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2,878,121

PHOTOGRAPHIC ELEMENTS AND PROCESSES

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This invention relates to photography and more particularly to photographic image-yielding elements and to processes of forming positive photographic images in such elements. Still more particularly, it relates to photographic films, plates and papers which have a water-permeable colloid layer having dispersed therethrough finely divided inert particles coated with a silicon compound containing at least one silicon-hydrogen bond.

An object of this invention is to provide new photographic image-yielding elements. Another object is to provide photographic image-yielding films and papers which are useful in inverse-transfer processes. Yet another object is to provide such sheet elements which are relatively inexpensive and can be manufactured from economical materials. A further object is to provide new inverse-transfer processes of producing photographic images. A still further object is to provide processes of forming images in the aforesaid elements. A still further object is to provide a process of forming positive images from developed or developing silver halide negative images. Still other objects will be apparent from the following description of the invention.

It has been found that a photographic image-yielding sheet element can be prepared by providing a sheet support, e. g., a film, foil, plate or paper with a light-insensitive, water-permeable colloid layer containing finely divided discrete solid particles of inert material having an average diameter not less than 1 μ and not greater than 10,000 μ and having on their surface a silanic compound containing at least one silicon-hydrogen bond, said silanic compound constituting from 0.1% to 100% by weight of the total weight of the uncoated particles.

Various types of water-permeable organic colloids can be used as the binding agents for the silanic compound coated particles including the naturally occurring types, e. g., gelatin, albumin, zein, agar-agar, alginic acid and casein; and synthetic types, e. g., polyvinyl alcohol, partially hydrolyzed polyvinyl esters, hydrolyzed ethylene/vinyl acetate copolymers; polyvinyl acetals, including sodium o-sulfobenzaldehyde polyvinyl acetal and benzaldehyde polyvinyl acetal; polyglycuronic acid and carboxymethyl cellulose.

Suitable materials for the discrete inert particles include colorless or white materials, e. g., silicon dioxide of the dense or solid type, inorganic silicates such as magnesium silicate, diatomaceous silicas, sodium aluminum silicate and calcium carbonate, barium sulfate and titanium dioxide, etc., or colored or black particles, e. g., carbon black, lamp black, etc.

The inert particles can be coated by adding an inert solvent solution or dispersion of the silanic compound to the finely divided particles. The amount of silanic compound used should in general constitute from 0.1% to 100% of the total weight of the uncoated particles. In the case of liquid silanic compounds, no solvent is needed and the inert particles and liquid silanic compound can be mixed in suitable proportions so that the latter are

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coated in an amount between 0.1% and 100% by weight based on the weight of the uncoated particles.

The silanic compound coated particles can be prepared for coating by simply admixing them with an aqueous solution or dispersion or with an organic solvent solution or dispersion of the water-permeable colloid. In order that the coated particles may be dispersed readily throughout an aqueous solution or dispersion of the water-permeable colloid, it is desirable to use a wetting or dispersing agent in an amount of 0.1 to 100% by weight based on the total weight of the silanic compound coated inert particles. Suitable such agents include saponin and those described in Blake U. S. Patent 2,400,532, namely, the oxyalkylene ethers of hexitol ring dehydration products, e. g., the polyoxyethylene sorbitan monolaurate, monostearate and monooleates which contain 2 to 20 oxyethylene groups divided in 3 chains; a salt of an alkyl-substituted aryloxy alkylene ether sulfonate, e. g., sodium p-tertiary-octyl phenoxy ethoxy ethyl sulfonate as disclosed in Baldisiefen U. S. Patent 2,600,831; sodium dodecyl, tetradecyl and octadecyl sulfate and the dioctyl ester of sodium sulfo-succinic acid.

The photographic image-yielding elements described above have an excellent light-insensitive image-receptive layer for the inverse transfer of soluble silver complexes from the unexposed and undeveloped portions of a contiguous light-sensitive silver halide water-permeable colloid layer, as more fully described below. The silanic compound coated particles not only act as nuclei for silver deposition in the light-insensitive water-permeable colloid layer containing them but accelerate the deposition. Since the coated particles do not migrate from or in the layer, an excellent image is deposited in and on the surface of the image-receptive layer containing such particles. A more dense image is formed than when uncoated particles (e. g., silica) are used, due to the —SiH groupings in the silanic compounds which reduce the silver complexes to metallic silver.

