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54 **Photographic element on a polymeric substrate with novel subbing layer.**

57 A radiation sensitive photographic element comprising a substrate with at least one polymeric surface and at least one photographic emulsion over the polymeric surface. The polymeric surface has adhered thereto a continuous gelled network or inorganic particles which provides a subbing layer having the potential for antistatic properties, antihalation properties and good coatability.

EP 0 250 154 A2

PHOTOGRAPHIC ELEMENT ON A POLYMERIC SUBSTRATE WITH NOVEL SUBBING LAYER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to photographic emulsions on substrates having a subbing or priming layer thereon.

2. Background of the Art

The construction of silver halide photographic elements has become an art that is an amalgum of many different sciences and technologies. Such varied disciplines as polymer chemistry, crystallography, physics, electrostatics, dye chemistry, coating technologies, and the like have to come into focus to produce what is to the consumer a simple snapshot.

Two complex problems that have traditionally been of concern to the photographic industry are adherence of the photographic emulsions to the substrates of choice (i.e., polymeric substrates such as polyester, polyolefin, or cellulosic ester bases and polymer coated paper bases such as white pigment filled polyolefin or polyvinylidene chloride coated paper). Another problem, particularly in high image content film which is processed mechanically is the development of static or triboelectric charges in the film which create spurious images.

Many different compositions, combinations of layers, and treatment of substrates have been proposed to effect better adhesion between emulsion layers and substrates as is evidenced by the number of patents in this technical area. A sampling of these patents include U.S. Patent Nos. 3,271,345, 2,943,937, 4,424,273, 3,791,831 and the like. A great amount of work has also been directed in the photographic sciences to the elimination of electrostatic charges on photographic film. Examples of the diverse work done in this area includes U.S. Patents 4,582,782, 3,884,699, 3,573,049 and the like.

Assorted handling problems (e.g., adhering of layers) are often addressed by the use of particulate matting agents in backside coatings or surface layers of photographic elements. Also sensitometric effects (e.g., lightscattering) are achieved by the use of particle-containing layers in photographic elements. These uses of particulate containing layers shown in U.S. Patents 4,343,873, 4,144,064, 3,507,678, 4,022,622 and the like.

Typical photographic supports comprise a base material (e.g., polyester, cellulose triacetate, or paper) with a subbing layer on at least one surface to assist in the adherence of the gelatin layers, including the emulsion layers, to the base. Conventional subbing layers are described in U.S. Patent Nos. 3,343,840, 3,495,984, 3,495,985 and 3,788,856.

SUMMARY OF THE INVENTION

The present invention relates to photographic elements having at least one silver halide emulsion layer over a substrate, where the substrate has at least one polymeric surface to which is adhered a layer comprising a gelled network of inorganic particles, preferably inorganic oxide particles.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to photographic elements. These elements comprise a substrate having at least one silver halide emulsion layer on a surface thereof. A surface with an emulsion thereon is hereinafter referred to as a major surface of the substrate. The silver halide emulsion generally comprises silver halide grains (also referred to as crystals or particles) carried in a water penetrable binder medium of a hydrophilic colloid. It has been found according to the practice of the present invention that the use of a gelled network of inorganic particles, preferably oxides, as a layer on a polymeric surface provides an excellent subbed (or primed) substrate for photographic emulsions. It has been found that this gelled particulate layer is capable

of providing one or more excellent properties to the photographic element including, but not limited to antistatic properties, ease of coatability of the particulate layer, photoinertness (harmless to the photographic emulsion and its properties), adhesion (both wet and dry, to both the substrate and the emulsion layers), and reduction in specular reflectance (i.e., antihalation properties).

5 The substrates of the invention may comprise any material having at least one polymeric surface which is to be used as the major surface of the substrate.

The silver halide photographic emulsions which are used in the present invention, as protective colloids, in addition to gelatin, acylated gelatins such as phthalated gelatin and malonated gelatin, cellulose compounds such as hydroxyethyl cellulose and carboxymethyl cellulose, soluble starch such as dextrin,
10 hydrophilic polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, and polyacrylamide, plasticizers for dimensional stabilization, latex polymers, and matting agents can be added. The finished emulsion is coated on a suitable support.

