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ARGENTOHALIDE COMPLEX FILM CONSTRUCTION

George de W. Anderson, near Bishops, Stortford, and Grahame J. Stehle, Ilford, England, assignors to Minnesota Mining and Manufacturing Company, St. Paul, Minn.

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ABSTRACT OF THE DISCLOSURE

This invention discloses a film having at least one layer containing a light insensitive argentohalide complex, said layer being free of protic solvent, photosensitive silver halide crystals and photosensitive silver ions, said complex providing light sensitive silver halide in said layer upon contact with a protic solvent. Such films can be utilized by contacting the layer containing the light insensitive argentohalide complex with a protic solvent, resulting in the generation of photosensitive silver halide, and exposing and developing photosensitive silver halide by conventional photographic technology.

This invention relates to coatings of non-light sensitive silver halide materials which can be made light sensitive and to the use of these coatings in the reproduction of light images.

The present invention provides a film construction which is essentially light insensitive but which can be made light sensitive prior to use. Moreover, this invention also provides a light insensitive film construction which can be repeatedly made light sensitive, imaged and non-light sensitive. The many uses for such a film construction will be obvious, and some of these uses are described hereinafter.

The novel film construction of this invention is characterized by at least one layer containing a light insensitive argentohalide complex (i.e. silver-halide complex), said layer upon contact with a protic solvent. No photosensitive photosensitive silver halide crystals and photosensitive silver ions, said complex providing light sensitivity in said layer upon contact with a protc solvent. No photosenstive silver halide crystals or silver ions can be tolerated in this layer, all of the silver being present in the form of the argentohalide complex. Such argentohalide complexes are shown in Table 1.8 on page 8 of The Theory of the Photographic Process, 3rd edition, C. E. K. Mees and T.H. James (Macmillan Co., N.Y., 1966), and include $AgCl_2^-$, $AgCl_4^{-3}$, $AgBr_3^{-2}$, $AgBr_5^{-4}$, $AgCl_3Br^{-3}$, $AgClBr_3^{-3}$, AgI_2^-, and AgI_4^{-3}. The films may consist of only the single layer itself, and hence would be considered self-supporting films, or they may comprise a substrate on which is coated one or more of such layers. The argentohalide complexes may be most conveniently prepared by reacting silver halide (i.e. silver chloride, silver bromide, silver iodide or a mixture thereof) with excess halide ions provided by a strongly ionizable halide, this reaction being conducted in a dipolar aprotic solvent medium to dissolve all the complex argentohalide and a sufficient amount of the strongly ionizable halide to generate enough halide ions to complex all of the silver as the desired argentohalide complex.

When the layer of the invention is dry, that is to say in the absence of a protic solvent, it is stable and light insensitive. It can be made light sensitive by treatment with a protic solvent to give free silver halide in the coating. Once the coating has been moistened to make it light sensitive, it can be exposed to light to give a latent image which can then be developed by an active developer, such as metol/hydroquinone or phenidone/hydroquinone developer and it is found that development takes place very quickly. A particularly convenient way of moistening the dry coating to make it light sensitive is to moisten it with the developer, since this has the great advantage of increasing light sensitivity. Also if a highly active developer is used, the development is virtually complete at the end of the exposure time. The developed image can then be fixed with a conventional fixer, such as an aqueous solution of sodium thiosulphate.

The advantages of the invented material will be apparent, since the dry coating of the material can be made light sensitive or light insensitive at will, simply by moistening or drying the coating with a protic solvent such as water. This change from light sensitive to light insensitive is limited by the fact that excess halide ions must be present and so one must ensure that the activation and development of the coating does not wash these out. With such a coating a number of light images can be developed one after another on the same coating.

The composition can be conveniently coated onto the photographic substrate from solution in a dipolar aprotic solvent and, when it has been dried, the coating is sufficiently light stable to be exposed to sunlight over prolonged periods without detectable change. The coating can, however, very easily be made light sensitive by being moistened with water, an alcohol or other protic solvent. The moistened coating has in fact, a surprising sensitivity to irradiation, particularly actinic irradiation, e.g. light and X-rays, in the same manner as photosensitive silver halide.

