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PROCESS FOR MINIMIZING CONTAMINANTS ON
A PHOTOGRAPHIC ELEMENT
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FIG. 1

ELIMINATION OF BASE CONTAMINATION

EMULSION COATED AT LOW pH
AUXILIARY LAYER COATED AT HIGH pH
FILM BASE

FIG. 2

ELIMINATION OF EMULSION CONTAMINATION

AUXILIARY LAYER COATED AT LOW pH
EMULSION COATED AT HIGH pH
FILM BASE

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3,123,492 PROCESS FOR MINIMIZING CONTAMINANTS ON A PHOTOGRAPHIC ELEMENT

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This invention relates to a process for preparing improved photographic elements. More particularly it relates to a method for reducing the effect of certain contaminants on the photographic element without adversely affecting the photographic properties of the element.

It is well known in the art of manufacturing photographic products that certain contaminants can have adverse effects on the photographic product. For example, metallic dusts in the emulsion or on the support can result in either locally desensitized or sensitized areas. A microscopic foreign particle can contaminate an area many times the size of the particle. The effect of contaminants is usually not perceptible until after the photographic material has been processed thus frequently running the film and causing great annoyance as well as loss of time and material.

Many times of metallic and other contaminants are known (see E. Zünd, Z. Wiss. Phot., vol. 49 (1954), pages 25-104, specifically pages 29-47). The effect of many of these contaminants cannot always be predicted. Likewise, a particular effect cannot always be traced with certainty to a specific contaminant. Factors such as the type of photographic emulsion, conditions of storage, developer used, density level after development, etc., are of great influence on the effect of certain contaminants. For example, a specific material may contaminate an X-ray film but not a cine positive film. Also, a contaminant can act as a sensitizer if the film is processed to low densities and as a desensitizer if the film is processed to high densities. The respective effects will be dark spots or markings in one case and markings of lower density in the other. Some marks resulting from contamination of films are visible only in a certain density range, usually the middle density range, between the values of about 0.5 and 1.0. At lower densities they may not be noticeable, and at higher densities they may be masked by the silver image. The above type of imperfections are extremely troublesome because they appear in an erratic fashion depending on the density of the developed silver.

One particular type of contamination is caused by discrete metallic particles present in the photographic emulsion or on the base support in a relatively reduced state, i.e., in a lower than maximum normal oxidation state. The presence of such particles may result in a reduction of silver ions to metallic silver while simultaneously the contaminant particle is oxidized to a higher oxidation state. The net result is the appearance of a localized sensitized area of higher density in the developed film, the sensitized area frequently being surrounded by an equally undesirable ring or halo of a desensitized area of lower density.

An object of this invention is to eliminate or minimize the effect of contaminants, in particular certain metallic contaminants, on photographic silver halide emulsions. Another object is to accomplish this result by utilizing standard photographic film manufacturing equipment. A further object is to eliminate the effect of such contaminants without materially affecting the photographic properties of a given emulsion. Still further objects will be apparent from the following description of the invention.

The above objectives of this invention are attained by a process for preparing a photographic element comprising a base support and coating over said support a first layer

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buffered to a pH within the range of 6.0 to 8.0 and coating over said first layer a second layer having a pH below 4.5 such that the pH of the final element is within the range of 4.0 to 7.0, one of said layers being a layer of a water-soluble colloid silver halide emulsion and the other being an auxiliary layer. By this process the deleterious effects of contaminants in the photographic emulsion or on the base support are minimized.

In reference to the accompanying drawings:

FIG. 1 illustrates the cross-section of a photographic element wherein the effects of contaminants on the base are minimized.

FIG. 2 illustrates the cross-section of a photographic element wherein the effects of contaminants in the emulsion are minimized.

The legends on the drawing are self-explanatory and make further explanation thereof unnecessary.

Generally, when the contaminants are present on subbed or unsubbed film base as in FIG. 1 they can be eliminated or minimized by coating on the base a relatively high pH, weakly buffered, thin, auxiliary undercoating layer, the auxiliary layer being overcoated with a photographic emulsion having a low pH. Contaminants in the emulsion as in FIG. 2 are eliminated or minimized by coating on a film base, an emulsion at a relatively high pH and a low pH, weakly buffered, auxiliary antiabrasion layer.