Supports which can be used include films of synthetic polymers such as polyalkyl acrylate or methacrylate, polystyrene, polyvinyl chloride, partial formalation polyvinyl alcohol, polycarbonate, polyesters
15 such as polyethylene terephthalate, and polyamides, films of cellulose derivatives such as cellulose nitrate, cellulose acetate, cellulose triacetate, and cellulose acetate butyrate, paper covered with α -olefin polymers or gelatin (a natural polymer), for example, and synthetic papers made of poly styrene; that is, any of transparent or opaque support commonly used in photographic elements can be used. Primed polymeric substrates are also useful, including gelatinprimed polymers (e.g., gelatin on poly(ethylene terephthalate)),
20 and poly(vinylidene chloride) copolymers or polyester. This includes polymeric materials loaded with pigments and particulates such as titania to improve the white background of the image and to provide antihalation or other sensitometric effects.

The substrates of the invention may be used with any type of photographic silver halides including, but not limited to silver chloride, silver bromide, silver chlorobromide, silver iodochlorobromide, silver
25 bromiodide and silver chloriodide grains, which may be in any of the many available crystal forms or habits including, but not limited to cubic, tetrahedral, lamellar, tabular, orthorhombic grains, etc.

Soluble silver salts and soluble halides can be reacted by methods such as a single jet process, a double jet process, and a combination thereof. In addition, a procedure can be employed in which silver halide grains are formed under the presence of an excess of silver ions (a so-called reverse mixing
30 process). A so-called controlled double jet process can also be employed in which the pAg of the liquid phase wherein the silver halide is formed is kept constant. Two or more silver halide emulsions which have been prepared independently may be used in combination with each other.

Soluble salts are usually removed from the silver halide emulsion after the precipitate formation or physical ripening of the silver halide emulsion. For this purpose, a noodle water-washing method can be
35 employed in which the soluble salts are removed by gelling the emulsions. A flocculation method utilizing inorganic salts containing polyvalent anions, anionic surface active agents, anionic polymers or gelatin derivatives can also be used.

Although so-called primitive emulsions which are not chemically sensitized can be used as the silver halide emulsions, the silver halide emulsions are usually chemically sensitized. This chemical sensitization
40 can be carried out, for example, by the methods as described in H. Frieser ed., Die Grundlagen der Photographischen Prozesse mit Silverhalogeniden, Akademische Verlagsgesellschaft, pp. 675-734 (1968).

That is, a sulfur sensitization method using sulfur-containing compounds capable of reacting with active gelatins and silver (e.g., thiosulfates, thioureas, mercapto compounds, and rhodanines), a reduction sensitization method using reducing substances (e.g., stannous salts, amines, hydrazine derivatives,
45 formamidinesulfinic acid, and silane compounds), a noble metal sensitization method using noble metal compounds (e.g., gold complex salts, and metal complex salts of Group VIII metals, such as platinum, rhodium, iridium, and palladium, of the Periodic Table), and so forth can be used singly or in combination with each other.

The sulfur sensitization method is described in detail, for example, in U.S. Patent Nos. 1,574,944,
50 2,410,689, 2,278,947, 2,728,668 and 3,656,955; the reduction sensitization method, in U.S. Patent Nos. 2,983,609, 2,419,974 and 4,054,458; and the noble metal sensitization method, in U.S. Patent Nos. 2,399,083, 2,448,060 and British Patent No. 618,061.

In photographic emulsions which are used in the present invention may be incorporated various compounds for the purpose of, e.g., preventing the formation of fog during the production, storage or
55 photographic processing of the light-sensitive material, or stabilizing photographic performance. That is, many compounds known as antifoggants or stabilizers, such as azoles (E.G., benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles,

nitrobenzotriazoles, and mercaptotetrazoles, (particularly 1-phenyl-5-mercaptotetrazole), mercapto-
 pyrimidines, mercaptotriazines, thioketo compounds (e.g., oxazolinethione), azaindenes (e.g., triazain-
 denes, tetraazaindenes (particularly 4-hydroxysubstituted-(1,3,3a,7)tetraazaindenes), and pentaazaindenes),
 benzenethiosulfonic acid, benzenesulfonic acid, and benzenesulfonic acid amide can be added.

5 Typical examples of such compounds and a method of using them are described, for example, in U.S.
 Patent Nos. 3,954,474, 3,982,947 and Japanese Patent Publication No. 28660/77.

The photographic emulsion layers of the light-sensitive material of the present invention may contain
 polyalkylene oxide or its derivatives (e.g., ethers, esters and amines), thioether compounds, thiomor-
 pholines, quaternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole deriva-
 10 tives, 3-pyrazolidones, hydroquinone or its derivatives, and the like for the purpose of increasing sensitivity
 or contrast, or accelerating development. For example, compounds as described in U.S. Patent Nos.
 2,400,532, 2,423,549, 2,716,062, 3,617,280, 3,722,021, 3,808,003 and British Patent No. 1,488,991 can be
 used.

