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LIGHT SENSITIVE ELEMENT FOR COLOR PHOTOGRAPHY

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FIG. 1.

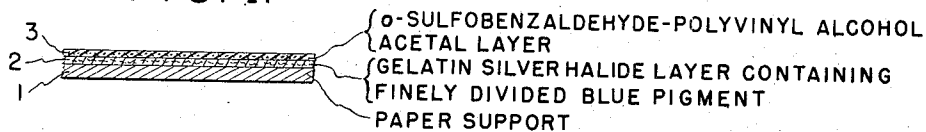


FIG. 2.

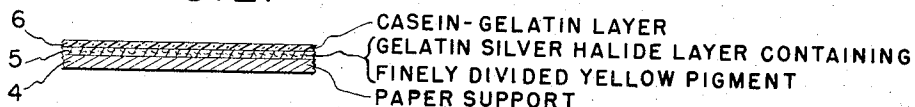
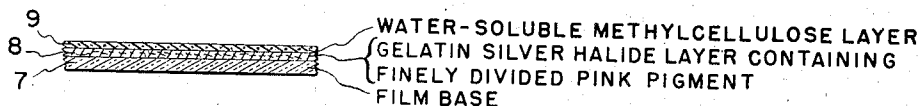


FIG. 3.



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LIGHT SENSITIVE ELEMENTS FOR COLOR PHOTOGRAPHY

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2 Claims. (Cl. 95—8)

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This invention relates to photography and, more particularly, to light-sensitive elements for color photography. Still more particularly it relates to photographic elements bearing pigmented light-sensitive silver halide layers which can be processed to form transferable pigment images. The invention also relates to processes of producing pigment images from such elements.

An object of this invention is to provide improved elements for the production of pigmented images. A further object is to provide light-sensitive photographic elements which have protected pigmented layers. A still further object is to provide such elements which are not deleteriously affected by photographic development of the silver halide layers. Still other objects will be apparent from the following description of the invention.

The novel photographic elements of this invention consist of a film, plate, or paper support which has superimposed thereon a gelatino-silver halide emulsion layer having intimately dispersed therethrough finely divided inert colored pigment particles, which layer bears a protective coating composed of a water-soluble, dilute alkali-insoluble, film-forming colloid. The useful colloids are freely water-permeable but insoluble in aqueous alkaline developer solutions containing 2% or more by weight of dissolved inorganic salts.

The outer coating protects the pigmented layer during handling and development of the photographic elements but it can be readily removed when it is desirable to prepare for transfer the pigmented image which is formed in the inner layer. The elements are exposed to light from an object field, e. g., light from a color separation negative, whereby a latent image is formed in the silver halide layer. They are then developed in an alkaline photographic developing bath whereby a silver image of good contrast forms in the silver layer. After fixing and washing, the elements are dried and then bleached in a hardening bleach. Each bleached component is rinsed briefly, squeegeed face down on a semi-rigid transparent support, such as methyl methacrylate sheets, cellulose acetate sheets, etc. After remaining in contact for a few minutes, each combination is immersed in warm water (110°–120° F.). The unhardened, pigmented colloid softens, its original support is removed, and excess softened colloid is washed away in the warm water leaving pigmented relief images. The images may be transferred to other transparent

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or opaque support in known manner analogous to that practiced in the process known as "carbon printing." Alternatively, a hardening developer may be used whereby no hardening bleach step is necessary. Similarly, relief images may be created on metal surfaces whereby a "resist" is formed for use in photomechanical processes.

Various water-soluble, dilute alkali insoluble colloids are known which are freely permeable to photographic developing, bleaching, and fixing solutions. Among such materials are the low substituted methyl and ethyl cellulose ethers, gelatin-casein mixtures, polyvinyl alcohol and polyvinyl alcohol acetals of aldehydes which contain SO₃M or COOM groups, where M is hydrogen or a water-soluble cation, e. g., sodium, potassium, ammonium, tetramethylammonium, morpholine, etc.

Colloids which are especially suitable are the polyvinyl acetals of aromatic monoaldehydes having sulfonic acid or carboxylic acid groups. Suitable acetals of this type can be prepared from polyvinyl alcohols and substantially completely hydrolyzed polyvinyl esters and aldehyde carboxylic or sulfonic acids, such as phthalaldehydic acid, ortho-, meta-, and para-benzaldehyde sulfonic acid, acetaldehyde disulfonic acid, naphthaldehyde sulfonic acids, e. g., 1-naphthaldehyde - 2 - sulfonic acid, 1 - naphthaldehyde - 4 - sulfonic acid, 2 - naphthaldehyde - 5 - sulfonic acid, and the corresponding carboxylic acids, by condensation in the presence of mineral acids or acid salts after the manner described in German Patent No. 643,650. Such acetals are insoluble in aqueous alkaline photographic developer solutions containing 2% or more by weight of dissolved inorganic salts. The condensation should be carried out until the vinyl alcohol groups have been acetalized to confer such solubility characteristics. The latter acetals possess a high resistance to solubilization by alkaline photographic developer solutions and acquire a hardened surface during development of the exposed silver halide layers.

