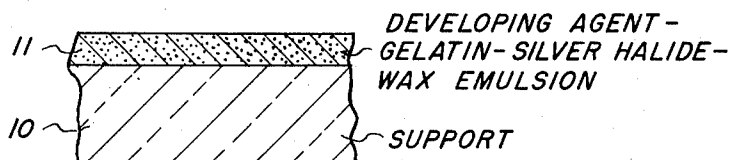


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PHOTOGRAPHIC EMULSION

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PHOTOGRAPHIC EMULSION

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This invention relates to light-sensitive photographic elements and their use in certain photographic reproduction processes.

The light-sensitive element of the invention includes a gelatino-silver halide emulsion containing one or more silver halide developing agents and in addition, a substantial amount of a water-insoluble wax such as paraffin, beeswax or carnauba wax. The silver halide developing agent in the emulsion is not especially critical and is selected according to the requirements of the particular reproduction process in which the emulsion is to be used. Similarly, the quantity of wax in the emulsion is such as to adapt the sensitive element to the given process. For example, a silver halide emulsion containing gelatin, paraffin and the gelatin tanning silver halide developing agent 3,4-dihydroxydiphenyl is adapted particularly for use in the reproduction processes described in U. S. Patents 2,596,756 and 2,716,059. In those processes a substantially unhardened gelatino-silver halide emulsion containing a gelatin tanning silver halide developing agent is exposed to a subject, treated with alkaline solution to form a hardened gelatin and silver image in the region of exposure and by pressing the developed emulsion layer against an absorbent sheet, a stratum of the less exposed emulsion areas adheres to the sheet and remains on the sheet when the emulsion and sheet are separated. In those processes, when no wax is employed one condition encountered is the tendency for the unhardened stratum of emulsion to not break away cleanly from the underlying unhardened emulsion area with the result that the image obtained on the receiving sheet does not have the desired sharpness and definition. A further difficulty lies in the tendency for the exposed and hardened image portions of the emulsion to adhere somewhat to the receiving sheet, making separation of the emulsion and the receiving sheet more difficult than desired.

We have discovered that if wax is incorporated into the silver halide emulsion layers used in the process of the mentioned patents, the result is that during the transfer step the substantially unhardened emulsion areas will fracture more readily when the emulsion and receiving sheet are separated, giving sharper images. Also, the mechanical separation of the emulsion from the receiving sheet is made less difficult.

Another use for the gelatino-silver halide emulsions containing developing agent and wax, for example, an emulsion containing silver halide developing agent, about 13 grams of gelatin and 40 grams of wax, is in the preparation of photographic reproductions by means of a photothermographic process. The emulsion is merely exposed to a suitable subject, treated with alkaline solution to develop the silver image in the emulsion layer, then placed in intimate contact with a sheet of paper or other material absorbent of molten wax. The sandwich is then exposed to heat rays with the result that a waxy silver image is obtained on the paper underlying the

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areas of the emulsion containing the silver image. This process does not require the silver halide developing agent to be present initially in the emulsion layer and the developing step can be carried out in the presence of the developing agent using an ordinary alkaline silver halide developing solution as will be described in the examples hereinafter.

In the accompanying drawing is shown in greatly enlarged cross-sectional view, the appearance of a photographic element having a wax-containing emulsion layer. In the drawing, layer 10 of the element is a support such as paper or a cellulose ester film base on which is coated the emulsion layer 11 containing developing agent, gelatin, silver halide and wax such as paraffin.

Example 1

An emulsion was provided containing gelatin, silver halide, 4-phenyl catechol, 4-methoxy-1-naphthol and dispersing agent as described in U. S. Patent 2,716,059.

Fifty grams of paraffin were melted at 50° C. and added to 500 cc. of a 10 percent gelatin solution containing 50 cc. of an 8 percent aqueous saponin solution with vigorous stirring followed by running the mixture through a colloid mill.