As binders or protective colloids to be used in the emulsion layers and intermediate layer of the
 15 lightsensitive material of the present invention, it is advantageous to use gelatins. In addition, other
 hydrophilic colloids can be used. For example, proteins such as gelatin derivatives, graft polymers of gelatin
 and other polymers, albumin, and casein, sugar derivatives such as cellulose derivatives (e.g., hydroxyethyl
 cellulose, carboxymethyl cellulose, and cellulose sulfate), sodium alginate, and starch derivatives, and
 various synthetic hydrophilic polymeric substances, homopolymers or copolymers, such as polyvinyl
 20 alcohol, polyvinyl alcohol partial acetal, poly(N-vinyl)pyrrolidone, polyacrylic acid, polymethacrylic acid,
 polyacrylamide, polyvinyl imidazole, and polyvinyl pyrazole can be used.

The light-sensitive material of the present invention is particularly effectively used as a black-and-white
 reflection light-sensitive material which is to be subjected to rapid processing. In addition, it can be used as
 an X-ray recording light-sensitive material, a photomechanical process light-sensitive material, a light-
 25 sensitive material to be used in a facsimile system, etc., and further, as a multilayer, multicolor photo-
 graphic light-sensitive material having at least two different spectral sensitivities.

The multilayer, multicolor photographic material usually comprises a support, and at least one red-
 sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive
 emulsion layer on the support. The order in which the above layers are arranged can be chosen
 30 appropriately. Usually the red-sensitive emulsion layer contains cyan dye forming couplers, the green-
 sensitive emulsion layer contains magenta dye forming couplers, and the blue-sensitive emulsion layer
 contains yellow dye forming couplers. In some cases, other combinations can be employed. Even in the
 case of the multilayer, multicolor photographic material, the effects of the present invention are exhibited
 significantly in a reflection light-sensitive material.

35 Spectral sensitizing dyes may be used in one or more silver halide emulsions useful on the subbed
 substrates of the present invention. These sensitizing dyes are well known in the art to increase the
 sensitization of silver halide grains to various portions of the electromagnetic spectrum such as the
 ultraviolet, blue, green, yellow, orange, red, near infrared, and infrared. These dyes may be used singly or
 in combination with other dyes to sensitize the emulsions.

40 The substrate of the invention bears a coating comprising a continuous gelled network of inorganic
 metal oxide particles. The particles preferably have an average primary particle size of less than about 500
 or 200 Å. As used herein, the term "continuous" refers to covering the surface of the substrate with virtually
 no straight-line penetrable discontinuities or gaps in the areas where the gelled network is applied.
 However, the layer may be and usually is porous, without significant straight-line pores or gaps in the layer.
 45 The term "gelled network" refers to an aggregation of colloidal particles linked together to form a porous
 three-dimensional network. Generally all of or the majority of linkages are from the material of the particles,
 but some binder may also be present. The term "porous" refers to the presence of voids between the
 inorganic metal oxide particles created by the packing of the metal oxide particles. The term "primary
 particle size" refers to the average size of unagglomerated single particles of inorganic metal oxide. The
 50 term "particle" includes spherical, non-spherical, and fibrillar particulate arrangements.

The coating should be thicker than a monolayer of particles. Preferably the coating comprises a
 thickness equal to or greater than three average particle diameters and more preferably equal to or greater
 than five particle diameters.

55 The articles of the invention comprise a substrate which may be transparent, translucent, or opaque to
 visible light having at least one polymeric surface, and have formed thereon a coating in the form of a
 continuous gelled network of inorganic oxide particles. When the coating is applied to transparent
 substrates to achieve increased light transmissivity, the coated article preferably exhibits a total average
 increase in transmissivity of normal incident light of at least two percent and up to as much as ten percent

or more, when compared to an uncoated substrate, depending on the substrate coated, over a range of wavelengths extending at least between 400 to 900 nm. An increase in light transmission of two percent or more is generally visually apparent and is sufficient to produce a measurable increase in energy transmissivity when the coated substrate is used. An increase in transmissivity is also present at
 5 wavelengths into the infrared portion of the spectrum.

The gelled network is a porous coating having voids between the inorganic oxide particles. If the porosity is too small, the antireflectance may be reduced. If the porosity is too large, the coating is weakened and may have reduced adhesion to the substrate. Generally, the colloidal solution from which the gelled network is obtained is capable of providing porosity of about 25 to 70 volume percent, preferably
 10 about 30 to 60 volume percent when dried. The porosity can be determined by drying a sufficient amount of the colloidal solution to provide a dried product sample of about 50 to 100 mg and analyzing the sample using a "Quantasorb" surface area analyzer available from Quantachrome Corp., Syosett, NY.

