

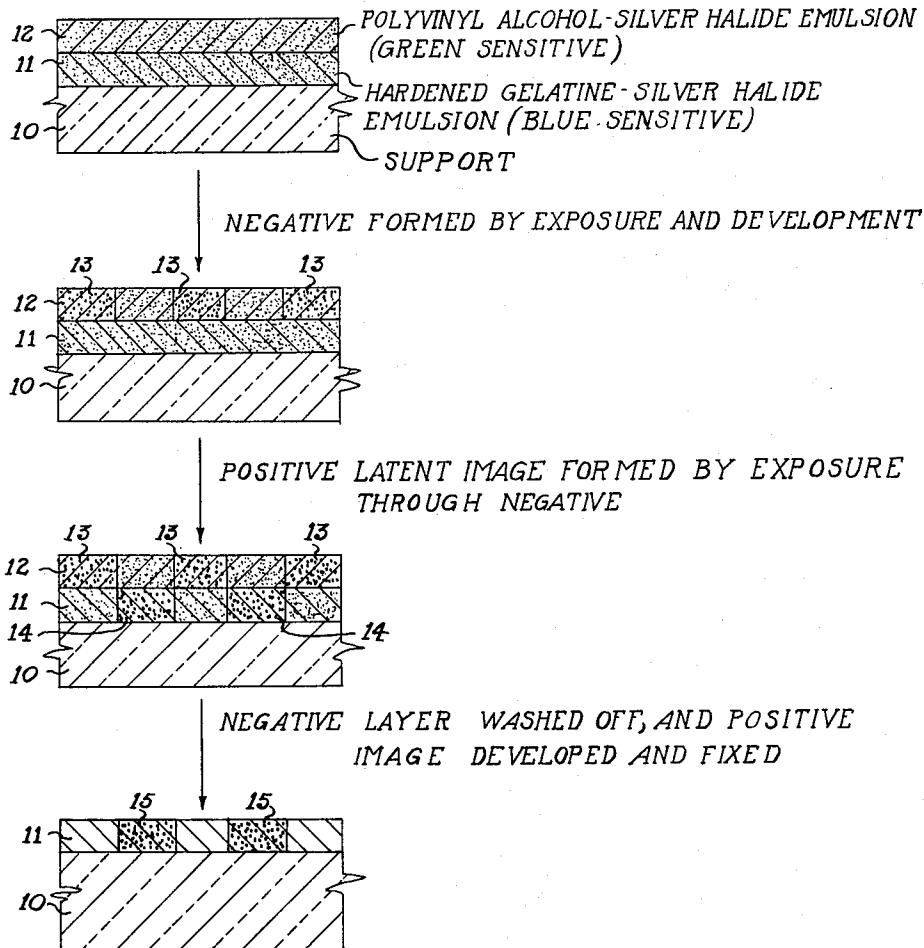
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TWO-LAYER INTEGRAL NEGATIVE POSITIVE PHOTOGRAPHIC MATERIAL

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TWO-LAYER INTEGRAL NEGATIVE POSITIVE PHOTOGRAPHIC MATERIAL

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5 Claims. (Cl. 95—8)

This invention relates to photography and particularly to a two-layer integral negative positive sensitive photographic material.

It is known that a positive image may be obtained by coating an unhardened negative gelatino-silver halide emulsion over a hardened positive gelatino-silver halide emulsion, exposing and developing the negative emulsion, flashing to print the positive and then washing off the negative layer before or after development of the positive. These suggestions have proven impracticable because of the difficulty of differentially hardening the two gelatin emulsions. The hardener in the bottom layer in time hardened the top layer to the point where the negative layer could not be washed off.

It is therefore an object of the present invention to provide a means for overcoming the defects in prior integral two-layer materials. A further object is to provide an integral negative positive material in which the top layer may be washed off without damaging the lower layer. A still further object is to provide a novel two-layer material and method of forming a positive image. Other objects will appear from the following description of my invention.

These objects are accomplished by using as the carrier for the top emulsion layer a colloid which is not hardened by the chemicals used to harden the gelatin in the lower layer, and which is removable with a solvent which does not remove the hardened gelatin.

The accompanying drawing shows sectional views of a photographic material at various stages in the process.

