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2,981,622

PHOTOGRAPHIC PROCESS

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This invention relates to a photographic process, and more particularly to a process in which a latent image is formed upon a material sensitized with a heteropolyacid of tungsten or molybdenum and subsequently developed into a visible image.

In my copending application Serial No. 448,990, now U.S. Patent No. 2,895,892, issued July 21, 1959, of which this is a continuation in part, it was shown that photographic processes could be built upon photosensitive systems composed of a heteropolytungstic acid and a carbonaceous reducing agent. The claims in that application related to a printing out process in which a visible image was formed by exposure alone. The present application relates to a process in which a latent image formed upon a heteropolyacid sensitized material is subsequently developed.

The formation and development of latent images, especially upon silver sensitized materials, has long been known. The replacement of silver as the photosensitive material by compounds of tungsten and molybdenum has a number of advantages. The first and most obvious advantage is a reduction in cost because molybdenum and tungsten are much cheaper elements than silver.

Another advantage lies in extended shelf life of photographic materials that can be prepared with the new sensitizers. This factor is of increasing importance because of the rising level of radioactivity not only in the background radiation but in natural products from which paper and other materials for the packing and preservation of photographic films and papers are made. The latent image of a silver sensitized material builds up under the continuous exposure to penetrating radiation into a fog that limits the shelf life. On the other hand, materials sensitized with the heteropolyacids, while sensitive to ionizing radiation, can be prepared so that the latent image produced by exposure to penetrating radiation retrogresses and does not build up into an objectionable fog. Such materials have an indefinite shelf life in spite of the increased background radiation and radioactivity of packing materials.

The advantage of prolonged shelf life also sets the new process apart from latent image processes built upon the use of such sensitizers as diazo compounds, mercury salts, lead salts, etc.

The process is useful for the conventional photographic purposes of making negatives and positive prints from negatives. As already disclosed in U.S. Patent No. 2,895,892, the heteropolyacids may be sensitized to longer wave lengths extending through the visible spectrum by derivatives of xanthene dyes, and thus the process may utilize orthochromatic materials. The process yields images with very fine grain, and thus is suitable for high resolution work. The process also is useful for routine reproduction of drawings and documents, recording in instruments using mirror galvanometers, etc.

Other uses and advantages will appear from the following more detailed disclosure.

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The photographic materials used in the process are sensitized with a combination of a heteropolyacid of tungsten or molybdenum, or mixtures of these, and a carbonaceous reducing agent.

5 Heteropolyacids suitable for use in the process are exemplified by silico-12-tungstic acid, $H_4SiW_{12}O_{40}$, boron-12-tungstic acid, $H_5BW_{12}O_{40}$, phospho-12-tungstic acid, $H_3PW_{12}O_{40}$, phospho-9-tungstic acid, $H_3PW_9O_{31}$, phospho-12-molybdic acid, $H_3PMo_{12}O_{40}$, silico-12-molybdic acid, $H_4SiMo_{12}O_{40}$, phospho-12-tungstomolybdic acids, $H_3PW_xMo_yO_{40}$, where x plus y equal 12. The heteropolyacids may be used singly or in admixture with each other. The term "heteropolyacid" is here used generically and includes both free acids and their salts in which one or more of the hydrogen ions shown in the formulae above have been replaced by another cation, usually an alkali metal ion. These salts are themselves acid in solution.

Carbonaceous reducing agents suitable from use in the process are illustrated by the following:

Polyhydric alcohols, exemplified by: ethylene glycol, propylene glycol, glycerine, 2-ethylhexanediol-1,3, sucrose, lactose, dextrine, starch, gum arabic, agar-agar, polyvinyl alcohol, triethanol amine, sorbitol.

Polyethers, exemplified by ethylene glycol diethyl ether, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether, benzyl cellulose, acetal.

Polyamids, exemplified by "nylon," albumen, casein, gelatin, glue, silk, wool, zein.