The gelatino-silver halide emulsion layers can be prepared in the usual manner and the finely divided inert pigments added to the emulsion at any time but preferably at the time it is prepared for coating. A practical method is to disperse the pigment in an aqueous solution of gelatin with the aid of a wetting or dispersing agent and the resulting gelatin solution is added to the gelatin silver halide emulsion and the flowable emulsion is coated in the usual manner onto a support, e. g., a transparent film or paper or onto

a layer of soft gelatin on the support, and dried. The pigments can be dispersed by mechanical comminution or grinding in a ball mill in the presence of the colloid by the aid of wetting agents until they have an average particle size of not more than $1\ \mu$ and not less than $0.1\ \mu$ in diameter. Different colored pigments may be used for producing individual images of any desired shade or alternatively blue-green, yellow, and magenta are used in different elements whereby composite multicolored pictures can be made from color separation negatives. The pigment particles may preferably be dispersed mechanically in comminuting and colloid mill apparatus of known type or colloido-chemically, preferably by the use of wetting and dispersing agents. Suitable wetting agents include alkali metal salts, e. g., sodium and potassium salts of n-alkane sulfuric acid esters and sulfonic acids of 8 to 18 carbon atoms, the alkali metal salts of alkylated naphthalene sulfonic acids, the N-alkyl and C-alkyl betaines wherein the alkyl groups contain 8 to 18 carbon atoms, and wetting agents of non-ionic type, e. g., the polyethylene glycols containing 8 or more ethylene units and their alkyl ethers and carboxylic acid esters, for example, nona- and dodecaethylene glycol and their mono- and di-methyl and ethyl ethers, and the hexitan derivatives, e. g., the polyoxyl alkylene ethers and esters of United States Patent 2,440,532.

The protective coatings can be deposited on the pigmented gelatin silver halide from an aqueous solution of the water-soluble, dilute alkali-insoluble colloids in the same manner in which emulsion, anti-abrasion, etc. layers are coated. The layers or coatings are then dried.

The invention will be further illustrated but is not limited by the following examples. The parts are by weight.

Example I

A paper support 1 as shown in Fig. 1 of the drawing is coated with a flowable gelatino-silver iodobromide emulsion containing 10% of gelatin and 5% of silver bromide and one part of finely divided "Monastral" Fast Blue BWD per 30 parts of gelatin, to form a layer 2 having a coating weight of 150 mg. of AgBr per square decimeter. A water-soluble o-sulfobenzaldehyde acetal of polyvinyl alcohol, prepared after the manner described in German Patent 643,650, was admixed in the following proportions:

o-Sulfobenzaldehyde acetal of polyvinyl alcohol	gram	1
Ethanol	cc	80
Water	cc	20

and the resulting solution was coated onto the silver halide layer to form a protective layer 3 having a coating weight of 20 milligrams per square decimeter.

The element is then processed as follows: Each pigmented element is exposed to its appropriate color record, such as a set of tricolor separation negatives, and developed for 2 to 5 minutes in a developer of the following composition:

N-methyl-p-aminophenol sulfate	grams	5.0
Na ₂ SO ₃	do	60.0
Hydroquinone	do	7.5
Na ₂ CO ₃	do	50.0
KBr	do	4.5
Water to	liter	1.0

After quick rinsing the element is fixed in the

following non-hardening fixer, then washed thoroughly and dried:

Sodium thiosulfate	grams	240.0
Sodium sulfite	do	10.0
Sodium bisulfite	do	25.0
Water to	liter	1.0

After drying, the individual element is processed to a pigmented relief image as follows:

Part A:

Potassium ferricyanide	grams	28.0
Potassium bromide	do	28.0
Potassium bichromate	do	28.0
Water to	cc	600.0

Part B:

Acetic acid (glacial)	cc	3.5
Hydrochloric acid (conc.)	cc	3.5
Formalin	cc	35.0
Water to	cc	100.0

For use, A and B are mixed as follows:

Water	cc	200.0
Part A	cc	30.0
Part B	cc	3.5

Each element is soaked for $1\frac{1}{4}$ minutes in the prepared bleach, rinsed for one minute, then squeegeed face down onto a freshly cleaned transparent sheet of methyl methacrylate or cellulose acetate, etc. which is somewhat larger than the paper elements. After standing in contact for five minutes, the "sandwiches" are immersed in water at 100° - 105° with the paper-backing side of the sandwiches uppermost.