My invention comprises in general the use of a two-layer material coated on a suitable support such as paper, film or glass, the two layers being capable of differential hardening. The lower layer is preferably a hardened gelatino-silver halide positive emulsion and the upper layer is preferably an emulsion of silver halide in a resin, not hardened by the usual gelatin hardeners, such as polyvinyl alcohol. The emulsions are preferably sensitive to different spectral regions so that the negative emulsion may be exposed without exposing the lower emulsion. Differential sensitivity may be obtained by the use of different silver halides, by optical sensitization or by the use of emulsions sensitive to the same spectral region but of different speeds. In the latter case a slow positive gelatin emulsion would be overcoated with a fast negative polyvinyl alcohol emulsion.

The following example illustrates my invention.

A high contrast low speed gelatino-silver chloride emulsion weighting 7600 grams and containing the equivalent of 100 grams of silver nitrate was sensitized in the blue region with a maximum at 495 m μ , hardened with 35 cc. of 20 per cent formaldehyde solution and coated on a paper support at a rate of 14 grams of emulsion per square foot of surface. After drying, the gelatin emulsion was coated with a silver bromoiodide emulsion suspended in a solution of a colloid mixture containing 91 per cent polyvinyl alcohol and 9 per cent of casein derivative. The silver bromoiodide emulsion weighed 4800 grams and

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contained 110 grams of colloid for each equivalent of 100 grams of silver nitrate. It was sensitized in the green region with a maximum at 550 m μ and coated at a rate of 20 grams of emulsion per square foot of surface.

After drying the emulsion coatings a direct reading positive print was obtained from a line drawing as follows:

The emulsion-coated paper was placed with the emulsion side against the back of the drawing. It was exposed 1/2 second through the front of the drawing to tungsten light filtered with a Wratten No. 21 filter to prevent exposure of the bottom layer. After exposure, a negative image was developed in the top layer by immersing the layer for 60 seconds in a developer of the following composition diluted 1 part of developer to two parts of water:

N-methyl-p-aminophenol sulfate	grams	3.1
Hydroquinone	do	12
Sodium sulfite, des.	do	45
Sodium carbonate, des.	do	67.5
Potassium bromide	do	1.9
Water to 1 liter.		

Development was stopped by placing the paper in 1.3 per cent acetic acid. The paper was then rinsed and exposed for 4 seconds to unfiltered tungsten light with the emulsion side toward the light. The negative polyvinyl alcohol layer was then removed by washing in warm water (90° F.) and the positive image in the lower layer was developed for 60 seconds in the above developer diluted 1 part of developer to 2 parts of water, fixed, washed, and dried.

The use of polyvinyl alcohol as peptizer for silver halide may be avoided by using the polyvinyl alcohol as an interlayer between two gelatin emulsion layers. In this embodiment the support is first coated with a suitably sensitized hardened positive gelatino-silver halide emulsion, and on this is coated a thin layer of polyvinyl alcohol or other water-soluble resin, followed by a hardened or unhardened gelatino-silver halide emulsion layer. After negative development of the top layer and printing exposure onto the bottom layer and development of that layer, the top layer and interlayer are removed by rinsing the film in water at about 70° F. A film of this type was prepared as follows:

A. A slow gelatino-bromoiodide of high contrast was prepared as by the procedure of Trivelli and Smith, Phot. J., 79, 330-8 (1939) and this emulsion was optically sensitized at 40° C. to green light with an optical sensitizer such as 5 (3-ethyl-2)3-(benzoxazolyldene)-ethylidene-3-N-heptyl-1-phenyl-2-thiohydantoin at the rate of 0.05 gram per mole of silver halide. After adding a suitable coating aid such as saponin, and formalin solution as a hardener at the rate of 0.50 gram HCHO per 500 grams of gelatin, the emulsion was coated on a non-curling film support at the rate of 0.004 mole of silver per square foot. This coating was set, dried and stored for the ensuing steps.

B. To 500 grams of a 10 per cent aqueous solution of polyvinyl alcohol obtained by hydrolysis of polyvinyl acetate were added 1000 cc. of distilled water and the mass was liquified at 90° C. by heating for 20 minutes with good stirring. This was cooled at 40° C. and the pH adjusted to between 5.5 and 6.0 with 10 per cent acetic acid. Then there were added 40 cc. of a 4 per cent sodium borate solution which has been buffered to pH 5.5 with acetic acid. This material was then coated over the emulsion layer of Part A above at rates as low as 0.10 gram of polyvinyl alcohol per square foot of film surface. Drying was carried out without setting by means of hot air. This part was retained for the ensuing manufacturing step.

