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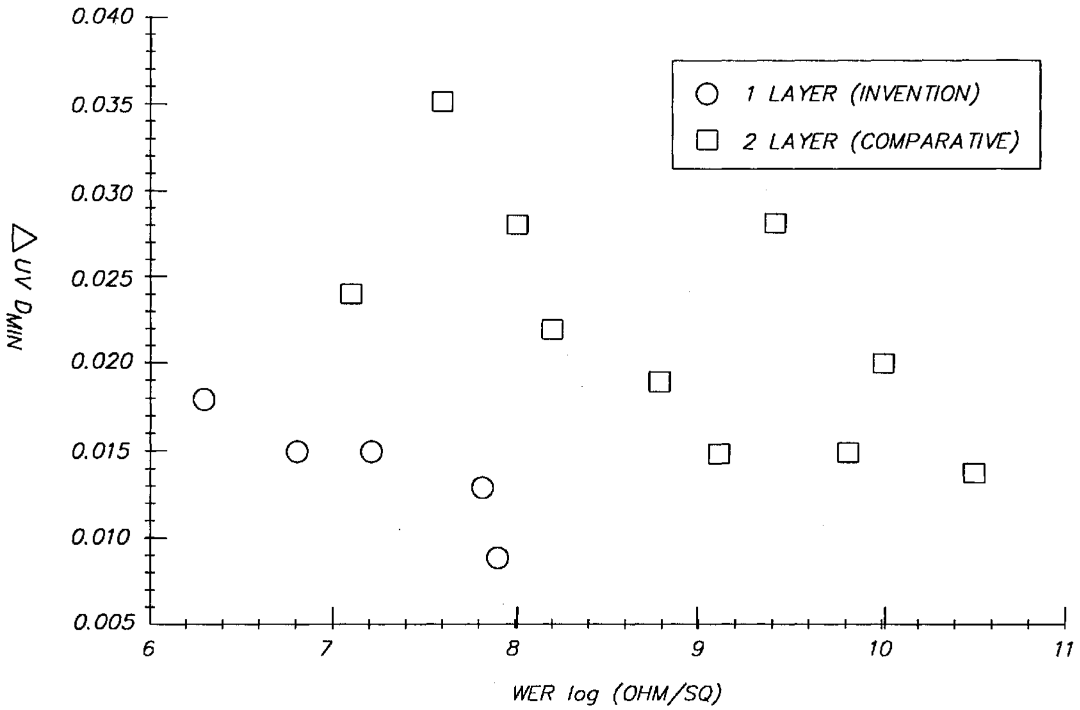
(54) Imaging element comprising an electrically-conductive backing layer containing acicular metal-containing particles

(57) The present invention is an imaging element including a support, at least one image-forming layer, and a transparent electrically-conductive, abrasion-resistant protective layer. The protective layer includes acicular, crystalline, single-phase, conductive metal-containing fine particles dispersed in a polyurethane binder at a volume ratio of conductive metal-containing particles to polyurethane binder of between 2.5 and 20 volume percent. The polyurethane binder has a tensile elongation to break of at least 50% and a Young's modulus at a 2% elongation of a least 50,000 lb/in^2.



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Description

FIELD OF THE INVENTION

[0001] This invention relates generally to imaging elements, and in particular, to photographic, thermographic, and photothermographic elements comprising a support, a silver halide imaging layer, and a transparent, electrically-conductive layer. More specifically, this invention relates to imaging elements having a transparent electrically-conductive outermost protective layer on the side of the support opposite to the imaging layer(s) which exhibits a high degree of scratch and abrasion resistance, excellent adhesion to the support, low dusting, and acceptable conveyance properties.

BACKGROUND OF THE INVENTION

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

[0003] One or more electrically-conductive antistatic layers can be incorporated into an imaging element in various ways to dissipate accumulated electrostatic charge, for example, as a subbing layer, an intermediate layer, and especially as an outermost layer either overlying the imaging layer or as a backing layer on the opposite side of the support from the imaging layer(s). A wide variety of conductive antistatic agents can be used in antistatic layers to produce a broad range of surface electrical conductivities. Many of the traditional antistatic layers used for imaging applications employ electrically-conductive materials which exhibit predominantly ionic conductivity, for example 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. 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. At high relative humidities an unprotected antistatic backing layer conataining such an ionic conducting material 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).

[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 or networks can be used more effectively than ionic conductors to dissipate charge because their electrical conductivity is independent of relative humidity and only slightly influenced by ambient temperature. Of the various types of electronic conductors disclosed in prior art, electronically-conductive metal-containing particles, such as semiconductive metal oxides, are particularly effective when dispersed with suitable polymeric binders. Antistatic layers containing granular, nominally spherical, fine particles of crystalline semiconductive metal oxides are well known and have been described extensively. 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 binary 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 electrically-conductive metal-containing granular particles including metal borides, carbides, nitrides, and silicides have been disclosed in Japanese

Kokai No. 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 a polyesterionomer binder can be combined with the colloidal vanadium oxide in the conductive layer to minimize degradation during processing as taught in U.S. Patent Nos. 5,380,584;5,427,835 ; 5,576,163; 5,360,706; and others .

[0006] When an electroconductive layer is the outermost layer on a support, it must be to protected against abrasion or scratching which may occur during handling of the photographic element in order to avoid degradation of its antistatic performance. Since the back side of an imaging element typically has more opportunity to come into direct contact with equipment surfaces and with mechanical parts during manufacture, winding and unwinding operations, use in a camera, processing, and printing or projecting the processed photographic element, it is particularly liable to abrasion damage or scratching. Scratches and abrasion marks not only degrade image quality during printing and projection processes but also in permanently damage processed photographic film. Numerous approaches to improving the resistance of the surface or outermost layers of photographic film to scratching and abrasion damage have been described in the prior art. As one of the more effective approaches, it is well known to provide at least one protective topcoat layer overlying the antistatic layer having physical properties such as increased hardness and reduced contact friction in order to enhance resistance to scratching and abrasion.

[0007] A photographic element having a conductive layer containing semiconductive tin oxide or indium oxide particles on the opposite side of the support from the silver halide sensitized emulsion layers with a polymer-containing intermediate backing layer overlying the conductive layer and an additional protective layer overlying the backing layer is disclosed in U.S. Patent No. 5,026,622. The outermost protective layer includes gelatin, a matting agent, a fluorine-containing anionic surfactant, and dioctyl sulfosuccinate. Another conductive three-layer backing having an antistatic layer containing granular semiconductive metal oxide particles; an intermediate backing layer containing a latex of a water-insoluble polymer, matting agent, polystyrenesulfonate sodium salt, and gelatin; and an outermost protective layer containing at least one hydrophobic polymer such as a polyester or polyurethane, fluorine-containing surfactant (s), matting agent(s), and an optional slipping aid is described in U.S. Patent No. 5,219,718. Further, a three-layer backing having an antistatic layer including conductive metal oxide granular particles or a conductive polymer and a hydrophobic polymer latex, gelatin, and an optional hardener is overcoated with an intermediate backing layer containing gelatin, a hydrophobic polymer latex, a matting agent, and backing dyes that is simultaneously overcoated with a protective layer comprising a fluorine-containing surfactant, a matting agent, gelatin, and optionally, a polymer latex is taught in U.S. Patent No. 5,254,448. Photographic elements including such multi-layer backings were disclosed to retain antistatic properties after processing, exhibit acceptable transport performance against Teflon coated surfaces, and have good "anti-flaw" properties.

[0008] Simplified two-layer conductive backings are taught in U.S. Patent Nos. 5,366,855; 5,382,494; 5,453,350; and 5,514,528. An antistatic layer containing colloidal silver-doped vanadium pentoxide and a vinylidene chloride-containing latex binder or a polyesterionomer dispersion coated on the opposite side of the support from the silver halide emulsion layer and subsequently overcoated with a protective layer including a coalesced layer containing both film-forming and non-film-forming colloidal polymeric particles, optional crosslinking agents, matting agents, and lubricating agents is disclosed in U.S. Patent No. 5,366,855. Such a protective layer was also disclosed to function as an impermeable barrier to processing solutions, to resist blocking, to provide good scratch and abrasion resistance, and to exhibit excellent lubricity. However, the addition of hard polymeric particles, such as poly(methylmethacrylate), to a film-forming polymer can produce brittleness in a coated layer. A photographic element containing an aqueous-coated antistatic layer containing conductive fine particles such as metal oxide particles, a butyl acrylate-containing terpolymer latex, and optionally, a hardening agent and a surfactant that is overcoated with a solvent-coated, transparent magnetic recording layer containing preferably nitrocellulose or diacetyl cellulose as the binder and carnauba wax as a lubricant is taught in U.S. Patent Nos. 5,382,494 and 5,453,350. Similarly, an antistatic layer containing conductive metal oxide granular particles in a hydrophilic binder applied as an aqueous or solvent dispersion and overcoated with a cellulose ester layer optionally containing ferromagnetic particles is described in U.S. Patent No. 5,514,528. A separate lubricating overcoat layer can be optionally applied on top of the cellulose ester layer.