The auxiliary layer as indicated above may be an antiabrasion overcoating layer weakly buffered at a pH within the range of 1.0 to 4.5. A thin layer, e.g., of gelatin, coated beneath the emulsion layer, weakly buffered at a pH within the range of 6.0 to 8.0 is also effective; as is a weakly buffered separator layer located between and adjacent to the emulsion layers in the case of multilayer coatings. The separator layer is buffered at a pH within the range of 1.0 to 8.0. Two or more of the above-described buffered auxiliary layers can be used in appropriate photographic elements.

In an embodiment of this invention a thin layer of a water-permeable colloid binder material, e.g., gelatin, is first coated on a film support, the pH of this layer being weakly buffered and being high enough to fully oxidize contaminant particles adhering to the surface of the base support, e.g., 6.0 to 8.0. A photographic emulsion is then coated over this layer, the emulsion pH being such that the pH of the final element is within the predetermined values described above. The emulsion coating can be overcoated with another similar or dissimilar layer, e.g., a second emulsion layer, a separator layer or an antiabrasion layer. The antiabrasion layer, too, can be buffered, if necessary, to further adjust the final pH of the element.

In photographic products that use two or more silver halide emulsion layers, e.g., multilayer black and white and color films, the pH of the several emulsions can be adjusted and, if necessary, buffered to different values so that the final over-all pH of the element is within the desired range. The auxiliary layers; in addition to providing a means for adjusting the pH of the photographic element; also fulfill other purposes, e.g., they can contain ingredients such as hardeners, wetting agents; dyes, pigments, matte, etc., that are not used specifically to adjust the pH of the emulsion.

While not being limited by the following discussion, it is believed that the improved photographic elements are obtained by preparing and coating a photographic emulsion at a pH sufficiently high so as to oxidize any metallic contaminants present in the emulsion or on the support to their highest normal oxidation state. The metallic contaminants are thereby rendered incapable of subsequent further oxidation and corresponding reduction of silver ions. Any metallic silver formed in the emul-

sion as a consequence of the contaminant oxidation is believed to be distributed throughout the mass of the emulsion, rather than remaining concentrated in the vicinity of the contaminant particles. The quantity of such silver is generally extremely slight so that it cannot be detected in this dispersed state.

While the metal contaminants are neutralized by the increase in emulsion pH, undesirable effects such as instability upon aging may result. To insure good photographic qualities, the pH of the emulsion should be reduced after the contaminants have been oxidized. This pH adjustment is accomplished by coating adjacent to the emulsion layer an auxiliary layer as described above which is weakly buffered at a pH such that the final pH of the element falls within the predetermined range of 4.0 to 7.0.

This invention is applicable to all types of photographic emulsions that are susceptible to contaminants of the type described above, i.e., contaminants in a lower than maximum normal oxidation state. The contaminants include, for example, iron, stainless steel, aluminum, nickel, copper, brass, carbon, etc. See the Zünd article. Typical such emulsions include negative, positive, X-ray, graphic arts emulsions, etc. They contain silver bromide or silver chloride or mixtures thereof and/or silver iodide in a suitable water-permeable colloid binder, preferably gelatin, or synthetic materials, or mixtures thereof to be hereinafter described. The emulsions are generally coated to a weight of 20 to 100 mg. of silver per square decimeter.

In place of the preferred gelatin binder for the emulsion and auxiliary layers there can be substituted other natural or synthetic water-permeable organic colloid binding agents. Such agents include water-permeable or water-soluble polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, polyvinyl ethers, and acetals containing a large number of extralinear- CH_2CHOH — groups; hydrolyzed interpolymers of vinyl acetal and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic acid ethyl esters, and styrene. Suitable colloids of the last mentioned type are disclosed in U.S. Patents 2,276,322, 2,276,323 and 2,397,866. The useful polyvinyl acetals include polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal and polyvinyl sodium o-sulfobenzaldehyde acetal. Other useful colloid binding agents include the poly-N-vinylactams of Bolton U.S. Patent 2,495,918; the hydrophilic copolymers of N-acrylamido alkyl betaines described in Shacklett U.S. Patent 2,833,650; and hydrophilic cellulose ethers and esters.

