and solvent washing or can be overcoated with adhesion promoting primer or tie layers containing polymers such as vinylidene chloride-containing copolymers, butadiene-based copolymers, glycidyl acrylate or methacrylate-containing copolymers, maleic anhydride-containing copolymers, condensation polymers such as polyesters, polyamides, polyurethanes, polycarbonates, mixtures and blends thereof, and the like. Other suitable opaque or reflective supports are paper, polymer-coated paper, including polyethylene-, polypropylene-, and ethylene-butylene copolymer-coated or laminated paper, synthetic papers, pigment-containing polyesters, and the like. Of these supports, films of cellulose triacetate, poly(ethylene terephthalate), and poly(ethylene naphthalate) prepared from 2,6-naphthalene dicarboxylic acids or derivatives thereof are preferred. The thickness of the support is not particularly critical. Support thicknesses of 2 to 10 mils (50 μm to 254 μm) are suitable for photographic elements in accordance with this invention.

[0032] Dispersions containing acicular, conductive metal-containing particles, a polymeric film-forming binder, and various additives in a suitable liquid vehicle can be applied to the aforementioned film or paper supports using any of a variety of well-known coating methods. Handcoating techniques include using a coating rod or knife or a doctor blade. Machine coating methods include air doctor coating, reverse roll coating, gravure coating, curtain coating, bead coating, slide hopper coating, extrusion coating, spin coating and the like, as well as other coating methods known in the art.

[0033] The electrically-conductive layer of this invention can be applied to the support at any suitable coverage depending on the specific requirements of a particular type of imaging element. For example, for silver halide photographic films, dry coating weights of the preferred acicular antimony-doped tin oxide in the conductive layer are preferably in the range of from 0.01 to 2 g/m². More preferred dry coverages are in the range of 0.03 to 1 g/m². The

conductive layer of this invention typically exhibits a surface resistivity (20% RH, 20°C) of less than 1×10^{12} ohms/square, preferably less than 1×10^{10} ohms/square, and more preferably less than 1×10^8 ohms/square.

[0034] Conductive layers of this invention can be incorporated into multilayer imaging elements in any of various configurations depending upon the requirements of the specific imaging element. In a photographic element, for example, the conductive layer can be applied to a support as a subbing layer on either side or both sides of the film support. When a conductive layer containing acicular metal-containing particles is applied as a subbing layer under a sensitized emulsion layer, it is not necessary to apply any intermediate layers such as barrier layers or adhesion promoting layers between it and the sensitized emulsion layer, although they can optionally be present. In the case of photographic elements for direct or indirect x-ray applications, the conductive layer can be applied on either side or both sides of the film support. In one such photographic element, a conductive subbing layer is applied to only one side of the support and the sensitized emulsion coated on both sides of the support. In another type of photographic element in which a sensitized emulsion layer is coated on one side of the support and a pelloid layer containing gelatin on the opposite side of the support, the conductive layer can be applied under the sensitized emulsion layer, under the pelloid as part of a multi-component curl-control layer or on both sides of the support. Additional optional layers can be present as well. In yet another type of photographic element, a conductive subbing layer can be applied either under or over a gelatin subbing layer containing an antihalation dye or pigment. Alternatively, both antihalation and antistatic functions can be combined in a single layer containing acicular conductive particles, antihalation dye, and a binder. This hybrid layer is typically coated on the same side of the support as the sensitized emulsion layer. The conductive layer of this invention also can be used as the outermost layer of an imaging element, for example, as a protective layer overlying an image-forming layer. When the conductive layer is applied over a sensitized emulsion layer, it is not necessary to apply any intermediate layers such as barrier or adhesion-promoting layers between the conductive overcoat layer and the imaging layer(s), although they can optionally be present. Alternatively, the conductive layer of this invention also can function as an abrasion-resistant backing layer applied on the side of the support opposite to the image-forming layer. Further, the conductive layer of this invention can be applied as an outermost layer on both sides of the support. Other addenda, such as polymer lattices to improve dimensional stability, hardeners or cross-linking agents, surfactants, and other well-known additives can be present in any or all of the above mentioned layers.