[0009] The inclusion of lubricant particles of a specified size, especially those having a fluorine-containing polymer, in a protective surface or backing layer containing a dispersing aid or stabilizer, a hydrophilic or resin-type binder and optionally, crosslinking agents, matting agents, antistatic agents, colloidal inorganic particles, and various other additives is described in U.S. Patent No. 5,529,891. Photographic elements incorporating such protective layers were disclosed to exhibit improved surface scratch and abrasion resistance as evaluated on a Taber Abrader.

[0010] Another method to improve the slipperiness and scratch resistance of the back surface of a photographic element is described in U.S. Patent No. 5,565,311. The incorporation of slipping agents containing compounds having both a long-chain aliphatic hydrocarbon moiety and a polyether moiety as a solution, emulsion or dispersion preferably in a backing protective layer containing a film-forming binder and an optional crosslinking agent overlying an antistatic layer is reported to provide improved slipperiness and scratch resistance and reduce the number of coated layers in the backing. The addition of a matting agent can improve scratch resistance as well as minimize blocking of the emulsion surface layer or emulsion-side primer layer by the backing layer. Further, the inclusion of an antistatic agent, such as conductive metal oxide particles, in a backing protective layer containing slipping and matting agents and optionally, nonionic, anionic, cationic, or betaine-type fluorine-containing surfactants is disclosed in U.S. Patent No. 5,565,311.

[0011] An abrasion-resistant protective overcoat including a selected polyurethane binder, a lubricant, a matting agent, and an optional crosslinking agent overlying a conductive backing layer wherein the abrasion-resistant protective overcoat contains a crosslinked polyurethane binder, which can provide a nonpermeable chemical barrier for antistatic layers containing antistatic agents that are degraded by photographic processing such as vanadium pentoxide, as described in U.S. Patent 5,679,505. Such a protective layer also was disclosed to be useful for overcoating antistatic layers containing electroconductive metal oxide granular particles which do not require protection from photographic processing solutions. It was further disclosed that because of the high volume loading of metal oxide particles required to obtain adequate antistatic properties, the physical properties of a single-layer conductive backing are substantially degraded and the use of an abrasion-resistant overcoat is needed to obtain suitable durability of the layers.

[0012] An electrically-conductive single layer backing having a combination of electrically-conductive fine particles, such as conductive metal oxide granular particles, and particular gelatin-coated water-insoluble polymer particles is disclosed in European Patent Application No. 749,040 to provide both a high degree of conductivity at low volumetric concentrations of conductive particles and a high degree of abrasion resistance. The use of a combination of insoluble polymer particles and a hydrophilic colloid with conductive metal oxide fine particles to prepare electrically-conductive layers that require lower volume fractions of conductive particles than conductive layers prepared using only a hydrophilic colloid as binder is disclosed in U.S. Patent No. 5,340,676. A similar beneficial result is disclosed in U.S. Patent No. 5,466,567 for electrically-conductive layers in which a combination of a hydrophilic colloid and pre-crosslinked gelatin particles is used as the binder for the electroconductive fine granular particles. However, the abrasion resistance of such gelatin-containing layers is unsuitable.

[0013] Electrically-conductive backing layers for use in thermally processable imaging elements are described in U. S. Patent Nos. 5,310,640 and 5,547,821. As described in U.S. Patent No. 4,828,971, backing layers useful for thermally processable imaging elements must provide adequate conveyance properties, resistance to deformation during thermal processing, satisfactory adhesion to the support, freedom from cracking and marking, reduced electrostatic charging effects, and exhibit no sensitometric effects. The use of electrically-conductive backings and protective overcoat layers for thermally processable imaging elements is described in U.S. Patent No. 5,310,640. In one preferred embodiment, a protective layer containing polymethylmethacrylate as binder and a polymeric matting agent is positioned overlying a conductive layer containing silver-doped vanadium pentoxide dispersed in a polymeric binder. The use of a single-layer conductive backing having antimony-doped tin oxide granular particles, a matting agent, and a polymeric film-forming binder is taught in U.S. Patent No. 5,547,821. Another preferred embodiment teaches the use of antimony-doped tin oxide granular particles in a conductive overcoat layer overlying the imaging layer. The reported Taber abrasion test results suggest that the relative level of abrasion resistance for the single-layer backings is inferior to that for the overcoated conductive backing layer described in U.S. Patent No. 5,310,640. Also, surface scattering and haze is higher for single-layer conductive backings than for overcoated conductive backings. Further, from the surface resistivity and dusting data reported in U.S. Patent No. 5,547,821, It can be concluded that it is particularly difficult to simultaneously obtain low dusting and high conductivity with single-layer conductive backings containing a polyurethane binder.

[0014] An electrically-conductive single-layer backing for the reverse side of a laser dye-ablative imaging element having conductive metal-containing particles, such as antimony-doped tin oxide particles, a polymeric binder, such as gelatin or a vinylidene chloride-based terpolymer latex, a matting agent, a coating aid, and an optional hardener is described in U.S. Patent No. 5,529,884. Surface resistivity values ($\approx 10^9$ Ω/sq) for the conductive backings were measured before and after the ablation process and exhibited virtually no change. No test data for abrasion or scratch resistance of the backing layers was reported.

[0015] Conductive backing and subbing layers for graphics films containing "short fibre", "needle-like" or "fibrous" conductive materials have been described in: U.S. Patent Nos. 5,122,445; 4,999,276; European Patent Appln. No. 404,091; and Japanese Kokai No. JP 04-97339. A suitable fibrous conductive material consisting of a fibrous nonconductive TiO_2 particle coated with a thin layer of conductive metal oxide is described in Japanese Kokai No. JP 59-006235. The preferred fibrous conductive particles were disclosed to exhibit average lengths of ≤ 25 µm, diameters of ≤ 0.5 µm, and length/diameter ratio of ≥ 3.

[0016] Conductive backings for silver halide photographic films containing fibrous conductive metal oxides of Zn, Ti, Sn, Al, In, Si, Mg, Ba, Mo, W or V or multi-component oxides thereof coated at a dry coverage of 0.3 g/m^2 with an optional fluorosurfactant are described in Japanese Kokai Nos. JP04-27937 and JP 04-29134. Other photographic films in which conductive $K_2Ti_6O_{13}$ whiskers available from Otsuka Chemical Co. under the tradename "Dentall WK-100S" are incorporated in subbing, backing or surface protective layers at dry coverages of 0.1-10 g/m^2 are described in Japanese Kokai No. JP63-98656. The conductive whiskers have a thin conductive antimony-doped tin oxide layer deposited on the surface of a nonconductive $K_2Ti_6O_{13}$ core particle. A laser scanner film containing conductive $K_2Ti_6O_{13}$ whiskers 0.05-1 µm in diameter and 1-25 µm in length dispersed in the emulsion layer is described in Japanese Kokai No. JP 63-287849.

[0017] A silver halide photographic film having a conductive backing or subbing layer containing acicular TiO_2 particles surface-coated with a layer of conductive antimony-doped SnO_2 and a transparent magnetic recording layer has been disclosed in a Comparative Example in U.S. Patent No. 5,459,021.. These acicular conductive particles have an average size of 0.2 µm in diameter and 2.9 µm in length and are commercially available from Ishihara Sangyo Kaisha under the tradename "FT-2000". However, conductive layers containing these acicular particles were disclosed to exhibit fine cracks which resulted in decreased conductivity, increased haze, and decreased adhesion.

[0018] An electrically-conductive protective layer having fibrous titanium dioxide or potassium titanate particles surface-coated with electroconductive metal oxide fine particles (e.g., Sb-doped SnO_2) in combination with at least one fluorine-containing surfactant is disclosed in U.S. Patent Nos. 5,122,445 and 5,582,959 and in Japanese Kokai No. A-63-098656.

[0019] Conductive backcoatings for photographic papers having acicular TiO_2 particles or $K_2Ti_6O_{13}$ whiskers coated with a thin layer of conductive antimony-doped SnO_2 fine particles have been described in European Patent Application No. 616,252 and Japanese Kokai No. JP 01-262537.