The photographic emulsions of this invention can contain color formers of the type used in multilayer color films. Suitable examples of color formers include, e.g., those disclosed in Mees, "The Theory of the Photographic Process," Revised Edition, The Macmillan Co., New York, 1954, pages 584 to 604. Also useful are the polymeric color formers disclosed in assignee's Chu et al., U.S. application Serial No. 113,100, filed May 29, 1961.

In addition, the emulsions can contain optical sensitizing dyes and non-optical sensitizing agents as well as all other ingredients necessary for making the emulsion types described above. As examples of non-optical sensitizing agents there may be mentioned sulfur sensitizers containing labile sulfur, e.g., allyl isothiocyanate, allyl diethyl thiourea, phenyl isothiocyanate and sodium thiosulfate; the polyoxyalkylene ethers in Blake et al., U.S. Patent 2,400,532, and the polyglycols disclosed in Blake et al., U.S. Patent 2,432,549. Other non-optical sensitizers such as amines as taught by Staud et al., U.S. Patent 1,925,508, and metal salts as taught by Baldisiefen, U.S. Patent 2,540,086, may also be used.

The emulsions can also contain known antifoggants, e.g., 6-nitro-benzimidazole, benzotriazole, triazaindenes, etc., as well as the usual hardeners, e.g., chrome alum, formaldehyde, dimethylol urea, mucochloric acid, etc. Other emulsion adjuvants that may be added comprise

matting agents, plasticizers, toners, optical brightening agents, etc.

Any suitable acid or alkali combination for emulsion layer and auxiliary layers can be used that brings the final pH within the stated predetermined pH values of between 4.0 and 7.0 and which has no significant adverse effect on the photographic or other properties of the coated film. Because there is usually a great difference in volume between the emulsion layer and the auxiliary layers, a suitably buffered system in the auxiliary layers is preferred. For example, an undercoat is generally coated to a weight of 0.5 to 5 mg. of gelatin per square decimeter and the antiabrasion layer to a weight of 1 to 10 mg. of gelatin per square decimeter. Such a buffered layer represents what is referred to as a pH "reservoir." The buffering capacity must be weak enough so that eventually the pH of the auxiliary layer is "overrun" and changed by the large volume of the emulsion layer to the predetermined optimum common value for the two layers. Suitable acids, bases, and buffers include, e.g., hydrochloric acid, sulfuric acid, etc., hydrochloric acid-potassium chloride, hydrochloric acid-sodium citrate, citric acid-sodium hydroxide, citric acid-disodium phosphate, formic acid-sodium hydroxide, acetic acid-sodium acetate, potassium phosphate-sodium hydroxide, potassium phosphate-borax, boric acid-borax, hydrochloric acid-borax, boric acid-sodium hydroxide, ammonium chloride-ammonium hydroxide, borax-sodium hydroxide, hydrochloric acid-sodium carbonate, borax-sodium carbonate, etc.; sodium hydroxide, ammonium hydroxide, etc. Preferably, the acids and low pH buffers are used in a thin coating to be applied over an emulsion having a relatively high pH. Likewise, the alkalies and high pH buffers are to be used in a thin substratum to be applied under an emulsion. Because of the extreme thinness of such substratum the emulsion pH generally requires only modest adjustment to yield the desired final pH of the coating, the volume of emulsion applied over the substratum being such that the high pH of this auxiliary layer is "overrun" easily without noticeable effect on the over-all pH.

The emulsions of this invention may be coated on any suitable support; such as, a macromolecular organic polymeric film, e.g., cellulose esters, cellulose mixed esters; super-polymers, e.g., polyvinyl chloride (co) vinyl acetate; polyvinyl acetals, e.g., formals, acetals, polystyrene; polyamides, e.g., polyhexamethylene adipamide; polyesters, e.g., polycarbonates, polyethylene terephthalate, polyethylene terephthalate/isophthalate, esters formed by condensing terephthalic acid and dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane-1,4-dimethanol (hexahydro-p-xylylene alcohol); paper, glass, etc.

The above-identified supports may be subcoated with suitable compositions as are known in the art to improve the adhesion of the photographic emulsion to the support. For example, the polyethylene terephthalate film base preferably bears a subcoating of a copolymer of vinylidene chloride, an acrylic ester and itaconic acid wherein said vinylidene chloride is present in an amount of at least 35% by weight of the copolymer. In the preparation of some film element embodiments it is desirable to coat a thin layer of gelatin over said subcoating layer.