C. A blue sensitive negative speed emulsion of a

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gelatino-bromiodide content was prepared according to the procedure, page 330, of Trivelli and Smith referred to above. This emulsion was coated with addition of a small amount of saponin solution and formalin as a hardener. This latter was at the rate of 0.50 gram per 500 grams of gelatin and the emulsion was coated at a temperature of 40° C. on the polyvinyl alcohol surface of step B above at the rate of 0.004 mole silver halide per square foot. After gelation, drying and reeling this film could be exposed and processed to a positive image.

My invention will be further understood by reference to the accompanying drawing.

As shown in the first stage of the drawing, a support 10 is coated with a hardened gelatino-silver halide emulsion 11 which may be blue-sensitive and an unhardened polyvinyl alcohol-silver halide emulsion which may be green-sensitive. After exposure of the top layer to a positive original a negative image 13 is formed in the emulsion layer 12. The bottom layer is then exposed through the negative image in the top emulsion layer, producing a positive latent image 14 in emulsion layer 11 as shown in the third stage of the drawing. The negative layer 12 is then washed off with warm water and the layer 11 is developed to form a positive image 15.

Instead of polyvinyl alcohol, other colloids not hardened by the usual gelatin hardeners, and removable in warm water may be employed, e. g., methyl cellulose, ethyl cellulose, hydrolyzed cellulose esters such as cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate, hydrolyzed to an acyl content of 19 per cent to 33 per cent, polyvinyl acetate having a high hydroxyl content, polyvinyl acetaldehyde acetals, and others.

A direct reading positive can also be obtained by making the first or regular exposure in a camera fitted with a prism, to secure lateral reversal. If reverse reading positives are desired for use for instance as intermediates in making diazo prints they can be obtained by contact printing with the emulsion in contact with the face of the drawing or by exposure in a camera having a conventional optical system.

My method may include the copying of continuous tone material by the proper selection of emulsion contrast in the negative and positive layers.

By "washing in warm water" I mean water at a temperature of about 70° F. to 120° F.

Other modifications may be made in my material and process within the scope of the appended claims.

I claim:

1. A light-sensitive photographic element comprising a support having thereon a gelatino-silver halide emulsion layer sensitive to at least one region, but less than all regions, of the visible spectrum, and on said silver halide emulsion layer a layer of polyvinyl alcohol-silver halide emulsion sensitive to a region of the visible spectrum to which said gelatin emulsion is insensitive, said gelatin emulsion being hardened to the extent of insolubility in water of about 70° to 120° F. and said polyvinyl alcohol emulsion being soluble in and removable with warm water at a temperature of about 70° to 120° F.

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2. The method of forming a positive image in a multi-layer photographic element comprising a support having thereon a layer of gelatino-silver halide emulsion hardened to the extent of insolubility in water of about 70° to 120° F. overcoated with a layer of unhardened polyvinyl alcohol-silver halide emulsion, which comprises forming a negative image in said unhardened polyvinyl alcohol-silver halide emulsion by exposure of only said polyvinyl alcohol emulsion to a positive original and development, forming a positive image in said hardened gelatin emulsion by exposure of said gelatin emulsion through the negative image in said polyvinyl alcohol emulsion and development, and washing off said polyvinyl alcohol emulsion and its accompanying negative image with warm water of about 70° to 120° F.

3. The method of forming a positive image in a multi-layer photographic element having thereon a blue sensitive gelatino-silver halide emulsion hardened to the extent of insolubility in water of about 70° to 120° F. overcoated with a green sensitive unhardened polyvinyl alcohol-silver halide emulsion, which comprises forming a negative image in said polyvinyl alcohol emulsion by exposure of said polyvinyl alcohol emulsion to green light under a positive original and development, forming a positive image in said hardened gelatin emulsion by exposure of said gelatin emulsion to blue light through the negative image in said polyvinyl alcohol emulsion and development, and washing off said polyvinyl alcohol emulsion and its accompanying negative image with warm water of about 70° to 120° F.

4. A light-sensitive photographic element comprising a support having thereon a gelatino-silver halide emulsion layer hardened to the extent of insolubility in water of about 70° to 120° F., and on said layer a silver halide emulsion layer of unhardened polyvinyl alcohol soluble in and removable with warm water at a temperature of about 70° to 120° F.

5. A light-sensitive photographic element comprising a support having thereon a blue-sensitive gelatino-silver halide emulsion hardened to the extent of insolubility in water of about 70° to 120° F., and on said emulsion an unhardened green-sensitive polyvinyl alcohol emulsion soluble in and removable with warm water at a temperature of about 70° to 120° F.

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