The preferred photographic elements of the invention have only one type of image-yielding layer or strata that is non-light-sensitive (i. e., free from light-sensitive materials; e. g., silver halide, bichromates and diazonium compounds) and such layer or strata preferably is outermost so that it can be brought into surface contact with a separate outer silver halide emulsion layer of a film, paper or plate. However, other useful elements of the invention have a light-sensitive silver halide water-permeable colloid layer on the light-insensitive water-permeable colloid layer containing the silanic compound coated inert particles. The latter composite elements are described in my copending application Ser. No. 237,687, filed July 19, 1951, now U. S. Patent 2,694,637, patented November 16, 1954, of which this application is a continuation-in-part. The silver halide emulsion layer in these composite elements preferably have a colloid binding agent which is relatively soluble in water as compared with the bottom layer so that the former can be washed off after image transfer has been accomplished. The lower layer may initially be relatively insoluble or it can be hardened chemically. When gelatin is the selected colloid, the bottom layer can be hardened with a gelatin hardening agent, e. g., chrome alum, formalin and dimethylolurea.

In the image-transfer processes of this invention, a latent image of silver halide in a water-permeable colloid layer is formed by the conventional method of exposure to an object field, e. g., an original scene, reproduction or to a photographic image. Either during or after the development of the latent silver image, an aqueous solution of a silver halide solvent, e. g., sodium thiosulfate, sodium thiocyanate and sodium sulfite and mixtures of two or more of such compounds is brought into contact,

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preferably in the absence of significant actinic radiations, while the light-sensitive layer is maintained in intimate surface contact with the image-receptive layer for a period of time sufficient to dissolve a small or large part of the underdeveloped silver halide, e. g., from 5 to 600 seconds. The silver complexes thus formed diffuse into the receptive layer containing the coated particles where the silanic compound and the photographic developer reduce the silver complexes and deposit metallic silver on the particles forming an image which is the reverse from the original latent image. The original silver halide layer is then removed. For instance, if the silver halide layer was in a separate film or paper, the two elements are simply separated. If the silver halide is in a differentially soluble layer, the entire original layer is washed away. Any residual stain in the image-receptive layer, which contains a deposited silver image, can be removed, if desired, by treatment with an aqueous solution or a fixing agent.

The invention will be further illustrated but is not intended to be limited by the following examples.

Example I

To a liter of aqueous gelatin containing 5% by weight of the latter, there was added 4.0 grams of silica particles having an average diameter of 0.015 micron which were coated with trichlorosilane that hydrolyzed to form a coating of $(\text{HSiO}_{1.5})_n$ where n is 1 or more and the coating constituted 15 to 20% of the total weight of the coated particles; said coated particles being added in the form of a dispersion in ethanol which was obtained by mixing in a high-speed blending mixer. The resulting gelatin dispersion was coated on a paper sheet to form a thin layer which was dried. A separate paper sheet was coated with a similar gelatin solution but free from coated particles to form a control sample. The coatings were dried.

Separate photographic contact printing paper samples bearing a chlorobromide gelatin emulsion layer were exposed to a transparent positive image in a film element and the resultant exposed element, samples of the light-insensitive papers bearing the gelatin layers containing the coated particles and samples of the light-insensitive papers free from such particles were separately immersed for 1.5 minutes in a developer solution at 68° F. made by admixing the following components

	Grams
N-methyl para-aminophenol sulfate	1.0
Hydroquinone	4.0
Sodium sulfite	15.0
Sodium carbonate	22.5
Potassium bromide	0.63
Water to make 1.0 liter	
Sodium thiosulfate	1.0

The exposed printing paper samples were removed from the developer together with the developer impregnated gelatin coated elements and separate samples of exposed element and gelatin element pressed together tightly with their gelatin surfaces in contact for 10 minutes. At the end of this period the layers were separated, fixed, washed and dried with the following results:

Image-Receptive Layer	Resultant Positive Image
Gelatin (no particles)	Very faint.
Gelatin+coated particles	Vigorous image with clean white areas.