The following examples serve to further illustrate but not limit the invention.

Example I

A photographic silver bromo-chloride emulsion was prepared containing 5.28% by weight of gelatin and 8.9% by weight of mixed silver halides in a ratio of 4 parts AgCl to 1 part of AgBr. Standard amounts of the usual final ingredients were added, such as wetting agent, hardener and preservative. The pH of the emulsion was raised to the value of 6.1 by adding 3.2 ml. of 3 N sodium hydroxide solution for each mole of silver halide. The emulsion was coated at 35° C. on polyethylene terephthalate film base made according to Alles and Saner,

U.S. Patent 2,627,088, and Alles, U.S. Patent 2,779,684, having a resin substratum of vinylidene chloride/acrylic ester/itaconic acid copolymer and a thin coating (about 0.5 mg. per square decimeter) of gelatin. The coating conditions were adjusted so that an emulsion coating weight of about 50 mg. of silver per square decimeter was obtained. The coated film was dried and overcoated with a gelatin antiabrasion coating of 2.5 mg. gelatin per square decimeter from a 1% by weight gelatin solution containing wetting agent and hardener. The pH of the gelatin solution had been adjusted to within the range of 1.45 to 1.5 by adding a mixture of 212.5 ml. of 3 N hydrochloric acid and 100 ml. of 3 N potassium chloride for every 100 g. of gelatin. After drying, the pH of the total element was determined as follows: A film sample measuring 5 inches by 8 inches was placed on a glass surface, emulsion side up, and taped down around the edges, the tape extending in about 1/4 inch along each side. Ten ml. of distilled water was spread over the entire film surface and the emulsion was allowed to soften for about 3 minutes. The softened emulsion was then scraped into a 50 ml. beaker and an additional 10 ml. of water was added. The slurry was heated to 35° C. under constant stirring, and the pH was measured with a Beckman model N pH meter, freshly buffered at pH 4.0.

The film described above was stored at room temperature and the pH of the emulsion was determined after one week and thereafter at monthly intervals. Throughout the test period of six months the pH remained within the limits of 4.6 ± 0.1 .

A control film element was made simultaneously in which the sodium hydroxide in the emulsion and the buffer in the antiabrasion overcoating were omitted. The emulsion was at the normal pH of 4.6 before coating and the overcoat solution was at the normal pH of 5.2 before application. The emulsion and the overcoat solution were applied in the order, and at the coating weights, described above for the test film. After one week and throughout the test period, the coated element had a pH within the range of 4.6 ± 0.1 when measured as described above.

The sensitometric characteristics of the two films were virtually identical and were well within the quality tolerance limits.

Test samples measuring about 6 inches by 42 inches were cut from the two films, were conditioned for 18 hours at a temperature of 60° C. to simulate long aging, were exposed uniformly and developed normally to an optical density of approximately 0.8 to 1.0. Close inspection of the developed samples showed as many as 50 contaminant spots per sample on the control film, whereas no such defects were visible on the film of this invention.

Example I

A polyethylene terephthalate film was prepared having a resin substratum as described in Example I and a thin gelatin layer buffered at a pH of about 7.0 ± 0.2 by adding to the gelatin solution (0.68% by weight gelatin) a mixture of sodium hydroxide and boric acid in a molar ratio of 6 to 5. The gelatin solution prior to buffering contained standard amounts of wetting agents, hardeners and other ingredients, and originally had a pH of about 5.8. This solution was coated at a coating weight of about 0.5 mg. gelatin per square decimeter over said resin substratum.

A silver bromo-chloride emulsion similar to the one described in Example I, with pH adjusted to 4.2 by the addition of 3 N hydrochloric acid, was coated on this film base at a coating weight of about 50 mg. of silver per square decimeter. After drying, an antiabrasion overcoating was applied in the form of a gelatin layer weighing 2.5 mg. per square decimeter. The antiabrasion coating solution had a pH of 5.2.

The finished structure was stored at room temperature over a period of several months. After one week and

thereafter monthly the pH was measured using the method described in Example I. It remained within the limits of 4.6 ± 0.1 .