The voids of the porous coating provide a multiplicity of subwavelength interstices between the inorganic particles where the index of refraction abruptly changes from that of air to that of the coating
 15 material. These subwavelength interstices, which are present throughout the coating layer, provide a coating which may have a calculated index of refraction (RI) of from about 1.15 to 1.40, preferably 1.20 to 1.30 depending on the porosity of the coating. When the porosity of the coating is high, e.g., about 70 volume percent or more, lower values for the RI are obtained. When the porosity of the coating is low, e.g., 25 volume percent or less, higher values for the RI are obtained.

The average primary particle size of the colloidal inorganic metal oxide particles is preferably less than
 20 about 200 Å. The average primary particle size of the colloidal inorganic metal oxide particles is more preferably less than about 70 Å. When the average particle size becomes too large, the resulting dried coating surface is less efficient as an antireflection coating.

The average thickness of the dried coating is preferably from about 300 to 10,000 Å, more preferably
 25 800 to 5000 Å and most preferably between 900 and 2000 Å. Such coatings provide good antistatic properties. When the coating thickness is too great, the coating has reduced adhesion and flexibility and may readily flake off or form powder under mechanical stress.

Articles such as transparent sheet or film materials may be coated on a single side or on both sides to increase light transmissivity, the greatest increase being achieved by coating both sides.

The process of coating the layer of the present invention comprises coating a substrate with a solution
 30 of colloidal inorganic metal oxide particles, the solution preferably containing 0.2 to 15 weight percent of the particles, the particles preferably having an average primary particle size less than about 500 or 200 Å, more preferably less than about 70 Å, and drying the coating at a temperature less than that which degrades the substrate, preferably less than about 200°C, more preferably in the range of 80 to 120°C. The
 35 coating provides the substrate with an average reduction in specular reflectance of at least two percent over wavelengths of 400 to 900 nm.

Coating may be carried out by standard coating techniques such as bar coating, roll coating, knife coating curtain coating, rotogravure coating, spraying and dipping. The substrate may be treated prior to coating to obtain a uniform coating using techniques such as corona discharge, flame treatment, and
 40 electron beam. Generally, no pretreatment is required.

The colloidal inorganic oxide solution, e.g., a hydrosol or organosol, is applied to the substrate of the article to be coated and dried at a moderately low temperature, generally less than about 200°C, preferably
 80-120°C, to remove the water or organic liquid medium. The coating may also be dried at room temperature, provided the drying time is sufficient to permit the coating to dry completely. The drying
 45 temperature should be less than at which the substrate degrades. The resulting coating is hygroscopic in that it is capable of absorbing and/or rehydrating water, for example, in an amount of up to about 15 to 20 weight percent, depending on ambient temperature and humidity conditions.

The colloidal inorganic oxide solution utilized in the present invention comprises finely divided solid inorganic metal oxide particles in a liquid. The term "solution" as used herein includes dispersions or
 50 suspensions of finely divided particles of ultramicroscopic size in a liquid medium. The solutions used in the practice of this invention are clear to milky in appearance. Inorganic metal oxides particularly suitable for use in the present invention include boehmite ($\alpha\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$), tin oxide (SnO_2), titania, antimony oxide (Sb_2O_5), zirconium oxide (ZrO_2), cerium oxide, yttrium oxide, zircon (ZrSiO_4), silica, and alumina-coated silica as well as other inorganic metal oxides of Groups III and IV of the Periodic Table and mixtures thereof. The
 55 selection of the inorganic metal oxide is dependent upon the ultimate balance of properties desired. Inorganics such as silicon nitride, silicon carbide, and magnesium fluoride when provided in sol form are also useful

Examples of commercially available inorganic metal oxides include "Dispural" and "Pural" boehmite available from Condea Petrochemie GmbH, "Catapal" SB, boehmite available from Vista Chemical Co., and "Nalco" ISJ-614, alumina sol, "Nalco" ISJ-611, antimony oxide sol, and "Nalco" ISJ-613, alumina-coated silica sol, available from Nalco Chemical Company.

5 The colloidal coating solution preferably contains about 0.2 to 15 weight percent, preferably about 0.5 to 6 weight percent, colloidal inorganic metal oxide particles. At particle concentrations about 15 weight percent, the resulting coating may have reduced uniformity in thickness and exhibit reduced adhesion to the substrate surface. Difficulties in obtaining a sufficiently thin coating to achieve increased light transmissivity and reduced reflection may also be encountered at concentrations above about 15 weight percent. At
10 concentrations below 0.1 weight percent, process inefficiencies result due to the large amount of liquid which must be removed and antireflection properties may be reduced.