[0035] In a particularly preferred embodiment, imaging elements comprising the electrically-conductive layers of this invention are photographic elements which can differ widely in structure and composition. For example, said photographic elements can vary greatly with regard to the type of support, the number and composition of the image-forming layers, and the number and types of auxiliary layers that are included in the elements. In particular, photographic elements can be still films, motion picture films, x-ray films, graphic arts films, paper prints or microfiche. It is also specifically contemplated to use the conductive layer of the present invention in small format films as described in Research Disclosure, Item 36230 (June 1994). Photographic elements can be either simple black-and-white or monochrome elements or multilayer and/or multicolor elements adapted for use in a negative-positive process or a reversal process. Suitable photosensitive image-forming layers are those which provide color or black and white images. Such photosensitive layers can be image-forming layers containing silver halides such as silver chloride, silver bromide, silver bromiodide, silver chlorobromide and the like. Both negative and reversal silver halide elements are contemplated. For reversal films, the emulsion layers described in U.S. Patent No. 5,236,817, especially examples 16 and 21, are particularly suitable. Any of the known silver halide emulsion layers, such as those described in Research Disclosure, Vol. 176, Item 17643 (December, 1978), Research Disclosure, Vol. 225, Item 22534 (January, 1983), Research Disclosure, Item 36544 (September, 1994), and Research Disclosure, Item 37038 (February, 1995) and the references cited therein are useful in preparing photographic elements in accordance with this invention. Generally, the photographic element is prepared by coating one side of the film support with one or more layers comprising a silver halide emulsion and optionally one or more subbing layers. The coating process can be carried out on a continuously operating coating machine wherein a single layer or a plurality of layers are applied to the support. For multicolor elements, layers can be coated simultaneously on the composite film support as described in U.S. Patent Nos. 2,761,791 and 3,508,947. Additional useful coating and drying procedures are described in Research Disclosure, Vol. 176, Item 17643 (December, 1978).

[0036] Imaging elements incorporating conductive layers of this invention also can comprise additional layers including adhesion-promoting layers, lubricant or transport-controlling layers, hydrophobic barrier layers, antihalation layers, abrasion and scratch protection layers, and other special function layers. Imaging elements incorporating conductive layers in accordance with this invention useful for specific imaging applications such as color negative films, color reversal films, black-and-white films, color and black-and-white papers, electrographic media, dielectric recording media, thermally processable imaging elements, thermal dye transfer recording media, laser ablation media, ink jet media and other imaging applications should be readily apparent to those skilled in photographic and other imaging arts.

[0037] The method of the present invention is illustrated by the following detailed examples of its practice. However, the scope of this invention is by no means restricted to these illustrative examples.

Preparation of Dispersions of Acicular Conductive Particles

[0038] A consistent method was used for preparing dispersions of acicular antimony-doped tin oxide used to formulate the coating solutions applied to the support for the Examples described below. This method includes the following general steps:

- (a) forming a slurry of the acicular conductive particles, vehicle, dispersant, and polymeric milling media
- (b) mixing the slurry of milling media and acicular conductive particles at high speed using a suitable disperser impeller in a mixing vessel or chamber
- (c) separating the dispersion of acicular conductive particles from the polymeric milling media by filtration

Dispersion Sample A

[0039] An aqueous slurry containing about 20 % solids by weight acicular conductive tin oxide powder was prepared by combining 50g of FS-10P (Ishihara Techno Corp.) with 500g deionized water by simple mixing and adjusting pH to > 8 using 1% NaOH solution. This premix slurry was combined with about 275g (300 cm³) of poly(styrene-co-divinylbenzene)-20/80 milling media having a mean diameter of 50 μm. The combined mixture of slurry and milling media was agitated for 96 hours in a cylindrical 1 liter water-cooled jacketed tank using a Dispermat laboratory-scale high-speed mixer with a Cowles-type saw tooth impeller (40 mm diameter) at an impeller shaft speed of 2000 rpm. A process temperature of nominally 20°C was maintained throughout processing. After 96 hours processing time, the dispersion of acicular tin oxide particles was separated from the milling media using a vacuum filtration system such as that described in U.S. Patent No. 5,662,279. This dispersion contained about 10 % solids by weight. A small sample of the dispersion was evaporated to dryness. The packed powder resistivity of the resulting powder was measured by a method similar to that described in U.S. Patent No. 5,236,737 and the result given Table 1. The average x-ray crystallite size of the acicular particles recovered from the dispersion, was determined by the method described in U.S. Patent No. 5,484,694 with the value given in Table 1. The average crystallite size of the FS-10P powder before dispersion was determined to be 19.5 nm. The powder was analyzed for trace metals by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and the results given in Table 2.

