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ENHANCED AND STABLE PHOTOGRAPHIC IMAGES

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ABSTRACT OF THE DISCLOSURE

Developed Lippmann films are enhanced and stabilized by replacing the free silver images which may have unusual geometric or dendritic forms with free mercury images with regular geometric form. The process is accomplished by contacting developed Lippmann film and silver images therein with aqueous solutions of mercuric iodide and potassium iodide which acts as a complexing agent. Reacting the mercuric iodide with the silver images changes the silver to silver iodide and leaves mercury images within the film. The complexing agent carries the silver iodide out of the film, leaving a film having only mercury images.

This invention concerns stable enhanced films and the production of enhanced and stable images in processed photographic films. Of particular importance is the enhancing of images or increasing of their light transmittance by treating silver images with an aqueous solution of mercuric iodide and relatively more soluble iodides, especially potassium iodide. Described herein are processes and solutions for treating developed and fixed plates and films, for enhancing the images, and for insuring that the enhanced images are stable.

In a Lippman photographic process, it has been discovered that silver is deposited in laminae having grains of different sizes. Some of these grains are rather large, and these large grains result in laminae having poor light transmittance. The large grains block necessary passage of light through the film and adversely affect reflective qualities of the film.

It is known that the uniformity of grains and the clarity of images may be improved by immersing silver images of processed Lippmann photographic films in mercuric chloride solutions. Mercuric chloride solutions bleach the film laminae and improve the light transmittance. It is also known that, at the same time, the mercuric chloride process results in the formation of unwanted AgCl and HgCl on the film. These compounds make the film light sensitive. Consequently, the improvement of images with the mercuric chloride process has the outstanding disadavntage of yielding a light senstive and unstable film.

The old mercuric chloride bleaching process is similar to the initial step of an intensification process used with ordinary photographic film. The latter process is used when a film is underexposed, and when, after developing, a relatively small amount of silver gives a poor image. By treating the film with a mercuric chloride solution, more light sensitive salts are allowed to form in the area of the weak image, and upon further exposure to light, these light sensitive salts intensify the image. Before exposure to light, the film appears bleached or lightened because some of the metallic silver has been changed to a salt. Previous enhancement processes in Lippman photography have used this bleaching step to produce temporarily enhanced or more transparent images. Of course, the end result of the intensification process produces the exact opposite of the desired effect of enhancement in the Lippmann process.

In Lippmann photography, an image may be defined as a series of metallic laminae stacked transversely across the film. The laminae are spaced apart the distance of one-half of the wavelength of the light which created the image. Silver in the images may be in the form of small spheres or ovoids, with radially extending filaments. Bleaching refers to making images more transparent or more light transmittant. Images having improved light transmittance are referred to as enhanced images.

This invention has, as one important objective, the provision of enhanced Lippmann films which are free from light sensitive salts. A second objective is the provision of a method for treating processed films having granular silver images to obtain enhanced images which are stable. A third objective is the provision of enhanced and stable images in photographic films. A further objective is the provision of improved solutions for treating silver images. This invention has, as an important purpose, the provision of solutions of mercuric iodide and soluble iodides for treating processed films. Another objective of this invention is the provision of solutions of mercuric iodides and alkali metal iodides for treating silver laminae. This invention has, as a further objective, the provision of mercuric iodide and potassium iodide solutions for treating processed films to result in enhanced and stable images. Other objectives will be apparent from the following description of this invention.

Broadly conceived, the objectives of the invention are achieved by treating the silver images in a conventional manner, in an aqueous bath of relatively insoluble mercuric iodide and soluble iodides. For economic reasons, alkali metal iodides are preferred as soluble iodides. Potassium iodide has proven particularly advantageous, probably due to its more favorable atomic diameter. While a theory of this invention is not necessary to an understanding of the invention, it would appear that potassium iodide enhances the solubility of the mercuric iodide. The potassium iodide further appears to facilitate the total replacement of silver with mercury and the complete removal of light sensitive salts from the film.

The concentration of the solution is determined by the solubility of the mercuric and potassium salts, but these salts have been found to possess adequate solubility for achieving minimum intervals of treatment times. In order to achieve optimum use of the expensive mercury salt, one preferably uses at least two moles of the potassium salt per mole of mercury salt. Preferably, six moles of the potassium salt are used per mole of mercury salt, but no advantages seem to flow from larger molar proportions of the potassium salt.