The thickness of the applied wet coating solution is dependent on the concentration of inorganic metal oxide particles in the coating solution and the desired thickness of the dried coating. The thickness of the wet coating solution is preferably such that the resulting dried coating thickness is from about 80 to 500 nm
15 thick, more preferably about 90 to 200 nm thick.

The coating solution may also optionally contain a surfactant to improve wettability of the solution on the substrate, but inclusion of an excessive amount of surfactant may reduce the adhesion of the coating to the substrate. Examples of suitable surfactants include "Tergitol" TMN-6 (Union Carbide Corp.) and "Triton" X-100 (Rohm and Haas Co.). Generally the surfactant can be used in amounts of up to about 0.5 weight
20 percent of the solution.

The coating solution may optionally contain a polymeric binder to aid in adhering the coating to the substrate. Useful polymeric binders include polyvinyl alcohol, polyvinyl acetate, polyesters, polyamides, polyvinyl pyrrolidone, copolyesters, copolymers of acrylic acid and/or methacrylic acid, and copolymers of styrene. The coating solution can contain up to about 20 weight percent of the polymeric binder based on
25 the weight of the inorganic metal oxide particles. Useful amounts of polymeric binder are generally in the range of 1 to 15 weight percent. These binders can reduce some of the beneficial properties (e.g., antistatic properties) of the coatings so are not most preferred.

The following procedures were used in making all samples used in the following Examples.

30

EXAMPLES

Examples 1-25

35 Sol-Gel Coating Procedure

Sol-gel solution was coated on film substrate using a wire-wound Meyer rod (either #4 or #6) drawn down by hand. Each coated sample was dried for 90 seconds in a 110°C oven. Wetting agent was added in a few cases to improve coating quality. These samples were tested for surface resistivity, yellowness index,
40 and water contact angle.

Conditions and compositions for each example were as follows:

175 micron poly(ethylene terephthalate) base with a poly(vinylidene chloride) (PVdC) primer were used except where noted. Deionized water was used wherever water is indicated.

45

Emulsion Coating Procedure

Sol-gel samples were coated with an X-ray photographic emulsion under red light using a #24 Meyer rod, drawn down by hand on a glass sheet over a tray of ice (in order to stimulate a chill zone). The
50 emulsion was 0.25 micron cubic grains of 64% AgCl and 36% AgBr with a narrow size distribution and was maintained in a constant temperature bath at 40°C. Each sample was cured for 5 minutes in a 32.5°C oven. All samples were then aged for one week at ambient temperature.

55

Wet Adhesion Testing

Emulsion coated samples were immersed in conventional photographic developer for 3 minutes, then conventional fixer solution for 5 minutes, followed by a 10 minute water wash. The wet samples were then scribed with a razor, rubbed firmly with a fingertip, and checked for loss of adhesion. Samples were graded 0 to 10 (perfect).

Additional Testing on Sol-Gel Coating

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Surface resistivity (a measure of surface charge conductivity), the water contact angle (a measure of surface wettability), and yellowness index (a measure of bulk yellowness) were also taken.

15 Example 1 Solution: 2.5% Nalco 2326 colloidal silica (50 Å average particle size) in anhydrous Reagent Alcohol (Baker Chemical)

20 Example 2 Solution: 2.5% Nalco 2326 in water

Example 3 Solution: 2.5% Nalco 2326 in water, 0.01% Tergitol TMN-6 as wetting agent

25 8.62 g Nalco 2326
41.38 H₂O
0.5 g 10% Tergitol TMN-6 (Union Carbide)

30

Example 4 Solution: 2.5% Nalco 2326 in water, 0.01% Triton X-100 as wetting agent

35 8.62 g Nalco 2326
41.38 g H₂O
0.5 g 10% Triton X-100 (Rohm & Haas)

40

Example 5 Solution: 2.5% Nalco 1115 colloidal silica (40 Å particle size) in water

45 8.33 g Nalco 1115
41.67 g H₂O

50 Example 6 Solution: 2.5% Nalco 2327 colloidal silica (200 Å particle size) in H₂O

55 3.13 g Nalco 2327
46.87 g H₂O

Example 7 Solution: 2.5% Nalco 1060 colloidal silica (600 Å particle size) in H₂O>