Dispersion Sample B

[0040] An aqueous slurry containing about 20 % solids by weight FS-10P acicular tin oxide powder was prepared as described above for Dispersion Sample A. This premix slurry was combined with about 275g (300 cm³) of poly(styrene-co-divinylbenzene)-20/80 milling media having a mean diameter of 50 μm and processed as for Dispersion Sample A but only for 72 hours. Small aliquots of the mixture of media and dispersion were removed after 24 and 48 hours of processing for measurement. The bulk of the dispersion of acicular tin oxide particles was separated from the milling media after 72 hours of processing using a vacuum filtration system as described for Dispersion Sample A. This dispersion contained about 14 % solids by weight. A small sample of this dispersion was evaporated to dryness. The packed powder resistivity and the average x-ray crystallite size of the acicular tin oxide particles recovered from the dispersions were determined and the values given in Table 1. The powder was analyzed for trace metals by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and the results given in Table 2.

Dispersion Sample C

[0041] An aqueous slurry containing about 20 % solids by weight FS-10P acicular tin oxide powder was prepared as described above for Dispersion Sample A except 2.2 g (1 % based on the dry weight of FS-10P) of a 45 % aqueous solution of Dequest 2006 (Monsanto Chemical Co.) was added to the slurry as a dispersing aid. This premix slurry was combined with about 275g (300 cm³) of poly(styrene-co-divinylbenzene)-20/80 milling media having a mean diameter of 50 μm and processed as in Dispersion Example B. Small aliquots of the mixture of media and dispersion were removed after 24 and 48 hours of processing for measurement. The bulk of the dispersion of acicular tin oxide particles was separated from the milling media after 72 hours of processing using a vacuum filtration system as described for Dispersion Sample A. This dispersion contained about 16 % solids by weight. A small sample of this dispersion was evaporated to dryness. The packed powder resistivity and average x-ray crystallite size of the acicular tin oxide particles recovered from the dispersions were determined and the values given in Table 1.

Dispersion Sample D

[0042] An aqueous slurry containing about 20 % solids by weight FS-10P acicular tin oxide powder was prepared

as described above for Dispersion Sample A except 4.4 g (2 % based on the dry weight of FS-10P) of a 45% aqueous solution of Dequest 2006 was added to the premix slurry as a dispersing aid. This premix slurry was combined with about 275g (300 cm³) of poly(styrene-co-divinylbenzene)-20/80 milling media having a mean diameter of 50 µm and processed as in Dispersion Sample A but only for 48 hours. After 48 hours processing, the dispersion of acicular tin oxide particles was separated from the milling media using a vacuum filtration system as described for Dispersion Sample A. This dispersion contained about 19 % solids by weight. A small sample of this dispersion was evaporated to dryness. The packed powder resistivity and average x-ray crystallite size of the acicular tin oxide particles recovered from this dispersion were determined and the values given in Table 1.