Four kilograms of a gelatin-paraffin dispersion thus prepared were then added to the above silver halide emulsion containing 1 mole of silver halide. Before coating on a support, an equal amount of 4% aqueous gelatin solution was added.

The resulting emulsion coating containing silver halide, developing agent, gelatin and paraffin, was then exposed by reflex printing methods to a two-tone subject so as to obtain appreciably more exposure in the highlight regions of the subject than in the shadow regions, processed with alkaline solution and a print obtained therefrom by pressing the developed emulsion layer against a paper receiving sheet. The emulsion layer and receiving sheet were then separated to obtain a direct positive image of silver, silver halide, gelatin and wax on the paper sheet. In the transfer step it was noted that due to the presence of the wax, the emulsion layer and receiving sheet separated more readily than when a comparable emulsion free of wax was used. Also, the image could be obtained under conditions of underexposure which was not possible with the control coating not containing wax. When additional copies were made by rewetting the developed emulsion layer with the alkaline solution and again pressing against other sheets of paper, separation of the emulsion layer from the paper sheet was facilitated.

The gelatin tanning silver halide developing agents particularly useful in the wax-containing emulsions adapted to the above transfer process are:

- 3,4-dihydroxy diphenyl
- 2,5-dihydroxy diphenyl
- 2,3-dihydroxy diphenyl
- 4-phenoxy catechol
- 4-(2,4-di-tert. amyl) phenoxy catechol
- 1,2-diethoxyl-4-phenoxy catechol

In addition to the gelatin tanning silver halide developing agents, the emulsion may also contain a non-tanning silver halide developing agent such as:

- 4-methoxy- α -naphthol
- N-methyl-p-aminophenol-x-sulfonic acid
- p-Hydroxy-anilino-methane sulfonic acid
- Pyrogallol dimethyl ether
- 8-hydroxy- α -naphthol

for the purpose set forth in U. S. Patent 2,716,059.

The gelatin of the emulsion is substantially unhardened,

that is, not substantially harder than a gelatin layer containing about 0.25 ounce of formaldehyde (40 percent formaldehyde solution diluted 1:3 with water) or 0.7 gram of dry formaldehyde per pound of gelatin when freshly coated or 0.1 ounce of the formaldehyde solution per pound of gelatin for a sample aged 3 to 6 months.

In the above process, the formation of the image on the receiving sheet is facilitated if the sheet has been treated prior to the transfer step with a silver halide fogging agent such as thiourea, thiosemicarbazine or thioacetamide, and has also been treated with a compound capable of retarding gelatin tanning such as sodium formaldehyde bisulfide, sodium formaldehyde sulfoxalate, etc., as described in the Chan et al. U. S. Patent application Serial No. 530,638, filed August 25, 1955.

In the above process, useful results are obtained when the emulsion contains about 1 part of a wax such as paraffin per 2 parts of gelatin.

Silver halide emulsion layers containing wax can be adapted to use in the mentioned thermographic process as shown in the following example.

Example 2

Forty grams of paraffin were melted and added to 100 cc. of a 10 percent gelatin solution. A dispersing agent was then added and the mixture stirred rapidly for 2 minutes. Two parts by weight of the dispersion thus prepared were then added to one part of a silver halide emulsion containing 1 mole of silver halide and 40 grams of gelatin. The resulting emulsion was then coated onto a film support and dried. The coated emulsion was exposed to a line negative, then developed with an ordinary paper developing solution to obtain a silver image in the exposed areas. The developed film was then placed with the emulsion side in contact with a sheet of paper and given a heat exposure through a dark red filter to prevent exposure of the residual silver halide. As a result, the emulsion in the region of the silver image melted and when the emulsion and paper were separated, an image composed of silver, gelatin and wax was obtained on the sheet of paper.

When the above process was carried out in the same manner except that the emulsion layer was dried after the development step, only a wax image transferred to the receiving sheet.

In the above process, stearic acid can be substituted for wax and similar results are obtained although the procedure is less preferred.