5 2.5 g Nalco 1060
 47.5 g H₂O

10 Example 8 Solution: 2.5% TX2588 (Nalco TiO₂ sol, 200 Å particle size) in H₂O

 8.93 g TX2588 + 0.5 g 10% Tergitol TMN-6 41.07 g H₂O
15

Example 9 Solution: 2.5% Nyacol SN-20 (colloidal SnO₂) in H₂O

20 5 g SN-20
 45 g H₂O

25

Example 10 Solution: 2.5% Nalco ISJ-611 (colloidal Sb₂O₅, 170 Å particle size) in H₂O

30 10.4 g ISJ-611
 39.6 g H₂O

35 Example 11 Solution: 2.5% Nalco ISJ-612 (alumina coated silica sol, 200 Å particle size) in H₂O

 4.17 g ISJ-612
 45.83 g H₂O
40

45 Example 12 Solution: 2.5% Nalco ISJ-613 (aluminum acetate coated silica sol, 200 Å particle size) in anhydrous reagent alcohol

 5.48 g ISJ-613
 44.52 g reagent alcohol
50

55

Example 13 Solution: 2.5% Nalco ISJ-614 (colloidal alumina [Al₂O₃], 200 Å particle size) in H₂O

5 12.5 g ISJ-614
 37.5 g H₂O

10 Example 14 Solution: 2.5% Nyacol colloidal ZrO₂ (50-100 Å particle size) in H₂O

 5.4 g ZrO₂
 44.6 g H₂O
15

20 Example 15 Solution: 2.5% Nyacol ZrO₂ (HNO₃ stabilized, 50-100 Å particle size) in H₂O

 6.16 g ZrO₂•HNO₃
 43.84 g H₂O

25

Example 16 Solution: 2.5% Nyacol ZrO₂ (acetic acid stabilized, 50-100 Å particle size) in H₂O

30 6.38 g ZrO₂•Acetic acid
 43.62 g H₂O
 #6 Meyer rod used

35

Example 17 Solution: 2.5% Nyacol CeO₂ (HNO₃ stabilized, 100-200 Å particle size) in H₂O

40 5.68 g CeO₂•HNO₃
 44.32 g H₂O

45

Example 18 Solution: 2.5% Nyacol CeO₂ (acetic acid stabilized, 100-200 Å particle size) in H₂O

50 8.17 g CeO₂•Acetic acid
 41.83 g H₂O

55

Example 19 Solution: 2.5% Nyacol Y_2O_3 (100 Å particle size, acetic acid stabilized) in H_2O

8.93 g Y_2O_3 •Acetic acid
 41.07 g H_2O
 #6 Meyer rod used

10

Example 20 Solution: 2.5% Nalco 2326 colloidal silica in anhydrous reagent alcohol. Base: 122 micron polystyrene, "Trycite 4000" (Dow Chemical)

15

Example 21 Solution: 2.5% Nalco 2326 in anhydrous reagent alcohol.
 Base: 122 micron polystyrene, nitrocellulose/gelatin primed.

20

Example 22 Solution: 2.5% Nalco 2326 in anhydrous reagent alcohol.
 Base: 100 micron PET, PVdC primed, gelatin subbed

25

Example 23

2.24% Nalco 2326
 0.25% Acrysol A-3
 0.0015% Triton X-100
 0.001% Victawet 12
 31.5% H_2O
 50.0% reagent alcohol

Coated during film making, using reverse roll air knife method, on PVdC primed 100 micron PET. The oven temperature was 106°C.

35

Example 24

2.25% Nalco 2326
 0.25% ISOBAM-10 (binder resin available from Kuraray Isoprene Chemical Co., Ltd., Tokyo, Japan)
 0.001% Triton X-100
 97.5% H_2O

Coating conditions same as in Example 23.

45

Example 25 Solution: 2.5% Nyacol colloidal zircon (ZrSiO_4) (100 Å particle size) in H_2O

50

5.18 g ZrSiO_4
 44.82 g H_2O

55

Results

All sol-gel solutions formed continuous coatings on the film substrates. When dry, the coatings adhere under firm rubbing with a fingertip. Emulsion coated acceptably over all sol gel samples and adhered during normal handling while dry. Failure was observed in certain samples during the wet adhesion test. These materials could undergo hand development and provide satisfactory images and gain some benefits of the present invention. All samples provided good dry adhesion.