After about one minute, the unhardened colloid next to the paper support becomes softened and the paper backing may be stripped away. The remaining unhardened, pigmented colloid may be then completely washed away by three or four minutes further washing with mild, continuous agitation in water from 100° - 110° . There remains finally pigmented relief images which adhere firmly to the transparent sheets.

After drying, the component images may be successively transferred in register to a single support in known manner.

Example II

A paper support 4 in Fig. 2 of the drawing is coated with a flowable gelatino-silver iodobromide emulsion containing 10% of gelatin and 5% of silver bromide and one part of thioflavine S per ten parts of gelatin to form a layer 5 having a coating weight of 175 milligrams of AgBr per square decimeter. A slightly alkaline 10% solution of a mixture of ten parts of casein and one part of gelatin in equal parts of ethanol and methanol is coated onto the silver halide emulsion layer to form outer layer 6. The element is exposed under a blue color separation negative which is processed in a manner similar to that described in Example I whereby a yellow image record is formed. It may be superimposed in register with the image record of Example I.

Example III

A cellulose acetate film base 7 as shown in Fig. 3 of the drawing is coated with an aqueous gelatino-silver iodobromide emulsion having uniformly dispersed therethrough finely divided particles of "Halopont" Pink 2BM. The ratio of gelatin to silver is 2 to 1 by weight and one gram of pigment is used for each five grams of gelatin. The resulting layer 8 has a coating weight

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of 200 milligrams of silver bromide per square decimeter. An aqueous solution of methyl cellulose is made by dissolving 20 parts of methyl cellulose containing 1.3 to 2.6 methoxy groups per glucose unit in 800 parts of a mixture of 10% ethanol and 90% water by weight. The resulting layer 9 is resistant to solution by aqueous alkaline photographic developers, yet can be readily and completely removed in water. The film is exposed under a green color separation negative and processed as described in Example I whereby a magenta image record is formed. The final image record when superposed in register on the other two color component records of Examples I and II results in a multi-color picture.

Various other inert colored pigments may be substituted for those described in the above examples. The phthalocyanine dyes are quite useful in the emulsion layers and are commercially available in various colors. Suitable additional specific pigments include "Monastral" Fast Blue GWD, "Monastral" Fast Green GWD, "Luxol" Fast Blue MBS, Halopont Blue BM, Halopont Brilliant Blue 2RN, "Lithosol" Yellow HLD, Halopont Blue RNM, Halopont Violet NM, Benzidine Yellow lakes, etc.

The gelatino-silver halide emulsion layers may contain, in addition to the colored inert pigments and the light-sensitive silver halide, e. g., silver chlorides, silver-chloride-bromide, silver-iodo-bromide, etc., various sensitizing dyes and other materials which are common in emulsion layers. Such additional materials include fog inhibiting agents, emulsion hardeners, emulsion preservatives, etc.

An advantage of the invention is that it provides improved elements for color photography. The elements are superior to those used in the preparation of pigment image photographs because the silver halide surfaces are protected and stress marks, abrasion marks, and the like are avoided. The outer layer does not come off during development which is desirable. By utilizing the relatively high order of sensitivity of silver salts as compared to dichromated colloids, for example, much shorter practical exposure times are possible. Physical abrasion of such sensitive layers is eliminated by the remov-

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able anti-abrasive layers. Presensitizing before use is not necessary, of course, as in the case of dichromated colloids.

What is claimed is:

1. A photographic element comprising a support, a gelatin silver halide emulsion layer on said support which layer has finely divided solid inert pigment particles having an average particle size of 1.0 to 0.1 micron uniformly dispersed therethrough and has superimposed thereon a layer composed of a water-soluble o-sulfobenzaldehyde acetal of polyvinyl alcohol said acetal being insoluble in alkaline photographic developer solutions containing 2% by weight of dissolved inorganic salts.

2. A photographic element comprising a support, an unexposed light-sensitive gelatin silver halide emulsion layer on the support, said layer having finely divided, solid, inert pigment particles possessing an average particle size of 1.0 to 0.1 micron uniformly dispersed therethrough and having superposed thereon a layer of an acetal of a vinyl alcohol polymer with a water-soluble aldehyde containing a group taken from the class consisting of carboxylic acid and sulfonic acid groups but which is otherwise unsubstituted, said acetal being insoluble in alkaline photographic developer solutions containing 2% by weight of dissolved inorganic salts.

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