Since the process as described in this example utilized an ordinary developing-out emulsion, a negative print was obtained with regard to the original subject. By employing a direct positive emulsion of a well-known type containing wax, a direct positive print can be obtained in the same manner.

The silver halide in the emulsion used in the mentioned photothermographic process is advantageously blue or green light-sensitive having little sensitivity in the infrared region to prevent exposure of the emulsion with wavelengths of light in the far red and infrared regions of the spectrum during the transfer step. Also, the process may be carried out in the manner above described by incorporating a silver halide developing agent such as hydroquinone or the developing agents of Example 1 in the emulsion layer together with wax, and initiating development with an alkaline solution free of developing agents such as dilute sodium carbonate solution.

In the described photothermographic process, useful results are obtained when the emulsion contains about 3

parts of paraffin per 1 part of gelatin. Accordingly, the emulsions useful in the processes of Examples 1 and 2 can contain about 0.5 to 3 parts of wax per part of gelatin, the emulsions containing the lower amounts of wax being preferred for the process of Example 1.

What we claim is:

1. A silver halide emulsion containing a mixture of gelatin, a silver halide developing agent, and about 0.5 to 3 parts of a water-insoluble wax per part of gelatin.

2. A substantially unhardened silver halide emulsion containing a mixture of gelatin, about 0.5 to 3 parts of a water-insoluble wax per part of gelatin, and a silver halide developing agent of the class consisting of 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl, 2,3-dihydroxy diphenyl, 4-phenoxy catechol, 4-(2,4-di-tert. amyl) phenoxy catechol and 1,2-diethoxalyl-4-phenoxy catechol.

3. A photothermographic process which comprises exposing to a subject a supported emulsion layer containing a mixture of gelatin, silver halide and about 3 parts of a water-insoluble wax per part of gelatin, developing the exposed emulsion layer with an alkaline solution in the presence of a silver halide developing agent to obtain a silver image in the emulsion layer, placing the developed emulsion layer in contact with an absorbent sheet and heating the emulsion layer in contact with the absorbent sheet for a time sufficient to transfer a wax image to the absorbent sheet.

4. The process of claim 3 wherein the exposed emulsion layer contains a silver halide developing agent and the development step is carried out with an alkaline solution.

5. The process of claim 3 wherein the silver halide emulsion is a direct positive silver halide emulsion.

6. A method of photographic reproduction which comprises exposing to a two-tone subject a substantially unhardened gelatino-silver halide emulsion layer containing a mixture of about 0.5 part of a water-insoluble wax per part of gelatin and a developing agent of the class consisting of 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl, 2,3-dihydroxy diphenyl, 4-phenoxy catechol, 4-(2,4-di-tert. amyl) phenoxy catechol and 1,2-diethoxalyl-4-phenoxy catechol, so as to obtain some exposure in the areas of the emulsion layer corresponding to the shadow areas of the subject and appreciably more exposure in the areas of the emulsion layer corresponding to the highlight areas of the subject, developing the exposed emulsion layer with an alkaline solution to obtain a hardened gelatin, wax and silver image in the region of exposure to the highlight area of the subject and substantially unhardened gelatin, wax, silver and silver halide in the region of the emulsion layer corresponding to the shadow region of the subject, pressing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist to cause only the shadow region of the emulsion to adhere to said sheet, and separating said sheet and emulsion layer to transfer only a stratum of said shadow region of the emulsion layer to said sheet.

7. The process of claim 6 wherein the receiving sheet has been treated prior to contact with the developed emulsion layer, with a silver halide fogging agent and a compound retarding gelatin tanning.

References Cited in the file of this patent

UNITED STATES PATENTS

2,059,829	Ward	Nov. 3, 1936
2,221,873	Knoefel	Nov. 19, 1940
2,596,756	Yutzy et al.	May 13, 1952
2,634,677	Klimkowski et al.	Apr. 14, 1953
2,691,587	Greig	Oct. 12, 1954