Table

Sample No.	Surface Resistivity [ohms/sq]	15 Second	Yellowness Index - YI	Emulsion
		Average Contact angle		Wet Adhesion
1	6.51×10^9	7	5.65	10
2	6.51×10^8	6	5.77	9
3	6.51×10^8	0	5.67	8
4	6.36×10^8	0	5.81	-
5	8.09×10^7	3	6.57	4
6	6.36×10^9	0	5.93	0
7	6.36×10^{10}	0	6.21	0
8	6.36×10^8	14	6.00	10
9	6.21×10^7	4	7.59	6
10	6.20×10^9	5	7.34	3
11	6.21×10^8	22	6.57	2
12	6.20×10^9	45	6.88	0
13	6.07×10^{10}	70	6.33	0
14	6.20×10^9	67	7.04	0
15	6.20×10^{10}	67	6.64	0
16	6.07×10^{10}	62	6.46	0
17	6.07×10^{10}	58	9.88	0
18	6.07×10^8	49	12.47	0
19	6.07×10^{10}	43	7.46	0
20	6.07×10^{10}	5	0.22*	9
21	6.07×10^{10}	6	0.80*	8
22	5.90×10^9	0	4.20	10
23	5.90×10^9	21	1.92	9
24	6.07×10^5	0	2.31	-
25	5.80×10^{11}	64	8.19	0

YI: The higher the number, the more yellow the film

* polystyrene is a hazy base, thus the low YI values

Examples 26-35 Coating Methods: Meyer bar handspread

Spin coated

Binders used:

RD-977 (vinylidene chloride/ethyl acrylate/itaconic acid terpolymer latex, i.e., "PVdC")

5 BAI (n-butyl acrylate/acrylonitrile/itaconic acid) BAIG (n-butyl acrylate/acrylonitrile/itaconic acid/glycidyl methacrylate)

ISOBAM (maleic anhydride/isobutylene copolymer)

RLS-375 (urethane)

RD-745 (phenolic resin)

10 Acrysol A-3 - Rohm & Haas (acrylic resin)

HPAR (acrylic resin)

PVA - Moviol 4-98 (polyvinyl alcohol)

P-70 - Toray Ind., Inc. (aqueous nylon)

FC-461 - 3M (fluorochemical)

15 AZ - (aziridine)

Dema (APB-2) (dimethyl amine/aminized polybutadiene)

Specific Examples: all use Nalco 2326 colloidal silica

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Specific Examples: all use Nalco 2326 colloidal silica

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	% Nalco 2326	% Binder	Binder Name	Film Substrate
	5	1.23	RD-977	PVdC primed PET
	2.5	.32	BAI	PVdC primed PET
30	9	1.0	BAI	PVdC primed PET
	9	1.0	BAI	Plain PET
	2.25	.2	BAIG	PvdC primed PET,
35				plain PET
	2.5	.83	RLS-375	PvdC primed PET
	2.25	.25	RD-745	Plain, PVdC
40				primed PET
	2.25	.25	ISOBAM	Plain, PVdC
				primed PET
45	2.25	.25	Acrysol A-3	Plain, PVdc
				primed PET
				acrylic sheeting
				Kel-F lenses
50	2.25-1.25	.25-1.25	H+HP	Acrylic sheeting
			HPAR	Kel-F lenses

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Nalco 2326/binder				Film
Proportion	Binder Name	% Solids	Substrate	
5 — 95/5	Moviol 4-98	2.2	100 μ m	PET (plain)
90/10	Moviol 4-98	2.2	100 μ m	PET (plain)
10 85/15	Moviol 4-98	2.2	100 μ m	PET (plain)
90/10	P-70	5.0	100 μ m	PET (plain)
15 95/5	FC-461	2.5 - 5.0	100 μ m	PET (plain)
90/10	FC-461	2.5 - 5.0	100 μ m	PET (plain)
20 95/5	RD-977	5.0	100 μ m	PET (plain)
25 98/2	AZ	5.0	100 μ m	PET (plain)
99.95/.05	Dema (APB-2)	2.5	100 μ m	PET (plain)
30 99.5/.5	Dema (APB-2)	2.5	100 μ m	PET (plain)
35 99/1	Dema (APB-2)	2.5	100 μ m	PET (plain)

Examples 36 - 43

These examples show the utility of sol gel coatings on coated paper base. Paper: Four types tested differing primarily in the weight of the paper and the thickness of the polyolefin surface coating

Batch	% Softwood		% Hardwood		% Pulpex E	% Parez 607	% Hycar 1562X003
45 1A	80		20		0	0	0
B	64		16		20	0	0
2A	48		12		40	0	0
50 B	72		18		10	0	0
3A	80		20		0	+3	+ 2.5
B	80		20		0	+3	+10
55 4A	80		20		+5	0	0
B	80		20		+5	+3	+ 5