Dispersion Sample E

[0043] A dispersion of acicular FS-10P was prepared using conventional high-energy, small media milling technology. An aqueous slurry containing about 20 % solids by weight FS-10P acicular tin oxide powder was prepared as above. To the premix slurry, 4.4 g (2 % based on the dry weight of FS-10P) of a 45% aqueous solution of Dequest 2006 was added as a dispersing aid. This premix slurry was combined with about 605g (255 cm³) of standard zirconium silicate milling media having an average diameter of about 500 µm (SEPR media from Quartz Products Corp. of Plainfield, NJ) in the milling chamber of a laboratory-scale 0.3 liter Dyno Mill (manufactured by Willy A. Bachofen AG Maschinenfabrik of Basel, Switzerland) and processed for 1 hour total residence time. The media separator gap in the media mill was adjusted to 100 µm clearance in order to retain the milling media in the milling chamber. After 1 hour residence time, the dispersion of acicular tin oxide particles was discharged from the mill. This dispersion contained about 21 % solids by weight. A small sample of this dispersion was evaporated to dryness. The packed powder resistivity and average x-ray crystallite size of the acicular particles recovered from this dispersion were measured and the values given in Table 1. X-ray fluorescence analysis of the powder revealed the presence of zirconium as a major contaminant. The powder was analyzed further for trace metals by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and the results given in Table 2.

Dispersion Sample F

[0044] An aqueous slurry containing about 20 % solids by weight FS-10P acicular tin oxide powder was prepared as described above for Dispersion Sample A except 4.4 g (2 % based on the dry weight of FS-10P) of a 45 % aqueous solution of Dequest 2006 was added to the slurry as a dispersing aid. This premix slurry was combined with about 700g (300 cm³) of zirconium silicate milling media having a mean diameter of about 50 µm and processed as in Dispersion Sample A but only for 24 hours. After 24 hours processing time, the dispersion of acicular tin oxide particles was separated from the milling media using a vacuum filtration system as described for Dispersion Sample A. This dispersion contained about 25 % solids by weight. A small sample of this dispersion was evaporated to dryness. The packed powder resistivity and average x-ray crystallite size of the acicular particles recovered from this dispersion were measured and the values given in Table 1. X-ray fluorescence analysis of the powder revealed the presence of zirconium as a major contaminant. The powder was analyzed for trace metals by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and the results given in Table 2.

Dispersion Sample G

[0045] A commercial dispersion of acicular conductive tin oxide particles available under the tradename "FS-10D" from Ishihara Techno Corporation was evaluated. The dispersion contained nominally 21 % solids by weight. A small sample of the dispersion was evaporated to dryness. The packed powder resistivity and average x-ray crystallite size of the acicular particles recovered from the dispersion were measured and the values given in Table 1. X-ray fluorescence analysis of the powder also revealed the presence of zirconium as a contaminant. The powder was analyzed for trace metals by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and the results given in Table 2.

Dispersion Sample H

[0046] Another sample of commercial "FS-10D" different from Dispersion Sample G was evaluated. The dispersion contained nominally 20 % solids by weight. A small sample of the dispersion was evaporated to dryness. The packed powder resistivity and average x-ray crystallite size of the acicular particles recovered from the dispersion were measured and the values given in Table 1. X-ray fluorescence analysis of the powder also revealed the presence of zirconium as a major contaminant. The powder was analyzed for trace metals by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and the results given in Table 2.

TABLE 1

Dispersions of acicular antimony-doped tin oxide particles					
Dispersion Sample	Processing Time (hr)	Media Type	Weight % Solids	Powder Resist (ohm-cm)	Crystallite Size (nm)
A	96	polymeric	9.8	110	19
B	72	polymeric	13.8	50	19
C	72	polymeric	16.1	50	19
D	48	polymeric	19.2	90	19
E	24	50 μ m	25.4	700	16
F	1	ZrSiO ₄			
		Std ZrSiO ₄	20.7	5200	15.5
G	unknown	unknown	20.5	625	10
H	unknown	unknown	19.9	2300	10

TABLE 2 Trace metal analysis of acicular tin oxide dispersions by ICP/AES

Dispersion Sample	A	B	C	D	E	F	G	H	FS-10P
Zr*	<30	<30	<30	---	6400	11000	410	1500	<30
Si*	<3000	<3000	<3000	---	<3000	<3000	750	910	270
Al*	240	150	180	---	120	1100	<100	360	110
Fe*	610	180	160	---	2900	150	48	280	150
Cr*	110	<30	<30	---	730	<30	<30	<30	<30
Ni*	74	<30	<30	---	580	<30	<30	<30	<30
Mn*	<30	<30	<30	---	85	<30	<30	<30	<30

* Contaminant levels are given in units of µg/g.