According to a preferred embodiment of this invention, the argentohalide complex is made by dissolving silver bromide or silver iodobromide in dimethylsulphoxide or dimethylformamide in the presence of excess bromide ions, which can be supplied by a strongly ionizable halide such as ammonium bromide, potassium bromide or other alkali metal halide or alkaline earth metal halide. Hydrogen bromide may also be used to supply the excess bromide ions. This solution is preferably mixed with a binder, such as a synthetic polymer e.g. acrylic acid/acrylic ester copolymer or gelatin, in order to obtain a tough layer which does not dissolve during aqueous processing. A binder providing a water permeable matrix may be advantageous. In addition, other organic compounds, for example a normally solid organic compound (e.g. phenylacetdimethylamide, polyvinylpyrrolidone, etc.) or a normally liquid organic compound (e.g. dinonylformamide, etc.) may be included to improve such properties as image quality. The resulting solution or suspension is coated onto photographic substrate which may, for example, be glass, paper or a transparent film base. It may also be cast in the form of a self-supporting sheet or film. Both the formulation steps and the coating operation may be carried out under normal room light, since the solution of the complex material in the aprotic solvent is not light sensitive. After drying, the coating or casting is also light stable.

According to another embodiment of the invention the complex is prepared by mixing a silver halide, such as silver bromide, with a strongly ionized halide such as ammonium bromide in water or other protic solvent and then crystallizing the complex from the solvent. In the case of silver bromide and ammonium bromide the complex compound has the composition $(NH_4)_2AgBr_3$, the argentohalide complex being $AgBr_3^{-2}$. The crystals of this complex compound are separated from the solvent, and ground, ball milled, homogenized or mixed by ultrasonic

vibrations in the presence of an inert aprotic organic solvent, such as ethyl methyl ketone, and a polymeric binder such as butyl acrylate/acrylic acid copolymer to give a suitable composition for coating on the photographic substrate. This method of operation has the advantages that the complex can be obtained in a relatively pure form so that the final coating has greater stability to atmospheric conditions such as humidity, and one has more control over the ultimate graininess of the silver in an image developed in the coating.

In order to use the coating in the reproduction of a light image, it is moistened with a protic solvent, for example, water or alcohol, and this apparently causes precipitation of silver bromide in a form which has a high sensitivity to light. Instead of applying the water or alcohol as a liquid to the surface of the coating, the coating can be moistened by exposing it to steam.

In order to improve the sensitivity of the moistened coating to particular wavelengths of light it may be dye sensitized. This may be effected by incorporating the sensitizing dye in the coating during the preparation of the complex material. Alternatively the sensitizing dye may be in solution in the liquid used for wetting the coating to make it light sensitive.

If desired chemical sensitizers such as for example gold or sulphur sensitizers, antifoggants and other silver halide additives may be incorporated in with the complex material in accordance with the invention before it is coated onto the substrate.

The invention has wide fields of use in the reproduction of light images. In fact, the coating of the invention can apparently be used in any application in which conventional silver halide materials are used. These include, for example, negative and positive black and white camera printing materials, microfilms, graphic arts films, color photography materials, X-ray films, and office copying materials.

The following examples are illustrations of the preparation and use of coatings in accordance with the invention.

EXAMPLE 1

To 88 ml. of dimethylsulphoxide were added 40 g. of ammonium bromide, 17.6 g. of polyvinylpyrrolidone, 17.6 g. of silver bromide and 0.88 g. of silver iodide. The mixture was brought into solution by warming to 40° C. with efficient agitation.

Meanwhile, 23.0 g. of gelatin was wetted with 18 ml. of water and set aside until the water was absorbed. 25 ml. of ethanol were added and the mixture allowed to stand for 1 hour. The mixture was then melted by warming and added to the above dimethylsulphoxide solution at 40° C., stirring until a clear solution was obtained. A further 50 ml. of ethanol was then added, again stirring to obtain a clear solution. This final addition made the viscosity of the solution suitable for coating.

Chrome alum (8 ml. of 8%) was added to the above solution as a hardener and the solution was then coated at 1.5 thou. wet thickness onto paper base and onto polyester film, and dried at 80 to 100° C. As neither the coating solution nor the coated layers are light sensitive, this operation was carried out in room lighting.

The film and paper materials so obtained were insensitive to light over a prolonged period. They became light sensitive when moistened with water.