Coating Method: Dip 12 × 20 cm sample in tray of sol gel solution
Place on paper toweling and drain by rolling with towel-wrapped bar
Dry in 85-95°C oven for 5 minutes Condition 24 hours in 50% R.H. before testing surface resistivity

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Coating Solution: 2.5% Nalco 2326 colloidal silica in H₂O + 0.1% by weight of solution Tergitol TMN-6 wetting agent

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	Paper	Surface Resistivity [ohm/sq]		Static Decay (seconds)	
		uncoated	sol gel coated	uncoated	coated
15	1A	2.7×10^{13}	1.4×10^{12}	1.41	0.16
	1B	5.9×10^{13}	5.9×10^{12}	2.35	0.67
	2A	5.8×10^{13}	8.2×10^{12}	3.59	1.43
	2B	3.4×10^{13}	1.2×10^{12}	0.95	0.19
20	3A	1.3×10^{13}	3.3×10^{12}	1.43	0.31
	3B	1.8×10^{13}	4.3×10^{12}	0.96	0.37
	4A	3.2×10^{13}	5.9×10^{11}	1.82	0.11
25	4B	2.3×10^{13}	4.1×10^{12}	2.68	0.44

The terms sol-gel and gelation, as they apply to the use of inorganic dispersions of particles in the formation of layers, are well understood in the art. Sol-gels, as previously described, comprise a rigidized dispersion of a colloid in a liquid, that is the gelled network previously described. Gelation is the process of rigidizing the sol-gel. This is often accompanied by extraction of the liquid. Gelation, as opposed to pyrolysis, does not necessarily require the addition of heat as room temperatures and normal humidity conditions will allow gelation to occur. These temperatures and humidity conditions will eventually remove sufficient amounts of the liquid for the colloidal particles to become more solid. Heat of course can be useful in speeding up the liquid extraction process as would gas flow directed against or parallel to the sol-gel coating.

The liquid extracted sol-gel coating (which will generally retain some significant amounts of liquid, e.g., at least 0.1% by weight up to 10% or 15% or more by weight in some cases) can be described in a number of various physical terms which distinguish it from other particulate constructions such as sintered, adhesively bound, or thermally fused particles. The association of the particles in a sol-gel system is a continuous sol-gel network which is known to mean in the art that the particles form an inorganic polymer network at the intersection of the particle (e.g., as with silica sol-gels), or an inorganic salt system. Bonding forces such as van der Waals forces and hydrogen bonding can form an important part of the mechanism of particle association. These characterizations of sol-gel compositions are quite distinct from the use of polymer binders which form a binding medium to keep particles associated and where the particles themselves do not exert direct bonding forces on one another.

As previously noted, the size of the colloid particles in the sol-gel is important. Processes where particulates are ball-milled generally produce particles of no less than about 1 micron. Unless a chemical process is used to form the particles of smaller size, which agglomerate to effectively form large particles which are then ball-milled to break up the agglomeration, the particle size limit of about 1 micron from physical processing tends to hold true.

Larger particles also cannot be used in sol-gel compositions to form an integral layer by only gelation processes. The large particles do not bond with sufficient strength to withstand any significant abrasion.

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Claims

1. A radiation sensitive photographic element comprising a substrate with at least one polymeric surface and at least one photographic emulsion over said at least one polymeric surface, said element being characterized by the fact that said at least one polymeric surface has adhered thereto a continuous gelled network of inorganic particles.
2. The element of claim 1 wherein said inorganic particles are inorganic oxide particles.
3. The element of claim 2 wherein said gelled network of inorganic oxide particles comprises a layer having an average thickness of between 300 and 10,000 Angstroms.
4. The element of claim 2 wherein said gelled network of inorganic oxide particles comprises a layer having an average thickness of between 80 and 5,000 Angstroms.
5. The element of claim 2 wherein said gelled network of inorganic oxide particles comprises a layer having an average thickness of between 900 and 2,000 Angstroms.
6. The element of claims 1-5 wherein said inorganic oxide particles are selected from the class consisting of yttria, ceria, silica, titania, chromia, zirconia, tin oxide, alumina and mixtures thereof.
7. The element of claims 1-5 wherein said layer comprises, as up to 20 percent by weight of the oxide particles, a polymeric binder.
8. The element of claim 6 wherein said layer comprises, as up to 20 percent by weight of the oxide particles, a polymeric binder.
9. The element of claims 1-5 wherein said layer consists essentially of inorganic oxide particles.
10. The article of claim 9 wherein said substrate is a polymeric film selected from the group consisting of polyester, and primed polyester.

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