[0047] The use of polymeric milling media produces less degradation of the electrical conductivity of the acicular conductive tin oxide particles based on the observed minimal increases in packed powder resistivity as well as the decreases for the Samples B and C processed for 72 hours compared to the value measured for the FS-10P powder before processing (i.e., 90 ohm-cm). These packed powder resistivity values are also much lower than those obtained for samples either processed for 24 hours using 50 µm ZrSiO₄ media or milled for only 1 hour using standard ZrSiO₄ media in a media mill. Further, these values are much lower than those for either of the commercial dispersion samples. A comparison of the x-ray crystallite size for the FS-10P samples dispersed using polymeric milling media with those for samples milled using ceramic media revealed similar trends. The crystallite size was smaller for the samples milled using the ceramic media and for the commercial dispersion samples. This decrease in crystallite size is consistent with degradation of the particle morphology resulting in a decrease in the aspect ratio. Further, the levels of contaminants such as Zr, Si, and Al resulting from erosion of the ceramic milling media and the levels of Fe, Cr, Ni, and Mn resulting

from wear of the stainless steel components of the milling equipment are substantially greater for those dispersions prepared using ceramic media and the commercial dispersions than for the dispersions prepared in accordance with this invention using polymeric media. Similar decreases in contamination levels for dispersions of other materials useful in imaging elements prepared using polymeric media have been described in U.S. Patent No. 5,478,705.

EXAMPLE 1 (a,b)

[0048] An antistatic layer coating formulation having acicular antimony doped tin oxide particles dispersed in water with a dispersed polyurethane binder, dispersing aids, coating aids, crosslinkers, and optional additives was prepared using Dispersion Sample A. The weight ratio of acicular tin oxide to polyurethane binder was nominally 1:4. The coating formulation is given below:

Component	Weight % (wet)
Polyurethane dispersion (Witcobond W-236, Witco Chemical Co.), 20%	12.68 %
Wetting aid (Triton X-100: Rohm & Haas), 1%	3.30 %
Dispersion Sample A, 9.8%	6.47 %
Water	77.55 %

[0049] The above coating formulation was applied to a moving 4 mil polyethylene terephthalate support using a coating hopper so as to provide nominal total dry coverages of 1075 and 645 mg/m² for Example 1a and 1b, respectively. The support had been coated previously with a typical subbing layer containing a vinylidene chloride-based terpolymer latex.

[0050] The electrical performance and optical transparency of the antistatic layers described herein were evaluated. Surface electrical resistivity (SER) of conductive layers were measured at nominally 20°C and 50% relative humidity using a two-point DC probe by a method similar to that described in U.S. Patent No. 2,801,191. Total optical (ortho) and ultraviolet densities ($D_{\min}$) were evaluated at 530 nm and 380 nm, respectively using a X-Rite Model 361T transmission densitometer. Net or $\Delta UV D_{\min}$ and net or $\Delta ortho D_{\min}$ values were calculated by correcting the total optical and ultraviolet densities for the contributions from the support. Descriptions of the antistatic layers, the surface resistivity values, and the net ultraviolet and optical densities are given in Table 3.

EXAMPLES 2 - 4 (a,b)

[0051] Antistatic layer coating formulations were prepared in a similar manner to Example 1, except Dispersion Samples B-D were used rather than Dispersion Sample A. Antistatic layers were applied to the support so as to provide nominal total dry coverages of 1075 mg/m² for Samples 2a, 3a, and 4a and 645 mg/m² for Samples 2b, 3b, and 4b. Surface resistivity values and net ultraviolet and optical densities are given in Table 3. The present Examples demonstrate that excellent antistatic properties can be achieved for a variety of dispersion conditions. A comparison of the SER values for Example 4 with those for Examples 1-3 demonstrates that significant improvements in dispersion quality and consequently, conductive layer properties can be achieved through optimization of the dispersion conditions (e. g., total energy input, processing time, dispersant selection, dispersant concentration, etc.) using polymeric media in accordance with this invention.