It has been found that the time required to enhance and stabilize the silver images is not greatly decreased by using concentrations of mercuric iodide greater than one mole. Thus, a very satisfactory treatment bath containing one mole of mercuric iodide and six moles of potassium iodide has proven very satisfactory, requiring a treatment period of only one hour. Since about nine moles of potassium iodide are soluble in a liter of water, one may use up to four and one-half moles of mercuric iodide without difficulty, but little advantage is obtained by using these more concentrated baths. On the other hand, when using one-half mole mercuric iodide and two moles of potassium iodide, a treatment of about twenty hours is required.

Due to conjoint presence of the KI and HgI, it appears that a complex mercuric iodide salt is formed in the aqueous bath. While operation of the chemical reactions is unnecessary to an understanding of this invention, the following reactions are visualized during the process:

(1) $HgI_2+2KI \rightarrow 2K^+ + (HgI_4)^-$

(2) $(HgI_4)^- \leftrightharpoons 4I^- + Hg^{++}$

(3) $Hg^{++}+Ag^{0}\rightarrow Ag^{+}+Hg^{+}$
(4) $Ag^{+}+I^{-}\rightarrow AgI\downarrow$
(5) $2Hg^{+}+2I^{-}\rightarrow Hg_2I_2\downarrow$
(6) $2AgI+2I^{-}\rightarrow (Ag_2I_4)^{-}$
(7) $Hg_2I_2+2I^{-}\rightarrow (HgI_4)^{-}+Hg^{0}\downarrow$

The reactions result in mercury taking the place in situ of all of the silver in the film emulsion, while all of the soluble complexes wash out of the emulsion. The large grains of silver and their radially extending filaments are completely removed, and spherical formed mercury is substituted, making well defined laminae which allow light to pass through the film. All salts which tend to make the film light senstive are held in solution and are removed from the film; no light sensitive salts remain in the film. Consequently, the end product is both enhanced and stable.

As an example, Lippmann images are formed in silver halide emusion on a photographic plate, and the plate is developed and fixed. Silver laminae in the plate are treated with an aqueous solution of one mole of mercuric iodide and six moles of potassium iodide. The plate is held in the solution for one hour, while the above stated chemical reactions may occur. Metallic mercury replaces silver in situ in the emulsion; silver forms a complex, and that complex and the remaining soluble mercury complexes wash out of the emulsion into the solution, leaving a stable Lippmann laminae.

Standard chemical tests reveal that all of the silver in the images is replaced by mercury from the solution, and that no light sensitive salts have remained in the film emulsion. Moreover, it has been determined that the precise locus and form of the image remains undisturbed at the end of the process.

While in the preferred embodiment of the invention the silver image is changed to a mercury image free from light senstive salts, it will be understood advantages flow from replacing any of the silver with mercury while, at the same time, achieving Lippmann films having less sensitivity to light than heretofore known bleached Lippmann films.

While the invention has been patricularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

I claim:

1. A developed enhanced and stabilized Lippmann film comprising mercury images and being free from silver images and from light sensitive silver salts and other metallic salts.

2. The method of producing enhanced and stable photographic images comprising contacting the silver images in exposed and developed Lippmann-type film with a solution of mercuric iodide and of a soluble iodide for a time sufficient in which to form and precipitate silver iodide and to form mercury images.

3. The method of producing enhanced and stable images on exposed and developed Lippmann-type photographic silver image film comprising contacting said film with an aqueous solution of mercuric iodide and at least one relatively more water soluble iodide, for a period of time sufficient for at least partially changing silver images to silver iodide, complexing the silver iodide and replacing silver images with mercury images.

4. The method of producing stable and enhanced exposed Lippmann-type photographic film containing silver images comprising contacting the images with a mercuric iodide and alkali metal iodide solution for a time sufficient for at least partially changing silver images to silver iodide, complexing the silver iodide and replacing silver images with mercury images.

5. The method of claim **4** wherein the solution comprises a solution of mercuric iodide and potassium iodide.

6. The method of claim **5** wherein the solution comprises an aqueous solution of from ½ to 4½ moles of mercuric iodide and from 1 to 11 moles of potassium iodide and wherein the film is contacted for from about one to twenty hours.

7. The method of claim **6** wherein the solution comprises an aqueous solution of one mole of mercuric iodide and six moles of potassium iodide and wherein the film is contacted for approximately one hour.

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