Example II

One gram each of silanic compound coated silica particles, types (a), (b) and (c), in the form of an ethanol dispersion (prepared as described in Example I) was added to separate 250 ml. samples of aqueous gelatin (5% by weight) containing 1.6 ml. of saponin and 1.5 ml. of 10.25% by weight aqueous solution of chrom alum:

(a) Silica particles having an average diameter of 0.015

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micron coated with $(\text{SiHO}_{1.5})_n$ where n is a positive integer of 1 or more in an amount of 15 to 20% by weight of the coated particles. (Manufactured by Linde Air Products Company as "Coated Silica 30.")

(b) Coated particles similar to (a) consisting of silica particles having an average diameter of 0.015 micron coated with $(\text{SiHO}_{1.5})_n$ where n is a positive integer of one or more (said coated particles being prepared from silica particles of such diameter which were made by Mallinckrodt Chemical Works.)

(c) Silica particles coated with 5% by weight of $\text{HO}[(\text{C}_2\text{H}_5)_3\text{HSiO}]_n\text{H}$ where n may be from 6 to 20. The resulting gelatin dispersions were coated on a baryta coated paper stock and the coating dried. The initial gelatin solution free of coated silica particles was coated on the same type of paper and the coating dried.

Separate photographic contact printing paper samples bearing a silver chlorobromide gelatin emulsion layer were exposed to a positive image in a film element and the papers together with samples of image-receptive papers (a), (b) and (c) were separately immersed for 1.5 minutes in a developer solution at 68° F., as described in Example I. The exposed impregnated photographic paper samples and impregnated samples (a), (b) and (c) were pressed together tightly with their gelatin surfaces in contact for 10 minutes. At the end of this period, the layers were separated and dried with the following results.

Image-Receptive Layer	Resultant Positive Image
Gelatin (no particles)	Faint image.
Gelatin+coated particles (a)	Strong blue-black image.
Gelatin+coated particles (b)	Do.
Gelatin+coated particles (c)	Do.

Each of the images in the papers of the foregoing table showed the same stain. However, in similar experiments the stain in each image-bearing layer was eliminated by fixing the positive prints for 3 minutes in a fixer made by admixing the following ingredients:

Sodium thiosulfate $\cdot 5\text{H}_2\text{O}$	grams	240
Sodium sulfite, desiccated	do	15
Borax $\cdot 10\text{H}_2\text{O}$	do	18
Glacial acetic acid	ml	12
Potassium alum $\cdot 24\text{H}_2\text{O}$	grams	20
Water to make 1 liter		

and washing the treated elements with water and drying.

Example III

One gram of silica coated particles in ethanol solution as described in Example I was added to a 250 ml. sample of medium viscosity polyvinyl alcohol (essentially completely hydrolyzed polyvinyl acetate), ethanol and water in the proportions 5:5:90% by weight, said solution containing 6.25 ml. of a 25% by weight aqueous solution of cetyl betaine. The resulting polyvinyl alcohol dispersion was coated onto a baryta coated paper stock and the thin layer dried. An identical polyvinyl alcohol solution containing no coated silica particles was coated onto baryta coated paper in like manner and the coatings dried to form control paper samples.

Samples of lithographic film having a gelatin silver chlorobromide emulsion layer on a cellulose acetate support were exposed in the manner described in Example I. The emulsion surface of the exposed samples was brought into intimate contact with the coated surface of two papers described in the previous paragraph and with the coated papers described in Example II in a commercial developing apparatus (an "Autostat" sold by The American Photocopy Equipment Company) having means for bringing the surfaces in contact and containing

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a developer solution at 68° F. of the following composition:

Water at 125° F.	ml.	750
Sodium sulfite (anhydrous)	grams	45.0
Hydroquinone	do.	16.0
Boric acid crystals	do.	5.5
Potassium bromide	do.	2.0
Sodium thiosulfate (anhydrous)	do.	15.0
"Serox" CD ¹ (1/50, C ₂ H ₅ OH, v./v.)	ml.	5.0
1-phenyl-5-mercaptotetrazole (1 gm. in 1000 cc. CH ₃ OH)	ml.	6.0
Sodium hydroxide	grams	24.0
Cold water to make 1.0 liter		

¹ A polyethylene ester of a tall oil acid (sold by Monsanto Chemical Company).

After 20 seconds of contact, the lithographic film samples were separated and the gelatin and polyvinyl alcohol image-receptive layers were treated in the fixing solution described in Example II for 3 minutes and dried with the results given in the following table:

Image-Receptive Layer	Resultant Positive Image
Gelatin (no particles)	Faint gray.
Gelatin+coated particles (a)	Brown.
Gelatin+coated particles (b)	Do.
Gelatin+coated particles (c)	Black.
Polyvinyl alcohol (no particles)	Faint gray.
Polyvinyl alcohol+coated particles (a)	Brown-black.