COMPARATIVE EXAMPLES 1-4

[0052] Antistatic layers were prepared in a similar manner to Examples 1-4, except the acicular tin oxide dispersions were not prepared by the method of the present invention. Comparative Examples 1 and 2 utilized Dispersion Samples E and F, respectively, containing the same acicular tin oxide powder (FS-10P) as in Dispersion Examples A-D, but dispersed according to methods of the prior art using either conventional (>350 μ m) zirconium silicate milling media or zirconium silicate micromedia (50 μ m). Comparative Examples 3 and 4 utilized Dispersion Samples G and H which are commercial dispersions of acicular antimony-doped tin oxide available under the tradename "FS-10D" from Ishihara Techno Corporation. Surface resistivity values and net ultraviolet and optical densities are given in Table 3. Based on the data presented in Table 3, antistatic layers containing acicular tin oxide dispersed according to the present invention and a polyurethane binder clearly exhibit significantly lower surface resistivity values compared to those for prior art dispersion methods. However, there is a relatively small effect on the optical transparency. Comparative Example 1 clearly demonstrates that dispersion by conventional small media milling of acicular tin oxide using ceramic milling media produces essentially non-conductive layers even after only 1 hr of milling. Comparative Example 2 further dem-

onstrates that the use of ceramic (ZrSiO_4) milling media similar in size to the polymeric media used to prepare Dispersion Samples A, B, C, and D also results in considerable degradation of the electrical performance of antistatic layers, even for processing times significantly less than those useful in the method of the present invention. For dispersion processing times longer than 48 hours, the present invention provided antistatic layers having significantly lower surface resistivity values than such antistatic layers prepared using the commercial "FS-10D" dispersions. In the case of Dispersion Sample D having a dispersion processing time of 48 hours, antistatic layers of the present invention (e.g., Examples 4a and 4b) provided comparable antistatic and optical performance to Comparative Examples 3(a and b) and 4(a and b). Further, the dispersion process of this invention generates significantly lower levels of contamination as shown in Table 2, minimizing potential adverse sensitometric effects when antistatic layers containing these dispersions are used in photographic elements.

EXAMPLES 5-8 and COMPARATIVE EXAMPLES 5-8

[0053] Antistatic coating formulations having an acicular tin oxide to polyurethane binder weight ratio of 1:3 were prepared in a manner similar to the above Examples and Comparative Examples. The antistatic layer coating formulations were applied to the support so as to provide nominal total dry coverages of 1075 and 645 mg/m^2 . Examples 5-8 utilized Dispersion Samples A-D prepared according to the method of this invention while Comparative Examples 5-8 utilized Dispersion Samples E-H prepared according to prior art. As demonstrated in Table 3, the dispersion method of the present invention provided superior antistatic layer performance for dispersion processing times longer than 48 hours.

EXAMPLE 9 (a-c)

[0054] An antistatic coating formulation having acicular, antimony doped tin oxide particles dispersed in water with gelatin, dispersing aids, coating aids, hardeners, crosslinkers, and optional additives was prepared using Dispersion Sample A. The antistatic layer coating formulation was applied to the support so as to provide nominal total dry coverages of 1075, 645, and 430 mg/m^2 . The weight ratio of acicular tin oxide to gelatin was nominally 30:70. The coating formulation is given below:

Component	Weight % (wet)
Gelatin 5%	42.70 %
Wetting aid (Triton X-100: Rohm & Haas), 1%	3.30 %
Dispersion Sample A, 9.8%	9.34 %
2,3-dihydroxy-1,4-dioxane, 1% (as a hardener)	7.47 %
Water	37.19 %

EXAMPLES 10-11 and COMPARATIVE EXAMPLES 9-12

[0055] Antistatic coating formulations were prepared in a similar manner to that of Example 9 using Dispersion Samples B and C for Examples 10 and 11, and Dispersion Samples E-H for Comparative Examples 9-12, respectively. Surface resistivity values and net ultraviolet and optical densities are given in Table 4. The present Examples further demonstrate that the dispersion method of this invention provides improved performance for antistatic layers having acicular tin oxide particles dispersed in a hydrophilic colloid binder in addition to the superior performance demonstrated by the antistatic layers of Examples 1-8 containing a hydrophobic film-forming binder.