[0020] Thermal recording media having 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 having an antistatic layer containing conductive ZnO, Si_3N_4 or $K_2Ti_6O_{13}$ whiskers are described in WO 91-05668.

[0021] The use of single-phase acicular conductive metal-containing nanoparticles in an abrasion-resistant conductive backing layer has been disclosed in co-pending U.S. Patent No. 5,719,016.

[0022] As indicated hereinabove, a wide variety of multi-layer backing for imaging elements that are electrically-conductive as well as abrasion and scratch resistant have been disclosed. However, there is still a critical need in the art for single-layer protective backings which provide electrical conductivity combined with abrasion and scratch resistance. Such single-layer protective backings also should resist the effects of humidity change, not exhibit adverse sensitometric or photographic effects, strongly adhere to the support, exhibit low dusting, exhibit no ferrotyping or blocking behavior, provide adequate support conveyance characteristics during manufacture and use, be unaffected by photographic processing solutions, and still be manufacturable at a reasonable cost. It is toward the objective of providing such improved single-layer protective backings that more effectively meet the diverse needs of imaging elements, especially silver halide photographic films and thermally-processable imaging elements than those of the prior art that the present invention is directed.

SUMMARY OF THE INVENTION

[0023] The present invention is an imaging element including a support, at least one image-forming layer, and a transparent electrically-conductive, abrasion-resistant protective layer. The protective layer includes acicular, crystalline, single-phase, conductive metal-containing fine particles dispersed in a polyurethane binder at a volume ratio of conductive metal-containing particles to polyurethane binder of between 2.5 and 20 volume percent. The polyurethane binder has a tensile elongation to break of at least 50% and a Young's modulus at a 2% elongation of a least 50,000 lb/in^2.

BRIEF DESCRIPTION OF THE DRAWING

[0024] Figure 1 shows the ultraviolet density versus internal resistivity for various backing layers.

[0025] For a better understanding of the present invention, together with other objects , advantages and capabilities thereof, reference is made to the following detailed description and claims.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The present invention provides an imaging element for use in an image-forming process comprising a support, at least one light- or heat-sensitive imaging layer, and at least one transparent electrically-conductive protective layer, wherein the electrically-conductive protective layer is comprised of electrically-conductive, crystalline, acicular metal-containing particles having a cross-sectional diameter ≤ 0.02 µm and an aspect (length to cross-sectional diameter) ratio $\geq 5:1$ dispersed in a polyurethane film-forming binder having a tensile elongation to breaking of at least 50% and a Young's modulus measured at 2% elongation of at least 50,000 lb/in^2 with an optional hardener or crosslinking agent, a lubricating agent, and a matting agent. In the case of photographic imaging elements, the electrically-conductive protective layer of this invention is located preferably on the side of the support opposite the sensitized emulsion layer (s) as a single-layer backing and may overlie an optional subbing layer. In the case of thermally-processable imaging elements, the transparent electrically-conductive layer can be a protective overcoat layer overlying an imaging layer, an abrasion resistant backing layer or an intermediate layer overlying a pelloid in a multielement curl control layer. These conductive protective layers function both to dissipate electrostatic charge resulting from triboelectric charging of the imaging element and to protect the imaging element from damage due to abrasion and scratching which may take place during manufacturing, use or processing of the imaging element. The electrical conductivity of the conductive protective layer of this invention is nominally independent of relative humidity. Further, electrical conductivity is not degraded by exposure to aqueous solutions exhibiting a wide range of pH values (e.g., $2 \leq pH \leq 13$) as are commonly used in photographic processing.

[0027] The conductive protective layers of this invention can be incorporated in many different types of imaging elements including, for example, photographic, thermographic, electrothermographic, photothermographic, dielectric recording, dye migration, laser dye-ablation, thermal dye transfer, electrostatographic, and electrophotographic imaging elements. Details with respect to the composition and function of this wide variety of different imaging elements are provided in U.S. Patent No. 5,719,016.

[0028] Photographic elements that can be provided with an electrically-conductive protective single-layer backing in accordance with this invention can differ widely in structure and composition. For example, they 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 films, especially CRT-exposed, autoreversal and computer output microfiche films. They can be black-and-white elements, color elements adapted for use in a negative-positive process or color elements adapted for use in a reversal process.

[0029] Conductive protective backing layers in accordance with this invention can be applied to a variety of supports. Such supports can be either transparent or opaque (reflective). Transparent support materials used in the practice of this invention may be comprised of any of a wide variety of synthetic high molecular weight polymeric films such as cellulose esters including cellulose diacetate, cellulose triacetate, cellulose acetate butyrate, cellulose proprionate; cellulose nitrate; polyesters such as poly(ethylene terephthalate), poly(ethylene naphthalate), polycarbonate; poly(vinyl acetal); polyolefins such as polyethylene, polypropylene; polystyrene; polyacrylates; and others; and blends or laminates of the above polymers. Transparent film supports can be either colorless or colored by the addition of a dye or pigment. Suitable opaque or reflective supports includepaper, polymer-coated paper, including polyethylene-, polypropylene-, and ethylene-butylene copolymer-coated or laminated paper, synthetic papers, and pigment-containing polyesters and the like. Of these support materials, 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.

[0030] In order to promote adhesion between the protective conductive backing of this invention and the support, the support can be surface-treated by various processes including corona discharge, glow discharge, UV exposure, flame treatment, e-beam treatment, as described in U.S. Patent No. 5,718,995 or treatment with adhesion-promoting agents including dichloro- and trichloro-acetic acid, phenol derivatives such as resorcinol and p-chloro-m-cresol, solvent washing or 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.

[0031] The principal advantage of the conductive backing of this invention derives from the use of a specific class of acicular, conductive, metal-containing particles in combination with a specific class of polyurethanes. The physical properties of polyurethanes in accordance with this invention ensure that the backing layer is hard and sufficiently tough to provide excellent abrasion and scratch resistance. The enhanced efficiency of conductive network formation by acicular particles relative to granular particles with comparable cross-sectional diameters permits the preparation of layers with greater conductivity at dry coverages comparable to those of granular conductive particles of prior art. Such an enhancement in efficiency permits the use of substantially lower dry weight coverages of acicular metal-containing particles to achieve a specified level of conductivity, or alternatively, a lower volume fraction of conductive particles relative to the film-forming polyurethane binder. This results in decreased optical losses resulting from haze and surface scattering and also can lead to decreased cutting tool wear and dirt generation in finishing operations during manufacturing. Further, an increase in the volume fraction of the polyurethane binder in the conductive layer results in improved adhesion to the underlying support, as well as included matte particles, and improved cohesion of the conductive layer itself and results in lower levels of dusting.

[0032] The acicular, conductive metal-containing particles used in accordance with this invention are single phase, crystalline, and have nanometer-size dimensions. Suitable dimensions for said acicular particles are less than 0.05 μm in cross-sectional diameter and less than 1 μm in length, preferably less than 0.02 μm in cross-sectional diameter and less than 0.5 μm in length, more preferably less than 0.01 μm in cross-sectional diameter and less than 0.15 μm in length. These dimensions tend to minimize optical losses by the coated layers due to Mie-type scattering by the particles. A mean aspect ratio of greater than or equal to 5:1 (length/cross-sectional diameter) is preferred and a mean aspect ratio of greater than 10:1 is more preferred. An increase in mean aspect ratio typically results in an improvement in volumetric efficiency of conductive network formation.

[0033] One particularly preferred class of acicular, conductive metal-containing particlesincludes acicular, semiconductive metal oxide particles. Acicular, semiconductive metal oxide particles suitable for use in the conductive backings of this invention exhibit a specific (volume) resistivity of less than $1x10^5$ ohm·cm, more preferably less than $1x10^3$ ohm·cm, and most preferably, less than $1x10^2$ ohm·cm. One example of such a suitable acicular semiconductive metal oxide is the acicular electroconductive tin oxide described in U.S. Patent No. 5,575,957 and available under the tradename "FS-10P" from Ishihara Techno Corporation which includes acicular particles of single phase, crystalline tin oxide doped with 0.3-5 atom percent antimony. The specific (volume) resistivity of this tin oxide ranges from 10-100 ohm·cm when measured as a packed powder using a DC two-probe test cell similar to that described in U.S. Patent No. 5,236,737. The mean dimensions of these acicular particles as determined by image analysis of transmission electron micrographs are approximately 0.01 μm in cross-sectional diameter (minor axis) and 0.1 μm in length (major axis) with a mean aspect ratio (length/diameter) 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 typical mean value for x-ray crystallite size determined in the manner described in U.S. Patent No. 5,484,694 is 200 angstroms 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 described in U.S. Patent No. 5,320,782. Additional examples of other non-oxide acicular metal-containing particles include select metal carbides, nitrides, silicides and borides.