Aldehydes, exemplified by formaldehyde, acetaldehyde, n-butyraldehyde, benzaldehyde.

Leucobases of triphenylmethane dyes, exemplified by 4-dimethylamino triphenylmethane, 4,4'-bis-dimethylamino triphenylmethane, 4,4',4''-tris-dimethylamino triphenylmethane, 4,4'-bis-diethylamino triphenylmethane.

Leucobases of xanthene dyes exemplified by 3,6-bis-dimethylamino xanthene, 3,6-bis-dimethylamino-9-(2-carboxyethyl) xanthene, 3,6-bis-diethylamino-9-(2-carboxyphenyl) xanthene, 3,6-bis-monethylamino-9-(2-carboxyphenyl) xanthene ethyl ester.

Suitable carbonaceous reducing agents may combine two or more of the chemical functions. Examples are, polyethylene glycol of average molecular weight 300, polyethylene glycol of average molecular weight 400, polyethylene glycol of average molecular weight 1500, polyethylene glycol of average molecular weight 4000, which combine the polyether and polyhydric alcohol functions; and glucose, which combines the polyhydric alcohol and aldehyde functions.

Without optical sensitizers the materials have their maximum sensitivity at wave lengths shorter than about 4500 A. Materials containing salts of the xanthene dye leucobases and of 4-dimethylamino-triphenylmethane are also sensitive to the longer wave lengths absorbed by the dyes corresponding to the leuco bases.

The photographic materials may be exposed by usual photographic methods.

The exposed sensitized material is developed preferably by a physical developer. Physical developers have long been known. Those employing salts of silver and mercury are most generally used, although others, such as palladium and gold developers, may be employed.

Materials sensitized with the heteropolytungstic acids should preferably be developed within a few days after exposure because the latent image retrogresses on these materials. Materials sensitized with heteropolymolybdic acids may be stored for some time after exposure and before development because on storage there is little retrogression of the latent image.

If it is desired to delay the development of a heteropolytungstic acid sensitized material for some time after exposure, the retrogression of the latent image may be

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arrested by treatment of the exposed material with a solution of a salt of a precious metal, such as silver, and washing. The photograph may then be stored for some time before development.

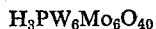
The following examples will make clearer the operation of the process.

Example 1

Water leaf paper is wet with an aqueous solution containing 2.5% of phosphotungstic acid, $H_3PW_{12}O_{40} \cdot 11H_2O$, and 2.5% of glucose, and dried and stored in the dark. This paper is printed for 20 seconds at an intensity of 280 microwatts per square centimeter of 3650 A. U. radiation from a hot mercury arc lamp. No visible image is formed by this exposure. Immediately after printing the image is developed in red light by the following sequence of treatments: N/20 silver nitrate solution for 5 minutes, rinse in water for 3 minutes, bathe in a solution of 1.1 g. potassium iodide and 2.7 g. of sodium sulfite in water to 100 ml. for 3 minutes, rinse in water for 1 minute, develop for 1 hour at 20° C. in a solution of 2 g. sodium sulfite, 0.33 g. silver nitrate, 3.2 g. sodium thiosulfate and 0.16 g. of 2,4-diaminophenol dihydrochloride in water to 100 ml., rinse for 1 minute, fix for 10 minutes in 20% sodium thiosulfate, wash for 10 minutes and dry. A permanent silver image is obtained.

Example 2

Paper is coated with a thorough mixture of equal volumes of a 10% solution of high viscosity, completely hydrolyzed polyvinyl alcohol (such as "Elvanol" 72-51) brought to an acidity of pH 1.5 with sulfuric acid, and a 2% solution of phosphotungstomolybdic acid,



and dried. Contact prints to form a latent image are made upon this by the light from a hot mercury lamp. Before development the paper is treated for 1 hour at 25° C. with 10% silver nitrate solution and rinsed with distilled water. The print then is developed for 10 minutes at 25° C. in a freshly mixed solution of 3 volumes of 5% silver nitrate and 10 volumes of a solution containing 1% of hydroquinone and 0.6% of citric acid; fixed in 35% sodium thiosulfate solution, washed and dried.