EXAMPLES 12-14 and COMPARATIVE EXAMPLES 13-16

[0056] Antistatic coating formulations were prepared in a similar manner to Examples 9-11 and Comparative Examples 9-12 except that the weight ratio of acicular tin oxide to gelatin was nominally 35:65. The coating formulation was applied to the support so as to provide nominal total dry coverages of 1075, 645, and 430 mg/m^2 . Values for surface resistivity, net ultraviolet and net optical densities are given in Table 4. Examples 12c and 14c exhibit surface resistivity values comparable to those of Comparative Examples 15a and 16a, demonstrating that comparable levels of electrical performance can be achieved by conductive layers prepared in accordance with this invention having acicular tin oxide dry coverages approximately 1/2 that of conductive layers containing acicular tin oxide dispersions prepared using methods of prior art.

TABLE 3. Acicular tin oxide in polyurethane

Sample	SnO ₂ Dispersion	Conductive Particle / Binder Weight Ratio	Dry Coverage (mg/m ²)	SER (log Ω /sq)	Δ UV Dmin	Δ ortho Dmin
Ex 1a	Sample A	1:4	1075	8.6	0.012	0.004
Ex 2a	Sample B	1:4	1075	8.5	0.011	0.005
Ex 3a	Sample C	1:4	1075	8.6	0.011	0.005
Ex 4a	Sample D	1:4	1075	9.6	0.014	0.004
Comp Ex 1a	Sample E	1:4	1075	13.0	0.014	0.007
Comp Ex 2a	Sample F	1:4	1075	13.5	0.012	0.007
Comp Ex 3a	Sample G	1:4	1075	9.5	0.004	0.001
Comp Ex 4a	Sample H	1:4	1075	10.8	0.006	0.003
Ex 1b	Sample A	1:4	645	9.2	0.007	0.003
Ex 2b	Sample B	1:4	645	9.1	0.008	0.003
Ex 3b	Sample C	1:4	645	9.4	0.007	0.005
Ex 4b	Sample D	1:4	645	10.9	0.011	0.003
Comp Ex 1b	Sample E	1:4	645	13.6	0.009	0.005
Comp Ex 2b	Sample F	1:4	645	13.6	0.008	0.005
Comp Ex 3b	Sample G	1:4	645	10.2	0.003	0
Comp Ex 4b	Sample H	1:4	645	10.7	0.007	0.003
Ex 5a	Sample A	1:3	1075	8.3	0.012	0.005
Ex 6a	Sample B	1:3	1075	8.0	0.012	0.006
Ex 7a	Sample C	1:3	1075	8.2	0.011	0.007
Ex 8a	Sample D	1:3	1075	9.0	0.016	0.002
Comp Ex 5a	Sample E	1:3	1075	13.7	0.020	0.008

	5	10	15	20	25	30	35	40	45	50
Comp Ex 6a				13.3	1075		1:3		Sample F	
	0.009	0.010		8.7	1075		1:3		Sample G	
	0.002	0.006		9.5	1075		1:3		Sample H	
Comp Ex 7a	0.003	0.010								
Comp Ex 8a										
Ex 5b				8.5	645		1:3		Sample A	
Ex 6b	0.004	0.008		8.5	645		1:3		Sample B	
Ex 7b	0.006	0.007		8.6	645		1:3		Sample C	
Ex 8b	0.005	0.007		9.3	645		1:3		Sample D	
Comp Ex 5b	0.003	0.012		13.4	645		1:3		Sample E	
Comp Ex 6b	0.006	0.014		13.5	645		1:3		Sample F	
Comp Ex 7b	0.007	0.008		9.0	645		1:3		Sample G	
Comp Ex 8b	0.001	0.005		9.5	645		1:3		Sample H	
	0.003	0.008								