Example IV

The procedure set forth in Example II was repeated, except that the control gelatin coating contained uncoated silica particles of the same average diameter with the following results:

Image-Receptive Layer	Resultant Positive Image
Gelatin+silica particles (uncoated)	Faint.
Gelatin+coated particles [(a) of Example II]	Strong.

Example V

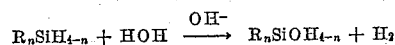
A liquid gelatino-silver bromide motion picture positive emulsion containing no hardener was coated over the image-receptive paper (a) and on the gelatin control (d) of Example II. The light-sensitive layer was dried and the resultant two-layer element was exposed to a transparent positive image in a film element and the two layer element was then immersed in a developer of Example I for 1.5 minutes at 68° F. After this immersion period the element was removed and placed, emulsion side down on a glass plate for 15 minutes to allow inverse-transfer development to take place. The element was then removed from the glass plate and the unhardened silver bromide layer containing the negative silver image was removed by flushing with hot water. The lower, hardened image-receptive layer was then found to bear a strong positive image record corresponding to the original transparent positive film image. Similar processing of the element prepared using the gelatin coated control (d) revealed only a faint trace of a positive image after hot water washing.

The invention is, of course, not limited to the use of the specific silanic compounds mentioned in the foregoing examples nor to the specific amounts given in such examples. A large number of other silanic compounds which possess at least one silicon-hydrogen bond can be substituted in like manner.

The utility of any particular silanic compound which contains a silicon-hydrogen bond can be determined by testing whether it or its hydrolysis products are capable of exerting a reducing action on or nucleating silver halide. The mechanism or theory as to why the silanic

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compounds are effective as chemical sensitizers for silver halide emulsions is not completely understood but it is believed that the silicon-hydrogen linkage must be capable of alkaline induced hydrolysis which is illustrated in the following equation for a useful class of silanic compounds:



where R_n is hydrogen, halogen, e. g., Fl, Cl and Br; alkyl of 1 to 30 carbon atoms, alkoxy of 1 to 30 carbon atoms, aryl, e. g., phenyl, tolyl, naphthyl, etc.; aryloxy, e. g., phenoxy, naphthoxy, etc., siloxy or combinations thereof, "n" being 1 to 3.

Among the additional suitable specific silanic compounds which can be used, there may be mentioned: alkyl silanes, e. g., methyl silane, dimethyl silane, trimethyl silane; ethyl silane, diethyl silane, triethyl silane, n-propyl silane, butyl silane; alkyl halogenosilanes, dimethylchlorosilane, ethyl dichlorosilane, diethylchlorosilane, propyl dichlorosilane; aryl silanes, e. g., diphenyl silane, triphenyl silane, and mixed alkyl aryl silanes, e. g., ethyl diphenyl silane, methyl phenyl silane and dihexyl phenyl silane; alkoxy, aroxy, alkoxy halogeno, and aroxy halogeno silanes, e. g., diethoxy silane, methyl dichlorodiethoxy silane and phenoxy silane; cyclic and linear polymeric siloxanes, e. g., cyclic tetrameric methyl siloxane and its linear analogue HO[CH₃(H)SiO]₄H. Hydrolysis products of the above listed silanes which retain a silicon-hydrogen bond may be used also.

Mixtures of two or more silanic compounds can be coated on the particles or mixtures of two differently coated particles can be dispersed in the aqueous colloid solution used to coat the image-receptive layers. Different types of carrier particles coated with either the same or different silanic compounds may also be used.

The quantity of silanic coated particles used in the water-permeable colloid may vary over a wide range of proportions. A practical range is from 0.1 mg. to 100 g. per 100 mg. of colloid. It is possible to prepare layers of active silanic compound coated particles with no water-permeable colloid binder by coating them onto a plastic support from a dispersion in a solvent having a solvent action on the support, e. g., acetone in the case of cellulose acetate. The particles can be dusted on a support which is heated to soften the surface. The particles can be forced into or imbedded in the softened surface by means of a roller.