[0034] It is important to note that those acicular electroconductive metal oxide particles containing an electroconductive outer shell deposited on a nonconductive acicular core particle are not suitable for use in conductive backings of this invention. Several serious deficiencies are manifested when such core/shell-type conductive particles are used in conductive backing layers for imaging elements. Because it is necessary to prepare the nonconductive acicular core particle and then coat it with fine conductive particles in a separate operation, the cross-sectional diameter of the resulting composite conductive particle is typically 0.1-0.5 μm or larger. The lengths of these composite particles typically range from 1-5 μm. Such large size particles produce an unacceptable increase in light scattering and haze, when used in a backing layer that is an outermost layer. Further, in the process of mechanically dispersing these core/shell-type composite particles to prepare coating solutions, the thin conductive shells can be damaged or even completely abraded from the core particle resulting in decreased conductivity for coated layers containing these damaged particles. In addition, the large particle size can produce fine cracks in coated layers that can result in decreased wet and dry adhesion to the support and overlying or underlying layers as disclosed in U.S. Patent No. 5,459,021. Such cracking also can lead to decreased cohesion of the conductive layer itself and can result in increased dust formation during manufacturing operations as well as during use of the imaging element. However, these deficiencies are notably absent from conductive backing layers of this invention.

[0035] The small average dimensions of acicular conductive metal-containing particles in accordance with this invention minimize the amount of light scattering which results in increased optical transparency and decreased haze in conductive backing layers. In addition to maintaining transparency, the small average dimensions of the acicular particles also promote the formation of a multitude of interconnected chains of particles into an extended network which in turn provides a multiplicity of electrically-conductive pathways, even in thin coated layers. The high aspect ratio of such acicular particles results in greater efficiency of conductive network formation compared to nominally spherical conductive particles of comparable cross-sectional diameter used in prior art conductive backings described, for example, in U.S. Patent No. 5,547,821 and European Patent Application No. 749,040. This increased efficiency of conductive network formation permits the use of lower volume fractions of conductive particles relative to polymeric binder in backings of this invention in order to obtain effective levels of surface electrical conductivity. It is an especially important feature of this invention that it permits the achievement of high levels of electrical conductivity with the use of relatively low volume fractions of acicular conductive metal-containing particles. Increasing the volume fraction of polymeric binder improves various binder-related properties of the backing layer such as adhesion to the support, cohesion of the layer, and retention of optional matte particles (resulting in lower dusting). Also, at the lower conductive particle to binder ratios possible with the acicular conductive metal-containing nanoparticles of this invention, transparency is increased and surface scattering (i.e., haze) is decreased. In addition, a lower volume fraction of conductive particles can result in decreased cutting tool wear and dust generation during photographic element manufacturing processes.

[0036] The acicular conductive metal-containing particles can constitute from 2.5 to 20 volume percent of the conductive backing of this invention. The amount of acicular conductive metal-containing particles contained in the conductive backing is defined in terms of volume percent rather than weight percent since the densities of the conductive particles may vary widely. For the acicular antimony-doped tin oxide particles described hereinabove, this corresponds to tin oxide particle to polyurethane binder weight ratios of from approximately 1:7 to 3:2. Use of significantly less than 2.5 volume percent of acicular conductive metal-containing particles will not provide a useful level of surface electrical conductivity. Use of significantly more than 20 volume percent of acicular conductive metal-containing particles defeats one of the objectives of this invention in that it results in increased dusting. Use of more than 70 volume percent of acicular conductive metal-containing particles defeats several other objectives of this invention in that it results in reduced transparency and increased haze due to scattering losses, diminished adhesion between the backing layer and the support, and decreased cohesion of the backing layer itself. Use of more than 20 but less than 70 volume percent accomplishes several of the objectives of this invention including improved conductivity, good transparency, adhesion, and haze but results in increased dusting. Thus, the conductive backing layer of this invention comprises acicular conductive metal-containing particles in the amount of preferably 20 volume percent or less and more preferably, 10 volume percent or less.

[0037] The use of polyurethane in abrasion and scratch resistant protective layers overlying antistatic layers containing metal-containing granular conductive particles has been disclosed, for example, in U.S. Patent Nos. 5,366,855, 5,547,821 and 5,679,505. However, the use of acicular metal-containing conductive particles in combination with a polyurethane film-forming binder to prepare the single-layer abrasion and scratch resistant conductive backing of the present invention results in backing layers with substantially improved antistatic, abrasion and scratch resistance, dusting, transparency, haze, and manufacturability properties Polyurethanes suitable for use in the protective conductive backing of the present invention are characterized as having a tensile elongation to break of at least 50% and a Young's modulus measured at 2% elongation of at least 50,000 lb/in^2. These physical property requirements for the polyurethane binder ensure that the backing layer is hard and sufficiently tough to provide excellent abrasion and scratch resistance and yet maintain sufficient adhesion to the acicular conductive metal-containing particles of this invention as well as to optional matte particles to minimize dusting during manufacturing operations and also to maintain excellent adhesion of the conductive backing layer of this invention to the support after processing. Aliphatic polyurethanes are preferred because of their excellent thermal and UV stability and freedom from yellowing. Suitable polyurethanes can be either aqueous-dispersible or solvent-soluble. The preferred polyurethane binder in accordance with this invention is coated as an aqueous dispersion of colloidal polyurethane particles.

[0038] The preparation of aqueous polyurethane dispersions is well-known in the art and involves chain extending an aqueous dispersion of a prepolymer containing terminal isocyanate groups by reaction with a diamine or a diol. The prepolymer can be prepared by reacting a polyester, polyether, polycarbonate, or polyacrylate having terminal hydroxyl groups with excess polyfunctional isocyanate. This product is then treated with a compound that has functional groups that are reactive with an isocyanate, for example, hydroxyl groups, and a group that is capable of forming an anion, typically a carboxylic acid group. The anionic groups are then neutralized with a tertiary amine to form the aqueous prepolymer dispersion.

[0039] In addition to the polyurethane binder and acicular conductive metal-containing particles, other components that are well known in the photographic art may also be present in the conductive backings of this invention. These additional components can include: matting agents, lubricating agents, crosslinking agents or hardeners, surface active agents including fluorine-containing surfactants, dispersing and coating aids, viscosity modifiers, charge control agents, soluble and/or solid particle dyes, co-binders, antifoggants, biocides, and others. Although preferred to be included in the electrically-conductive protective layer, matting agents, lubricating agents, surface active agents including fluorine-containing surfactants, soluble and/or solid particle dyes, and others may optionally be contained in auxiliary layers either overlying or underlying the conductive layer of this invention. Although the present invention provides an electrically-conductive protective single-layer backing which exhibits excellent adhesion, abrasion resistance, durability, and transparency, and can also function as a transport control layer, it may be advantageous to include auxiliary layers in the backing. In particular, auxiliary layers functioning to improve transport control are contemplated. Further, an optional topcoat layer overlying the conductive protective layer can be provided in order to reduce the level of dusting when volume loadings of acicular conductive metal-containing particles between 20 and 70 volume percent are required for specific imaging applications.

[0040] Crosslinking agents that react with functional groups present in polyurethane, for example, carboxyl groups, can be optionally added to improve the hardness of the backing layer. Suitable crosslinking agents for the polyurethane binders of this invention include polyfunctional aziridines, carbodiimides, epoxies, and the like. A crosslinking agent can be used at 0.5 to 30 weight percent based on the weight of polyurethane binder. A crosslinking agent concentration of 2 to 15 weight percent is preferred.

[0041] A suitable lubricating agent can be optionally included in the conductive protective layer of this invention to produce a coefficient of friction that ensures good conveyance characteristics during both manufacturing processes and use of the finished imaging element. Various suitable conventional lubricating agents are known, including higher alcohol esters of fatty acids, higher fatty acid calcium salts, metal stearates, silicone compounds, paraffins, and the like as described, for example, in U.S. Patent Nos. 2,588,756; 3,121,060; 3,295,979; 3,042,522; 3,489,567. For satisfactory conveyance characteristics, the lubricated backing surface should exhibit a coefficient of friction of from 0.10 to 0.40. However, a more preferred range is from 0.15 to 0.30. If the coefficient of friction of the backing layer is below 0.15, it is possible that long, slit rolls of photographic film could become unstable in storage or during shipping. If the coefficient of friction is greater than 0.30 during manufacturing or becomes greater than 0.30 after processing, which is common if water soluble lubricants are used, the conveyance characteristics are degraded. Aqueous dispersions of nonsoluble lubricant particles are particularly preferred, especially lubricant particles of the type described in U.S. Patent No. 5,529,891. Aqueous dispersed particles of carnauba wax, polyethylene oxide, microcrystalline waxes, paraffin wax, silicones, stearates, and amides can be incorporated directly into the aqueous coating formulations containing dispersions of polyurethane binder particles and acicular conductive metal-containing particles used to coat the single-layer backings of this invention. This avoids the need to apply a separate lubricant overcoat that could potentially degrade the surface conductivity of the backing. Aqueous dispersions of carnauba wax and stearates are preferred as lubricating agents because of their effectiveness in controlling friction at low concentrations and their excellent compatibility with aqueous dispersed polyurethanes.