TABLE 4. Acicular tin oxide in gelatin

Sample	SnO ₂ Dispersion	Conductive Particle / Binder Weight Ratio	Dry Coverage (mg/m ²)	SER (log Ω/sq)	Δ UV Dmin	Δ ortho Dmin
Ex 9a	Sample A	30/70	1075	7.3	0.019	0.006
Ex 10a	Sample B	30/70	1075	8.5	0.017	0.006
Ex 11a	Sample C	30/70	1075	9.8	0.019	0.005
Comp Ex 9a	Sample E	30/70	1075	12.8	0.016	0.006
Comp Ex 10a	Sample F	30/70	1075	13.3	0.014	0.002
Comp Ex 11a	Sample G	30/70	1075	11.7	0.013	0.004
Comp Ex 12a	Sample H	30/70	1075	11.7	0.013	0.003
Ex 9b	Sample A	30/70	645	7.8	0.015	0.004
Ex 10b	Sample B	30/70	645	9.2	0.015	0.004
Ex 11b	Sample C	30/70	645	10.3	0.015	0.004
Comp Ex 9b	Sample E	30/70	645	13.0	0.010	0.003
Comp Ex 10b	Sample F	30/70	645	12.9	0.011	0.004
Comp Ex 11b	Sample G	30/70	645	12.1	0.011	0.003
Comp Ex 12b	Sample H	30/70	645	11.6	0.011	0.002
Ex 9c	Sample A	30/70	430	9.6	0.011	0.004
Ex 12a	Sample A	35/65	1075	7.4	0.020	0.009
Ex 13a	Sample B	35/65	1075	7.6	0.019	0.008
Ex 14a	Sample C	35/65	1075	7.9	0.016	0.006
Comp Ex 13a	Sample E	35/65	1075	12.8	0.008	0.004
Comp Ex 14a	Sample F	35/65	1075	13.9	0.012	0.005

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Claims

1. An imaging element comprising:

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a support;

an image-forming layer superposed on the support; and

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an electrically-conductive layer superposed on the support; said electrically-conductive layer comprising a film-forming binder and acicular, crystalline single-phase, conductive metal-containing particles, said particles having a diameter less than or equal to 0.02 μm and an aspect greater than or equal to 3:1; wherein the electrically-conductive layer is formed by dispersing the acicular particles using polymeric milling media having a mean particle size less than 350 μm to form a colloidal dispersion, combining the colloidal dispersion with the film forming binder to form a mixture, coating the mixture onto the support and drying the mixture to form the electrically-conductive layer.

2. The imaging element of claim 1, wherein the acicular crystalline single phase conductive metal-containing particles comprise from 1 to 70 volume percent of said electrically-conductive layer.
3. The imaging element of claim 1, wherein the acicular crystalline single-phase conductive metal-containing particles
5 comprise from 1 to 50 volume percent of said conductive layer.
4. The imaging element of claim 1, wherein said particles comprise a dry weight coverage of from 5 to 1000 mg/m².
5. The imaging element of claim 1, wherein said electrically-conductive layer has a surface resistivity of less than 1
10 x 10¹⁰ ohms per square.
6. The imaging element of claim 1, wherein the acicular, crystalline single-phase, metal-containing particles comprise a packed powder resistivity of 10³ ohm-cm or less.
7. The imaging element of claim 1, wherein the acicular, crystalline single-phase, metal-containing particles comprise
15 acicular doped tin oxide particles, acicular antimony-doped tin oxide particles, acicular niobium-doped titanium dioxide particles, acicular metal nitrides, acicular metal carbides, acicular metal silicides, acicular metal borides and acicular tin-doped indium sesquioxide.
8. The imaging element of claim 1, wherein the fine polymeric milling media comprise cross-linked polystyrene, sty-
20 rene copolymers, polycarbonates, vinyl acetals, vinyl chloride polymers, polyurethanes, polyaramides, high density polyethylenes, polypropylenes, polyacrylates or fluoropolymers.
9. The imaging element of claim 1, wherein the mean particle size of the fine polymeric milling media is less than or
25 equal to 50 µm.
10. The imaging element of claim 1, wherein said film-forming binder of the electrically-conductive layer comprises
30 water-soluble polymers, gelatin, cellulose derivatives, water-insoluble polymer, a water-dispersible polyesterion-omers, vinylidene chloride-based terpolymers or water-dispersible polyurethanes.