A sample of the paper coating was moistened with water during 15 seconds and exposed behind a negative. The exposed material was then developed for 10 seconds in undiluted Ilford P.Q. Universal developer, rinsed, fixed in sodium thiosulphate solution and washed in running water. Sensitometric tests were carried out, using an exposure of 3390 meter candle seconds to a lamp of color temperature 3040° K. behind a continuous wedge. These indicated a speed of 0.005 A.S.A.

A second sample of the paper coating was moistened with undiluted Ilford P.Q. Universal developer and exposed behind a negative. Development was virtually complete at the end of exposure (2 seconds) and the material was then rinsed, fixed and washed as before. Sensitometric tests carried out as above indicated a speed of 0.1 A.S.A.

A third sample of the paper coating was moistened with undiluted Ilford P.Q. Universal developer, then bathed in an M/1000 aqueous solution of 3-carboxymethyl-5-(3'-methylthiazolidin-2'-yl - β - methylethylidene-) rhodanine (ammonium salt) and then exposed and processed as before. Sensitometric tests carried out as described above indicated speed 0.2 A.S.A., fog 0.02 and gamma 1.0. Wedge spectrograms were prepared showing that the increase of speed was due to dye sensitization. The undyed material was sensitive to about 500 mμ while the material dyed as above was sensitive to about 570 mμ.

A sample of the film coating was moistened with Ilford P.Q. Universal developer, exposed and processed as described above. This showed a resolving power of 50 lines/mm.

EXAMPLE 2

A solution for coating was prepared as in Example 1, but in place of dimethylsulphoxide, 176 ml. of dimethylformamide was employed. The solution was then coated at 1.5 thou. wet thickness onto Baryta coated paper base. When moistened with Ilford P.Q. Universal developer (undiluted), sensitometric tests indicated a speed of 0.1 A.S.A.

EXAMPLE 3

A solution for coating was prepared as in Example 1, place of polyvinylpyrrolidone, phenylacetdimethylamide (26.4 g.) was incoroparted. The solution was then coated at 1.5 thou. wet thickness onto Baryta coated paper base. When moistened with Ilford P. Q. Universal developer (undiluted), sensitometric tests indicated a speed of 0.1 A.S.A.

EXAMPLE 4

Precipitated silver bromide (47 g.) suspended in water (150 ml.) was heated to just below the boiling point of the water. Ammonium bromide (160 g.) was then added and the mixture stirred until the silver bromide had completely dissolved. On cooling this solution to 50° C., a complex argentobromide crystallized out as glistening white needles. These were filtered off, separated as completely as possible from the mother liquor and dried.

A butyl acrylate/acrylic acid copolymer (3 g., 21.6% acrylic acid) was dissolved in dry ethyl methyl ketone (60 ml.). Ammonium bromide (1 g.) was added and the mixture was ground in an orbital grinder for 30 minutes. Ammonium argentobromide (10 g.) as prepared above was then added to the mixture which was then ground for a further two hours. The suspension was coated onto a Baryta coated paper at a wet thickness of 0.002 inch and dried.

When this coating was soaked in water for 20 seconds, exposed to 2840 meter candle seconds of tungsten light through a photographic negative, and developed for 25 seconds in a standard commercial Phenidone-hydroquinone developer (P.Q. Universal developer at a dilution of 1 part of developer to 4 parts of water) followed by fixation in sodium or ammonium thiosulphate solution, it gave a print having an image density of 0.9 upon a stable white background.

EXAMPLE 5

A polyvinyl butyral resin (0.5 g. Butvar B. 76) and polyvinylpyrrolidone (5.0 g.) were dissolved in dry chloroform (50 ml.). Ammonium bromide (2 g.) was then added and the mixture was stirred for five minutes. Ammonium argentobromide (10 g.), prepared as described in Example 1 was added and the mixture was ground for three hours in an orbital grinder. This dispersion was then coated onto a Baryta coated paper at a wet thickness of 0.002 inch and dried.

This coating was soaked in a Phenidone-hydroquinone developer (P.Q. Universal at a dilution of 1 part of developer to 4 parts of water) for 20 seconds and exposed to 7,100 meter candle seconds of tungsten light through a photographic negative. Further development for 25 seconds in the same developer followed by fixation in sodium or ammonium thiosulphate solution gave black images of density 0.8 upon a stable white background.