[0042] In addition to lubricants, matting agents commonly are incorporated in a backing layer to improve conveyance characteristics of photographic elements during manufacturing, use, processing, and printing or projecting. Further, matting agents reduce the potential for the backing layer to cause ferrotyping when brought in contact with the surface of emulsion layer(s) under the pressures typically present in roll films. The term "ferrotyping" is used herein to describe the condition in which a backing layer, when brought in direct contact with a surface layer on the emulsion-side of the photographic element under pressure, as in a tightly wound roll film, adheres to the emulsion-side layer sufficiently strongly such that some sticking is observed when the layers are separated. In severe cases of ferrotyping, damage to the surface of the emulsion-side layer can occur when the backing and emulsion-side layers are separated. Such damage can result in adverse sensitometric effects as well.

[0043] Single-layer conductive backings of the present invention can optionally include matting agents to minimize the possibility of ferrotyping or blocking. Suitable matting agents include inorganic particles such as silica, alumina-coated silica, calcium carbonate or other mineral oxides, glass spheres or polymeric particles such as ground polymers, high melting point waxes or matte beads. Polymeric matte beads are preferred because of their uniformity in shape and size distribution. Matte particles should have a mean diameter of from 0.75 to 2.5 μm. Suitable dry coverages of matte particles range from 1 to 100 mg/m^2. However, the preferred range of coating weights of matte particles for use in protectiveconductive backings of this invention is from 15 to 65 mg/m^2.

[0044] It is well-known to include at least one of a wide variety of surfactants or coating aids in an outermost protective layer overlying the emulsion layer(s) or in an outermost backing layer as charge control agents to help dissipate accumulated electrostatic charge. A wide variety of ionic-type surfactants have been evaluated as charge control agents including anionic, cationic, and betaine-based surfactants of the type described, for example, in U.S. Patent Application Serial Nos. 08/991,288 and 08/991,493 filed December 16, 1997.

[0045] Aqueous dispersions of acicular conductive metal-containing particles can be prepared in the presence of appropriate levels of optional dispersing aids, colloidal stabilizing agents or polymeric co-binders by any of various mechanical stirring, mixing, homogenization or blending processes well-known in the art of pigment dispersion and paint making. Alternatively, dispersions of acicular metal-containing particles can be obtained commercially, for example, a stabilized dispersion of acicular electroconductive antimony-doped tin oxide nanoparticles at nominally 20 weight percent solids is available under the tradename "FS-10D" from Ishihara Techno Corporation. Dispersions of acicular conductive metal-containing particles formulated with binders and additives can be coated onto a variety of photographic supports described hereinabove by any of a variety of well-known coating methods. Handcoating techniques include using a coating rod, coating 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 well known in the art.

[0046] The electrically-conductive backing 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 acicular antimony-doped tin oxide in the conductive backing layer typically are in the range of from 0.005 to 1.5 g/m^2. Preferred coverages are in the range of 0.01 to 0.75 g/m^2 and more preferred coverages are in the range of 0.05 to 0.5 g/m^2.

[0047] The internal electrical resistivity (WER) of the single-layer electrically-conductive backing of this invention is either comparable to or superior to that of multi-layer conductive backings of prior art which have a protective overcoat overlying the antistatic layer. The electrically-conductive backing layer of this invention typically exhibits a surface resistivity of less than $2x10^{10}$ ohms/square, preferably less than $1x10^9$ ohms/square, and more preferably less than $1x10^8$ ohms/square.

[0048] Single conductive, abrasion and scratch-resistant protective layers of this invention can be incorporated in various types of imaging elements for specific imaging applications such as color negative films, color reversal films, black-and-white films, color and black-and-white papers, electrophotographic media, as well as thermally processable imaging elements including thermographic and photothermographic media, thermal dye transfer elements, laser dye ablation elements, laser toner fusion media, and the like. Suitable image-forming layers are those which provide color or black and white images. Such image-forming layers can contain silver halides such as silver chloride, silver bromide, silver bromoiodide, 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) and Research Disclosure, Vol. 225, Item 22534 (January, 1983), and Research Disclosure, Item 36544 (September, 1994), and Research Disclosure, Item 37038 (February, 1995) are useful in preparing photographic elements in accordance with this invention.

[0049] Photographic elements having conductive backing layers of this invention can be either simple black-and-white or monochrome elements or multilayer and /or multicolor elements. Generally, the photographic element is prepared by coating the film support on the side opposite the conductive backing layer with one or more photosensitive image-forming layers comprising a dispersion of silver halide crystals in an aqueous solution of gelatin 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).

[0050] The present invention is further illustrated by the following examples of its practice. However, the scope of this invention is by no means restricted to these specific illustrative examples.

COMPARATIVE EXAMPLE 1

[0051] A multi-layer conductive backing having an antistatic layer and a separate polyurethane-containing protective overcoat was prepared in a manner similar to that taught in U.S. Patent No. 5,679,505. An antistatic layer coating formulation containing colloidal silver-doped vanadium pentoxide gel dispersed in water with an aqueous polyesterionomer dispersion, and a wetting aid was prepared at 0.077% total solids. The coating formulation is given below:

Component	Weight % (wet)
Polyesterionomer binder (AQ29D: Eastman Chemicals)	0.028%
Wetting aid (Triton X-100: Rohm & Haas)	0.021%
Colloidal vanadium pentoxide	0.028%
Water	balance

[0052] The above coating formulation was applied to a moving 4 mil polyethylene terephthalate support using a coating hopper to give a nominal total dry coverage of 11 mg/m^2. The support was previously coated with a subbing layer containing a vinylidene chloride-based terpolymer latex. The antistatic layer was subsequently overcoated with a polyurethane-based protective topcoat layer containing lubricating and matting agents. The polyurethane protective topcoat formulation is given below:

Component	mg/m^2
Polyurethane binder (Witcobond W-232: Witco Chemical Co.)	973.3
Lubricant (Michemlube 160: Michelman Inc.)	0.6
Matte, poly(methylmethacrylate), 2μm beads	33.0
Wetting aid (Triton X-100: Rohm & Haas) Polyfunctional aziridine crosslinker (Neocryl CX-100:	7.5
Polyvinyl Chem. Ind.)	61.9

COMPARATIVE EXAMPLE 2

[0053] A multilayer backing was prepared in a similar manner to Comparative Example 1 except that the antistatic layer has granular tin oxide particles dispersed with a terpolymer latex comprising poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) and was coated to give a nominal total dry coverage of 645 mg/m^2. The granular tin oxide used was an antimony-doped tin oxide having an antimony dopant level at least 8 atom percent and having an X-ray crystallite size less than about 100 Å and an average equivalent spherical diameter less than about 15 nm as taught in U.S. Patent No. 5,484,694. The coating formulation is as follows:

Component	Weight % (wet)
Terpolymer latex, poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid)	0.395%
Wetting aid (Triton X-100: Rohm & Haas)	0.033%
Granular tin oxide (SN100D: Ishihara Sangyo Kaisha, Ltd.)	2.236%
Water	balance

COMPARATIVE EXAMPLE 3

[0054] A multilayer backing was prepared as in Comparative Example 2 except that the antistatic layer has acicular conductive tin oxide of the present invention at a lower weight fraction than the granular conductive tin oxide of prior art. The coating formulation is as follows:

Component	Weight % (wet)
Terpolymer latex, poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid)	0.481%
Wetting aid (Triton X-100: Rohm & Haas)	0.033%
Acicular tin oxide powder (FS-10P: Ishihara Techno Corp.)	1.44%
Dispersing aid (Dequest 2006: Monsanto Chemical Co.)	0.036%
Water	balance

EXAMPLES 1-7 and COMPARATIVE EXAMPLES 4-6

[0055] Electrically-conductive protective single-layer backings were prepared using acicular conductive tin oxide in accordance with this invention dispersed with a polyurethane binder having a tensile elongation to break of at least 50% and a Young's modulus measured at a 2 % elongation of at least 50,000 lb/in^2. Tensile elongation and Young's moduli were determined according to procedures set forth in ASTM D882 by the method described in U.S. Patent No. 5,679,505 assigned to the same assignee as the present Application and are listed for select commercial polyurethanes in Table 1. Coating formulations essentially identical to the protective topcoat formulation used for Comparative Examples 1-3 were prepared except that the indicated weight fraction (See Table 2) of polyurethane binder was replaced with acicular conductive tin oxide. The nominal total dry coverage of the conductive single-layer backing was equivalent to the total dry coverage of the non-conductive protective topcoat in Comparative Examples 1-3. In addition to acicular tin oxide and polyurethane binder, the single-layer backings contained optional matte beads, lubricant, crosslinker and wetting aid as for Comparative Examples 1-3. The volume fraction of acicular tin oxide ranged from about 3.5 to 17 percent (of total) for Examples 1-7; was nominally 2.5 percent for Comparative Example 4; and about 20 percent for Comparative Examples 5 and 6.