Various types of supports may be used for the image-receptive layers containing silanic compound coated particles. Suitable supports include films and plates composed of cellulose derivatives, e. g., cellulose acetate, propionate, butyrate, acetate-butyrate, and nitrate; super-polymers, e. g., nylon, polyvinyl chloride, poly(vinyl chloride co vinyl acetate), polystyrene, polymethylene terephthalates, e. g., polyethylene terephthalate; thin aluminum sheets; paper and cardboard, etc. Of course, various sublayers may be present to anchor the layers to the base as is common in photographic film and plate manufacture.

Any of the conventional photographic developing solutions can be used in carrying out the process. Suitable developing agents and solutions are described in Mees "The Theory of the Photographic Process" published by The Macmillan Company, New York (1946), pages 338-369 and particularly page 352.

The novel image-receptive elements of this invention are useful in the reproduction of various images. Thus, they are useful in copying printed matter. In this case an image-receptive paper is used with a separate exposed film bearing a light-sensitive silver halide latent image. The image-receptive papers are especially useful in direct-positive photography. The receptive paper and light-sensitive film or paper being separate elements but

the development being completed in contact with simultaneous inverse-transfer.

An advantage of the invention is that it provides new and practical light-insensitive image-receptive films, sheets, plates and papers which are economical to make and simple to use. The image-receptive elements are stable over long periods of time. They give more dense images than when uncoated particles are used. The coated particles can be made long prior to coating operations and do not require storage in the absence of actinic radiations. The preparation of silanic compound coated particles is a simple and inexpensive operation in contrast to the difficult operation of producing colloidal or complex particles heretofore used. A further advantage is that the particle size of the particles can easily be selected before the silanic coating operation, thus allowing a large selection of types of particles of reproducible and controlled sizes from the many such particles which are common items of commerce. The silanic coated particles are dry powders which are easily stored and handled and offer many other advantages such as ease of controlling concentration of active ingredient through changes in type and amount of silanic coating.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An image-receptive element for photographic reproduction comprising a sheet support bearing a light-insensitive water-permeable organic colloid layer having dispersed therethrough finely divided inert solid silica particles having an average diameter from 0.001 to 10.0 microns coated with a silanic compound having at least one silicon-hydrogen bond, said compound constituting 0.1 to 100% of the weight of the uncoated silica particles; said coated particles being present in the amount of 0.1 mg. to 100 grams per 100 mg. of the colloid.

2. An element as set forth in claim 1 wherein the said colloid layer is the only image-yielding layer in the element.

3. An element as set forth in claim 2 wherein said support is paper.

4. An element as set forth in claim 2 wherein said colloid layer is outermost.

5. An image-receptive element for photographic reproduction comprising a sheet support bearing a light-sensitive water-permeable colloid silver halide layer and a contiguous light-insensitive water-permeable organic colloid layer having dispersed therethrough finely divided inert solid particles having an average diameter from

0.001 to 10.0 microns coated with a silanic compound having at least one silicon-hydrogen bond, said compound constituting 0.1 to 100% of the weight of the uncoated particles; said coated particles being present in the amount of 0.1 mg. to 100.0 grams per 100 mg. of the colloid.

6. An element as set forth in claim 5 wherein the particles are silica.

7. An element as set forth in claim 6 wherein said support is paper.

8. A photographic reproduction process which comprises impregnating with a developer solution an exposed silver halide layer and a contiguous light-insensitive layer of finely divided inert solid particles having an average diameter from 0.001 to 10.0 microns coated with a silanic compound having at least one silicon-hydrogen bond, said compound constituting 0.1 to 100% of the weight of the uncoated particles, maintaining said layers in surface contact until the images are developed and removing the original silver halide layer.

9. A photographic reproduction process which comprises impregnating with a developer solution an exposed silver halide layer and a contiguous light-insensitive water-permeable organic colloid layer having dispersed therethrough finely divided inert solid particles having an average diameter from 0.001 to 10.0 microns coated with a silanic compound having at least one silicon-hydrogen bond, said compound constituting 0.1 to 100% of the weight of the uncoated particles, said coated particles being present in the amount of 0.01 mg. to 100 grams per 100 mg. of the colloid, maintaining said layers in surface contact until the images are developed and removing the original silver halide layer.

10. A process as set forth in claim 8 wherein the light-sensitive layer is on a separate support from the light-insensitive layer and the light-insensitive layer is outermost on its separate support.

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