When using the films of this invention, if one moistens the layer without removing the excess of halide ions provided by the ionizable halide, the latent image formed upon exposure of the photosensitive silver halide can be erased simply by drying the layer, e.g. by heating. The layer may then be remoistened with protic solvent, exposed and developed without a trace of the original latent image. This erasability feature permits the use of a protic solvent in the coating composition for preparing the film product, since in a reverse reaction halide ion derived from excess ionizable halide converts any silver halide to the argentohalide complex upon drying. For this reason, aqueous gelatin solution may be included in the coating composition if a gelatin binder is desired in the layer.

Various other embodiments of the present invention will be apparent to those skilled in the art without departing from the scope thereof.

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

1. A light-insensitive film comprising a substrate having at least one layer thereon containing a light-insensitive argentohalide complex capable of providing light-sensitive silver halide in said layer upon contact with a protic solvent, said halide being selected from the group consisting of chloride, bromide and iodide.

2. The film of claim **1** in which said layer contains a binder.

3. The film of claim **1** in which said binder is gelatin.

4. The film of claim **1** in which said layer contains phenylacetdimethylamide.

5. The film of claim **1** in which said layer contains polyvinylpyrrolidone.

6. The film of claim **1** in which said layer contains dinonylformamide.

7. The film of claim **1** in which said layer contains a sensitizer.

8. The film of claim **1** in which said light insensitive argentohalide complex is ammonium argentobromide.

9. A light-insensitive film having at least one layer containing a light-insensitive argentohalide complex and a halide ionizable in protic solvent, said complex providing light-sensitive silver halide in said layer upon contact with a protic solvent, each said halide being selected from the group consisting of chloride, bromide and iodide.

10. A light-insensitive film having at least one layer containing a light-insensitive argento halide complex capable of providing light-sensitive silver halide in said layer upon contact with a protic solvent, said halide being selected from the group consisting of chloride, bromide and iodide.

11. A method for preparing the film of claim **10** which comprises reacting silver chloride, silver bromide, silver iodide, or a mixture thereof in a dipolar aprotic solvent with a strongly ionizable halide to dissolve a sufficient amount of said strongly ionizable halide to generate enough halide ions to complex all of the silver in the form of the dissolved argentohalide complex, adding a film-forming binding agent thereto, applying the resulting admixture onto a surface to form a light insensitive film, and drying said film.

12. The method of claim **11** in which said film is cast onto said surface, dried and removed therefrom as a self-supporting film.

13. The method of claim **11** in which said film is coated onto the surface of a film base and dried thereon to form a coated film product.

14. A method for preparing the film of claim **1** which comprises reacting silver chloride, silver bromide, silver iodide or a mixture thereof in a protic solvent with a strongly ionizable halide to dissolve a sufficient amount of the strongly ionizable halide to generate enough halide ions to complex all of the silver in the form of the dissolved argentohalide complex, separating said complex from said protic solvent, admixing said complex with a film-forming binding agent, applying the resulting admixture onto a surface to form a light insensitive film, and drying said film.

15. The process of claim **14** in which said separated complex is admixed with a film-forming binder agent in an aprotic solvent.

16. A method of image reproduction comprising

(a) providing a light-insensitive film having at least one layer containing a light-insensitive argentohalide complex capable of providing light-insensitive silver halide in said layer upon contact with a protic solvent,

(b) contacting said layer with said protic solvent to provide said silver halide in said layer,

(c) exposing said layer to imagewise radiation to expose said silver halide, and

(d) developing said exposed layer.

17. The method of claim **16** in which said protic solvent is water or alcohol.

18. The method of claim **16** in which said protic solvent is an aqueous developer.

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WILLIAM D. MARTIN, Primary Examiner

M. SOFOCLEOUS, Assistant Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,600,175 Dated August 17, 1971

Inventor(s) George de W. Anderson and Grahame J. Stehle

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 44, delete "layer upon contact with a protic solvent. No photosensitive" and insert --layer being free of protic (i.e. non-aprotic) solvent,--;

Column 1, line 47, "protc" should be --protic--;

Column 4, line 31, after "Example 1," insert --but in--;

Column 4, line 33, "incoroparted" should be --incorporated--;

Signed and sealed this 25th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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