TABLE 1

Polyurethane		Description	Modulus, lb/in^2	Elongation to Break, %
W-232	(Witco Corporation)	Invention	103,000	150
W-234	(Witco Corporation)	Comparative	31,000	350
W-240	(Witco Corporation)	Invention	118,000	70
W-242	(Witco Corporation)	Invention	73,000	50
Sancure 898	(B.F. Goodrich Co.)	Invention	115,000	210
Sancure 815D	(B.F. Goodrich Co.)	Invention	180,000	220
Sancure 12684	(B.F. Goodrich Co.)	Invention	86,000	320
Neorez 972	(Zeneca Resins)	Comparative	5,100	500

COMPARATIVE EXAMPLE 7

[0056] An electrically-conductive backing layer was prepared as in Example 6, except Witcobond W-234, which exhibits a Young's modulus measured at a 2 % elongation of less than 50,000 lb/in^2 (See Table 1), was used as the binder. The backing layer containing Witcobond W-234 as binder exhibited unsuitable dusting properties.

EXAMPLES 8 AND 9

[0057] Coating formulations were prepared as in Example 3 and coated onto a moving poly(ethylene naphthalate) support, rather than a poly(ethylene terephthalate) support, using a coating hopper to provide a nominal total dry thickness of 0.6 µm for the conductive backing layer. For Example 8, the poly(ethylene naphthalate) support was previously coated with a subbing or primer layer comprising a vinylidene chloride-based terpolymer latex. For Example 9, the poly(ethylene naphthalate) support was surface-treated with a corona discharge at a treatment level of 250 Watts immediately prior to applying the coating formulation.

EXAMPLE 10

[0058] A conductive backing layer formulation was prepared comprising a polyurethane binder, matte beads, lubricant, and a wetting aid but without the optional polyfunctional aziridine crosslinker included in the backings of Examples 1-9. This modified coating formulation was applied to a moving poly(ethylene terephthalate) support having to a vinylidene chloride subbing layer using a coating hopper to give a nominal dry composition indicated below.

	mg/m^2
Polyurethane binder (Witcobond W-232: Witco Chemical Co.)	671.3
Acicular tin oxide (FS-10D: Ishihara Techno Corp.)	361.4
Lubricant (Michemlube 160: Michelman Inc.)	0.7
Matte, polymethyl methacrylate 2µm beads	35.1
Wetting aid (Triton X-100: Rohm & Haas)	8.0
Polyfunctional aziridine crosslinker (Neocryl CX-100: Polyvinyl Chem. Ind.)	0

EXAMPLES 11 AND 12

[0059] Conductive backing layers were prepared using a weight ratio of acicular tin oxide to Witcobond W-232 polyurethane binder of 40/60 as in Example 4. However, the layers were applied to give nominal total dry coverages of 540 and 800 mg/m^2, respectively.

TABLE 2.

DESCRIPTIONS OF SAMPLES

sample	backing structure	conductive particle	particle/ binder ratio	binder for separate antistat layer	binder for outermost layer
Comp Ex 1	2 layer	V_2O_5	50/50	AQ29D	W-232
Comp Ex 2	2 layer	granular tin oxide	85/15	terpolymer	W-232
Comp Ex 3	2 layer	Acicular tin oxide	75/25	terpolymer	W-232
Comp Ex 4	1 layer	Acicular tin oxide	15/85	-	W-232
Ex 1	1 layer	Acicular tin oxide	20/80	-	W-232
Ex 2	1 layer	Acicular tin oxide	25/75	-	W-232
Ex 3	1 layer	Acicular tin oxide	35/65	-	W-232
Ex 4	1 layer	Acicular tin oxide	40/60	-	W-232
Ex 5	1 layer	Acicular tin oxide	45/55	-	W-232
Ex 6	1 layer	Acicular tin oxide	55/45	-	W-232

TABLE 2. (continued)

DESCRIPTIONS OF SAMPLES					
sample	backing structure	conductive particle	particle/ binder ratio	binder for separate antistat layer	binder for outermost layer
Comp Ex 5	1 layer	Acicular tin oxide	65/35	-	W-232
Comp Ex 6	1 layer	Acicular tin oxide	65/35	-	Sancure 898
Ex 7	1 layer	Acicular tin oxide	35/65	-	Sancure 898
Comp Ex 7	1 layer	Acicular tin oxide	55/45	-	W-234

[0060] Samples having variousconductive backing layers, optional protective topcoat layers, and various film supports as described hereinabove were evaluated with regard to their electrical performance, optical transparency, adhesion performance, dusting and abrasion resistance, and their conveyance characteristics.

Electrical Resistivity

[0061] Surface electrical resistivities (SER) of the above conductive backings were measured at about 20°C and nominally 50% relative humidity using a two-point DC probe by the method described in U.S. Patent No. 2,801,191. Internal resistivities of multi-layer backings were measured by a wet electrode resistivity (WER) technique (See R.A. Elder, "Resistivity Measurements on Buried Conductive Layers", 1990 EOS/ESD Symposium Proceedings, pp. 251-254). Internal resistivities of single-layer backings were also measured to permit direct comparison with multilayer backings by minimizing differences arising from the two different measurement techniques. Internal resistivities also were measured for samples after processing by the standard C-41 photographic process.

[0062] A significant advantage provided by the present invention is the enhanced electrostatic charge dissipation capability resulting from the greatly improved surface conductivity produced by incorporating the conductive particles into an outermost single-layer backing. Surface and internal resistivities of multilayer backings of prior art and single-layer conductive backings of this invention are compared in Table 3. Surface resistivities of the multilayer backings are significantly higher than their internal resistivities (e.g., Comparative Examples 1 and 2). However, surface and internal resistivities are nearly identical for single-layer backings. For most coating formulations, surface resistivities of the single-layer backings of this invention are comparable to or less than the internal resistivities of multilayer backings for similar total dry weight coverages of conductive particles even though the volume fraction of conductive particles can be substantially lower for the acicular conductive metal-containing particles in the conductive backings of this invention. Examples 1-6 exhibit decreasing resistivity with increasing volume fraction of conductive material as expected. However, the single-layer conductive backing of Comparative Example 4 is essentially insulating for an acicular tin oxide volume fraction of about 2.5 percent. Although improved conductivity can be obtained at volume loadings above 20 % as shown by Comparative Examples 5 and 6, dusting becomes a significant problem at high volume fractions of conductive metal-containing particles. Further, as shown in Table 3, there is little or no change in WER after processing.

TABLE 3

	SER, raw (log Ω/sq)	WER, raw (log Ω/sq)	WER, processed (log Ω/sq)
Comp Ex 1	12.9	7.5	7.5
Comp Ex 2	8.2	7.1	
Comp Ex 3	7.4*	8.5	
Comp Ex 4	12.2	12.0	11.6
Example 1	10.3	10.0	10.8
Example 2	8.1	7.9	
Example 3	8.0	7.8	8.0
Example 4	7.8	7.6	

* SER measured prior to overcoating with polyurethane protective layer

TABLE 3 (continued)

	SER, raw (log Ω/sq)	WER, raw (log Ω/sq)	WER, processed (log Ω/sq)
Example 5	7.4	7.2	
Example 6	7.0	6.8	
Comp Ex 5	6.5	6.2	6.9
Comp Ex 6	6.5	6.4	
Example 7	7.4	7.4	
Comp Ex 7	8.1	7.9	8.6
Example 11	8.3	8.0	
Example 12	7.7	7.8	

[0063] The unexpected result that the surface resistivity for the single-layer backings can be lower than the internal resistivity for multilayer backings at comparable acicular tin oxide dry weight coverages but lower volume fractions of acicular tin oxide possibly may be related to intermixing and swelling of the conductive layer when it is overcoated with a separate protective layer in the case of multilayer backings. The effect of intermixing and swelling is expected to be more significant for lower volume fractions of conductive particles. For example, the resistivity of the conductive backing of Comparative Example 3, having acicular tin oxide dispersed in a terpolymer latex binder at a corresponding weight ratio of 3:1, was measured prior to overcoating with a separate protective layer. The internal resistivity measured after overcoating increased to 8.5 log ohm/sq from 7.4 log ohm/sq before overcoating.