Test samples measuring about 6 inches by 42 inches conditioned, exposed and developed as described in Example I showed no contamination defects. A control coating made as described in Example I exhibited many contamination spot defects under identical test conditions. The sensitometric characteristics of the two films were virtually identical over the entire test period.

Example III

A silver iodo-bromide photographic emulsion containing 187 g. of gelatin for every mole of silver salt, comprising 98.5 molar equivalents of silver bromide and 1.5 molar equivalents of silver iodide, was made. The pH of the prepared emulsion was 6.55. The emulsion was divided into 6 parts and coated on cellulose acetate photographic base at a coating weight of 60 mg. of silver per square decimeter. Part 1 was coated without further modification, whereas the pH of parts 2 through 6 was raised to the value of 8.0 by adding a sufficient quantity of 3 N sodium hydroxide solution.

An antiabrasion overcoating solution was prepared containing 3% by weight of gelatin and standard ingredients such as wetting agent and hardener, and having a pH of 5.1. The solution was split into 6 parts designated A through F. Part A was not altered, but parts B to F were modified by adding 100 ml. of 2.75 N potassium chloride solution for every 100 grams of gelatin and enough 3.0 N hydrochloric acid to adjust the pH to the values of 4.5, 4.0, 3.5, 3.0 and 2.5 respectively. These solutions were then coated over the six emulsion coatings at a gelatin coating weight of 10 mg. per square decimeter. Overcoating A was applied over coating 1, B over 2, C over 3, etc.

The pH of the coatings and the sensitometric properties after aging at normal conditions for one week are reported in the following table:

Coating No.	Emul. pH	Abr. pH	Coated pH	Relative Speed	Contrast	Fog
1A-----	6.55	5.10	5.60	100.0	3.46	0.05
2B-----	8.00	4.50	5.60	107.0	3.37	0.05
3C-----	8.00	4.00	5.55	103.0	3.49	0.07
4D-----	8.00	3.50	5.55	97.3	3.44	0.05
5E-----	8.00	3.00	5.55	92.0	3.42	0.06
6F-----	8.00	2.50	5.10	83.0	3.42	0.05

It is noted that coatings 2B, 3C and 4D had sensitometric properties very close to those of the control coating 1A. All of the experimental coatings were virtually free of contaminant spots after a conditioning test as described in Example I, whereas coating 1A exhibited many such contaminant spots.

The novel film elements of this invention are useful for standard photographic purposes depending on the particular emulsion or combination of emulsions present. The elements are useful in making negatives, positives, X-ray, graphic arts films, etc., including black and white and color films.

This invention is advantageous because defects in photographic emulsions caused by metallic contaminants are eliminated. Such defects are eliminated by a simple, inexpensive process which utilizes standard photographic manufacturing equipment and materials. The film elements obtained thereby exhibit essentially no change in their photographic properties, e.g., sensitivity, contrast or fog, over similar untreated photographic emulsions.

What is claimed is:

1. A process for preparing a photographic element wherein the deleterious effects of contaminants in the photographic emulsion or on the base support are minimized which comprises coating over at least one side of a base support a first layer buffered to a pH within the range of 6.0 to 8.0 and coating over said first layer a

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second layer having a pH below 4.5 such that the pH of the final element is within the range of 4.0 to 7.0, one of said layers being a layer of a water-soluble colloid silver halide emulsion and the other being an auxiliary layer.

2. A process according to claim 1 wherein said first layer is said water-soluble colloid silver halide emulsion layer and said second layer is an auxiliary thin gelatin layer.

3. A process according to claim 1 wherein said first layer is an auxiliary thin gelatin undercoating and said second layer is said water-soluble colloid silver halide emulsion layer.

4. A process as defined in claim 1 wherein at least two water-permeable colloid silver halide emulsion layers are coated over at least one side of said support and adjacent to each of said emulsion layers is at least one auxiliary layer.

5. A process as defined in claim 1 wherein said support is polyethylene terephthalate coated on a surface beneath said first layer with a layer of a copolymer of vinylidene

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chloride, an acrylic ester and itaconic acid, said vinylidene chloride being present in an amount of at least 35% by weight of the copolymer.

6. A process as defined in claim 1 wherein said base support is a macromolecular organic polymer film.

7. A process as defined in claim 6 wherein said support is a polyester film.

8. A process as defined in claim 7 wherein said support is polyethylene terephthalate.

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