Example 3

Paper is coated with a thorough mixture of equal volumes of a 10% solution of high viscosity, completely hydrolyzed polyvinyl alcohol, brought to an acidity of pH 1.5 with sulfuric acid; and a 1.2% solution of phospho-12-molybdic acid, and dried. Contact printing is done upon this by the light from a hot mercury lamp to form a latent image. Before development the paper is treated for 1 hour at 25° C. with 10% silver nitrate solution, rinsed with distilled water and developed and fixed as in Example 2.

Example 4

Paper is coated with a solution containing 5% of high viscosity, completely hydrolyzed polyvinyl alcohol, such as "Elvanol" 72-51, and 1.5% of silico-12-tungstic acid, the acidity having been adjusted with sulfuric acid to pH 3. Printing is done by a carbon arc lamp, and the latent image developed promptly for 10 minutes at 25° C. in a solution freshly mixed from 3 volumes of 5% silver nitrate and 10 volumes of a solution containing 1% of hydroquinone and 0.6% of citric acid. The developed print is fixed in 35% sodium thiosulfate to remove all silver salts, washed and dried.

Example 5

Paper is coated with a solution containing 5% of high viscosity, completely hydrolyzed polyvinyl alcohol and 1% of phospho-12-tungstic acid, the reaction having been

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adjusted with sulfuric acid to pH 2. A contact print to form a latent image is made by exposure of about 30 seconds to sunlight, and the latent image developed promptly as in Example 4. This paper has very high contrast.

Example 6

Paper sensitized and printed as in Example 3 is developed for 30 minutes at 25° C. in a solution composed of 1 volume of 10% aqueous oxalic acid and 1 volume of 0.1 of 1% chloroauric acid, washed in running water and dried. The image is purple, in contrast with the silver developed images, which are black.

The above examples illustrate the practice of the process. Many other applications will occur to those skilled in the art, and it is obvious that various changes may be made in the specific details of the invention without departing from the spirit and scope thereof.

I claim:

1. The photographic process comprising the steps of irradiating a photosensitive photographic material sensitized with a combination of a heteropolyacid of a metal chosen from the group of molybdenum and tungsten and a carbonaceous reducing agent chosen from the group consisting of polyhydric alcohol, polyether, polyamid, aldehyde, leucobase of a triphenylmethane dye, leucobase of a xanthene dye to form a latent image and developing the irradiated photographic material to produce a visible image.

2. The process of claim 1 wherein said heteropolyacid is phosphotungstic acid.

3. The process of claim 1 wherein said heteropolyacid is phosphomolybdic acid.

4. The process of claim 1 wherein said heteropolyacid is phosphotungstomolybdic acid.

5. The process of claim 1 wherein said heteropolyacid is silicotungstic acid.

6. The process of claim 1 wherein said heteropolyacid is silicomolybdic acid.

7. The photographic process comprising the steps of irradiating a photosensitive photographic material sensitized with a combination of a heteropolyacid of a metal chosen from the group consisting of molybdenum and tungsten and a carbonaceous reducing agent chosen from the group consisting of polyhydric alcohol, polyether, polyamid, aldehyde, leucobase of a triphenylmethane dye, leucobase of a xanthene dye to form a latent image and developing the latent image into a visible image by physical development which deposits from a solution containing a metallic salt a light absorbing metallic substance upon the irradiated portions of the photosensitive photographic material.

8. The process of claim 7 wherein said physical developer contains the salt of a noble metal and deposits such metal to form the image.

9. The process of claim 7 wherein said physical developer contains a salt of silver and deposits metallic silver to form the image.

10. The process of claim 7 wherein said physical developer contains a salt of gold and deposits metallic gold to form the image.

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