Optical density

[0064] Another important requirement is that the conductive backings of this invention have minimal impact on optical transparency of the imaging element. It is particularly important that single-layer backings containing high volume fractions of conductive metal-containing particles exhibit little haze or surface scattering. Total optical and ultraviolet densities (D_{min}) were evaluated at 530 nm and 380 nm, respectively with a X-Rite Model 361T densitometer. Net or Delta UV D_{min} and Delta ortho D_{min} values were calculated by correcting the total optical and ultraviolet densities for the contributions of the uncoated support which then corresponds to the contribution of either the combined conductive and protective layers in the case of multilayer backings (i.e., Comparative Examples 1-3) or of the single-layer backing (i.e., Examples) which are given in Table 4.

TABLE 4

	Δ UV Dmin	Δ ortho Dmin
Comp Ex 1	0.014	0.004
Comp Ex 2	0.024	0.013
Comp Ex 3	0.015	0.004
Comp Ex 4	0.005	0.002
Ex 1	0.006	0.002
Ex 2	0.009	0.004
Ex 3	0.013	0.006
Ex 4	0.014	0.007
Ex 5	0.015	0.008
Ex 6	0.015	0.010
Comp Ex 5	0.018	0.012
Comp Ex 6	0.023	0.012
Ex 6	0.019	0.008
Comp Ex 7	0.013	0.009
Ex 7	0.019	0.008
Ex 11	0.010	0.005
Ex 12	0.012	0.006

[0065] Thus, incorporation of acicular tin oxide particles in the outermost single-layer backing of this invention does not adversely affect the optical properties of the conductive backing. In all instances, both the net optical and ultraviolet

D_{min} values measured for single-layer backings of the present invention are lower than those measured for multilayer backings of prior art comprising a conductive layer containing granular tin oxide overcoated with a separate polyurethane-containing protective layer (e.g., Comparative Example 2).

[0066] In order to optimize antistatic layer performance it is generally necessary to balance the relationship between optical density and resistivity. In order to reduce resistivity, it is necessary to increase the volume fraction of metal-containing conductive particles, which results in increased optical density. Figure 1 depicts the relationship between delta ultraviolet density and internal resistivity for conductive backings comprising either acicular or granular tin oxide particles and Witcobond W-232 polyurethane binder. The values for WER and UV D_{min} for the single-layer backings of this invention are those for Examples 1-5. The values of WER and UV D_{min} for the multilayer backings are those for Comparative Examples 2 and for examples disclosed in commonly assigned, concurrently filed U.S. Patent Application No. (Kodak Docket No. 76,266). As shown in Figure 1, single-layer conductive backings of this invention are strongly preferred for optimization of both resistivity and ultraviolet density for antistatic backing layers.

Adhesion

[0067] Dry adhesion of the conductive backings was evaluated by scribing a small cross-hatched region into the coating with a razor blade. A piece of high-tack adhesive tape was placed over the scribed region and quickly removed from the coating. The relative amount of coating removed is a qualitative measure of the adhesion of the coating to the support. Wet adhesion was evaluated using a procedure which simulates wet processing of silver halide photographic elements. A one millimeter wide line was scribed into the backing or overcoat layer. The sample was then placed in KODAK Flexicolor developer solution at 38 °C for 3 minutes and 15 seconds. The sample was removed and then placed in a Flexicolor developer bath and a weighted rubber pad (approximately 3.5 cm diameter) with a 900 g applied weight was rubbed vigorously across the sample in the direction perpendicular to the scribe line. The amount of additional material removed is a relative measure of the wet adhesion of the coating. No removal was judged as excellent, from 1 to 10 percent removal as good, 10 to 20 percent as fair, and greater than 20 percent as poor. Adhesion results for the multilayer and single-layer conductive backings described hereinabove are given in Table 5. The test results demonstrate that the conductive single-layer backings of the present invention exhibit excellent dry adhesion throughout the specified particle to binder weight ratio range for both poly(ethylene terephthalate) and poly(ethylene naphthalate) supports. Wet adhesion was generally equivalent to or superior to the multi-layer structures.

TABLE 5

	dry adhesion	wet adhesion
Comp Ex 1	excellent	fair
Comp Ex 2	excellent	poor
Comp Ex 3	excellent	-
Comp Ex 4	excellent	good
Ex 1	excellent	excellent
Ex 2	excellent	excellent
Ex 3	excellent	-
Ex 4	excellent	-
Ex 5	excellent	excellent
Comp Ex 5	excellent	excellent
Comp Ex 6	excellent	excellent
Ex 6	excellent	-
Comp Ex 7	excellent	excellent
Ex 7	excellent	good
Ex 8	excellent	fair
Ex 9	excellent	fair

Dusting and Abrasion Resistance

[0068] In addition to improved antistatic performance of the single-layer conductive backing of this invention it is a further objective of this invention to provide improved resistance of the conductive backing layer to scratching and abrasion. To evaluate the abrasion resistance of such a "multi-functional" backing layer, samples of support to which the backing was applied were placed on a Taber Abrader and abraded in accordance with ASTM method D1044. The

Taber abrader results for multilayer backings of prior art and multi-functional single-layer backings of this invention are compared in Table 6.

[0069] The addition of low volume fractions of inorganic materials, such as metal-containing particles, to a polymeric layer is well known to improve abrasion resistance of the polymeric layer. However, addition of higher volume fractions of conductive metal-containing particles required to achieve sufficient conductivity may be anticipated to degrade the physical properties of the backing which could result in increased brittleness and also in dusting behavior. Dusting can result from a cohesive failure of the backing layer or from decreased adhesion of optional matte particles caused by insufficient polymeric binder volume fraction. The extent of dusting by multilayer and single-layer backings described hereinabove was evaluated using the procedure described in U.S. Patent No. 5,547,821. A qualitative scale ranging from 1-4 was used to rate the degree of dusting. For photographic imaging elements, particularly those which must be perforated, only very low levels of dusting can be tolerated. A ranking of 1 was judged as "excellent", less than 2 as "good", from 2-3 as "poor", and from 3-4 as "very poor". A comparison of the dusting and Taber abrader test results for multilayer backings and the multi-functional single-layer backings of this invention is given in Table 6. In general, differences in the test results for the various backing layers are more evident for dusting than for Taber abrader testing. For example, Comparative Example 5 exhibited a significant increase in dusting compared with Examples 1-6 and still exhibited (abraded) percent haze values similar to those of Examples 1-6. Consequently, dusting performance can be considered to be a significant criteria for rating "durability" of the backing layers.

TABLE 6

	Dusting Rating	Taber Abrasion (% haze)
Comp Ex 1	1	17.8
Comp Ex 2	1	12.1
Comp Ex 3	1	16.0
Comp Ex 4	1	-
Ex 1	1	13.6
Ex 2	1	12.7
Ex 3	1	-
Ex 4	1	12.5
Ex 5	1	12.1
Comp Ex 5	3	12.3
Comp Ex 6	3.5	-
Ex 6	1	11.7
Comp Ex 7	2	-
Ex 7	1	-
Ex 8	1.5	-
Ex 9	1	-

[0070] The dusting and abrasion test results in Table 6 show that single-layer conductive backings of the present invention have dusting levels comparable to multilayer conductive backings of prior art, which include an abrasion-resistant overcoat to protect the conductive layer from physical damage. Comparative Examples 5 and 6 demonstrate that the level of dusting can become significant for acicular, conductive tin oxide particle volume fractions of approximately 20 percent or greater. In addition, the test results in Table 6 demonstrate that excellent durability can be obtained when single-layer conductive backings of the present invention are applied to surface-treated supports. Further, excellent durability can be obtained for the backings in which the optional hardener or crosslinking agent was omitted. Comparative Example 7 demonstrates an increase in dusting for a backing layer comprising a polyurethane binder not in accordance with this invention. Taber abrader test results suggest that the single-layer backings of this invention typically exhibit abrasion-resistance comparable or superior to multilayer backings of prior art. Also, single-layer backings of this invention exhibit comparable abraded haze values.

Coefficient of Friction

[0071] In one preferred embodiment, it is desirable for the single-layer conductive backing to function also as a transport control layer wherein matte particles and/or lubricating agents can be included. It is required that incorporation of the conductive acicular tin oxide not adversely affect conveyance characteristics. As described hereinabove, addition of high volume fractions of metal-containing conductive particles to a backing layer can reduce cohesion of the layer as well as reduce adhesion of matte particles in the layer. In addition, depending on the particular properties and volume fraction of the conductive particles incorporated in the backing layer, an increase in level of adsorption of lubricant(s) by or an increase in surface roughness of the backing could take place. Such changes can influence the coefficient of friction and thus, the conveyance properties of an imaging element having such a backing layer. Consequently, coefficient of friction was evaluated for several single-layer conductive backings of this invention as well as multilayer conductive backings of prior art. For example, the paper clip test coefficient of friction values were 0.36 and 0.33 for Comparative Examples 2 and 3, respectively, compared with 0.3 for Example 2. The values for dynamic coefficient of friction were 0.24 for Comparative Example 2 and 0.25 for Example 5.

[0072] As demonstrated by the above examples, the use of acicular metal-containing particles at low volume fraction loadings in combination with specific polyurethane binders can provide highly conductive, transparent single-layer backings which are useful for a wide variety of imaging elements. Further, the single-layer multifunctional protective backings of the present invention allow simplification of an imaging element manufacturing process by reducing the number of coated layers required to obtain desired performance.

Claims

1. An imaging element comprising a support, at least one image-forming layer, and a transparent electrically-conductive, abrasion-resistant protective layer comprising acicular, crystalline, single-phase, conductive metal-containing fine particles dispersed in a polyurethane binder at a volume ratio of conductive metal-containing particles to polyurethane binder of between 2.5 and 20 volume percent; wherein said polyurethane binder has a tensile elongation to break of at least 50% and a Young's modulus at a 2% elongation of a least 50,000 lb/in^2.

2. The imaging element of claim 1, wherein said acicular, crystalline, single-phase, electrically-conductive metal-containing fine particles are selected from the group consisting of acicular electroconductive tin oxide, tin-doped indium sesquioxide, aluminum-doped zinc oxide, niobium-doped titanium dioxide, oxygen-deficient titanium suboxide, TiO_x, where $x<2$, titanium oxynitride, TiO_xN_y, where $(x+y) \leq 2$, metal carbides, metal nitrides, metal silicides and metal borides.

3. The imaging element of claim 1, wherein said acicular, crystalline single-phase, conductive metal-containing particles comprise a dry weight coverage of from 0.005 to 1.5 g/m^2.

4. The imaging element of claim 1, wherein said tranparent electrically-conductive protective layer has a surface resistivity of less than or equal to 2×10^{10} ohm per square.

5. The imaging element of claim 1, wherein said acicular, crystalline single-phase, metal-containing particles exhibit a packed powder resistivity of 10^3 ohm-cm or less.

6. The imaging element of claim 1, wherein said support is selected from the group consisting of cellulose esters, polyesters, polyolefins, polystyrene and polyacrylates.

7. The imaging element of claim 1, wherein said support is surface-treated by means of corona discharge, glow discharge, UV exposure, electron beam treatment, flame treatment, solvent washing, or adhesion-promoting agents.

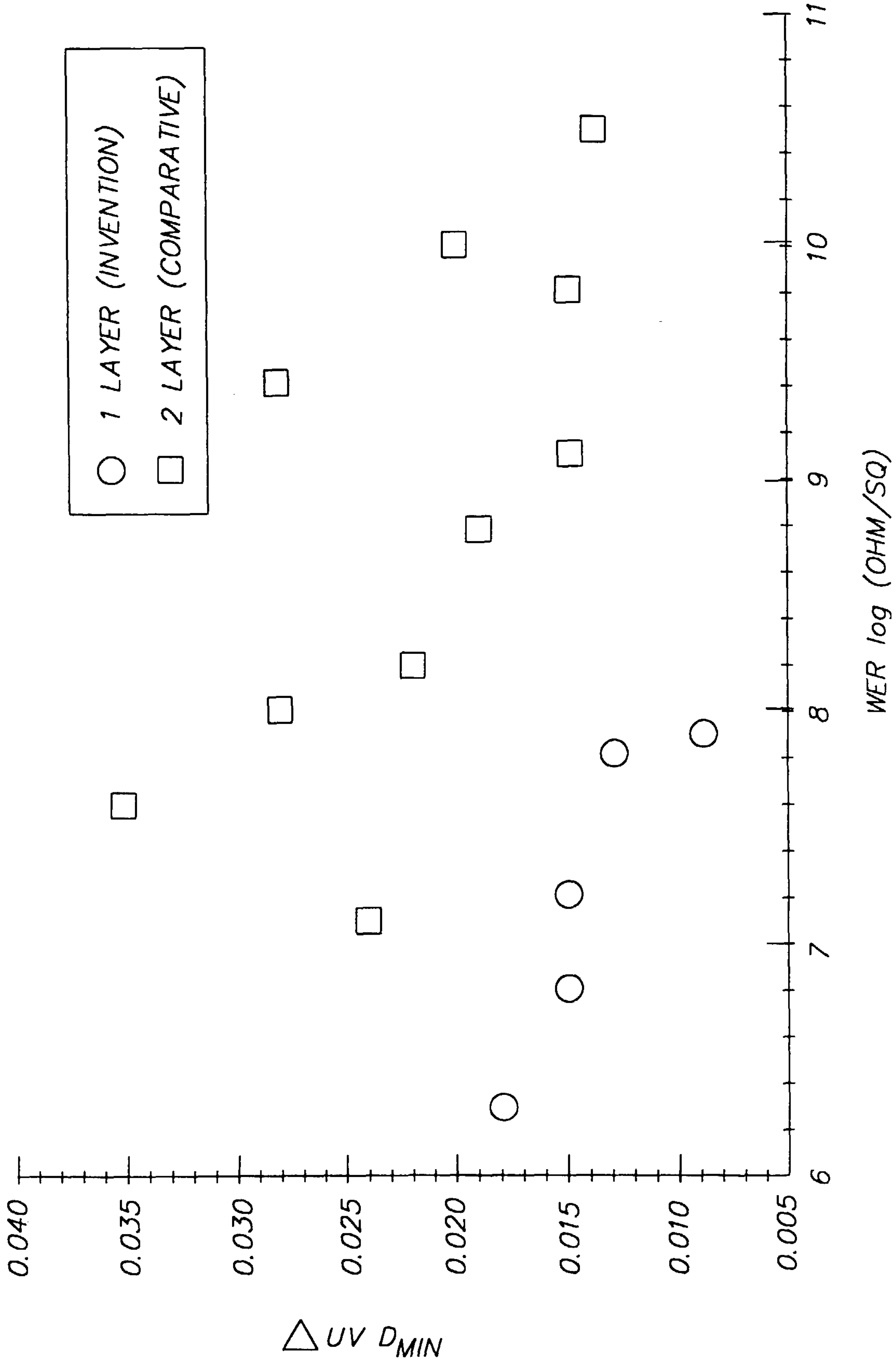
8. The imaging element of claim 1, wherein the acicular conductive metal-containing particles comprise from 2.5 to 20 volume percent of the conductive backing layer.

9. The imaging element of claim 1, wherein the protective layer further comprises matting agents, lubricating agents, crosslinking agents, surface active agents, dispersing aids, coating aids, viscosity modifiers, charge control agents, particle dyes, antifoggants or biocides.

10. A photographic film comprising:

    (1) a support having a first side and a second side;
    (2) a least one silver halide emulsion layer superposed on the first side of said support; and
    (3) a transparent, electrically-conductive, abrasion-resistant, backing layer superposed on the second side of the support comprising acicular, crystalline, single-phase, conductive metal-containing fine particles dispersed

in a polyurethane binder at a volume ratio of conductive metal-containing particles to polyurethane binder of between 2.5 and 20 volume percent; wherein said polyurethane binder has a tensile elongation to break of at least 50% and a Young's modulus at a 2% elongation of a least 50,000 lb/in^2.


○ 1 LAYER (INVENTION)
□ 2 LAYER (COMPARATIVE)
WER log (OHM/SQ)
6
7
8
9
10
11
△UV D_{MIN}
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005