Jan. 16, 1968 E. C. YACKEL ETAL 3,364,024

PHOTOGRAPHIC PROCESS

Filed June 24, 1963

Fig. 1

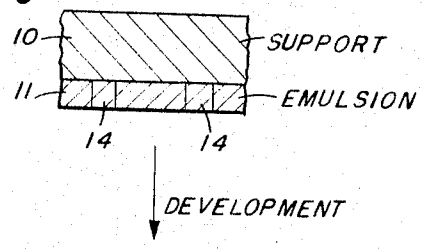


Fig. 2

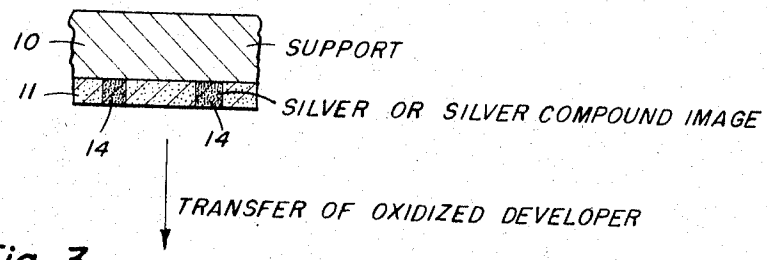


Fig. 3

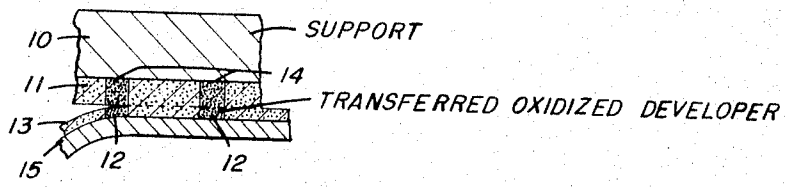


Fig. 4

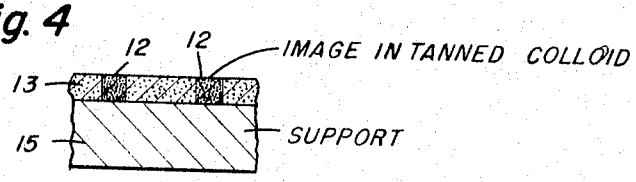
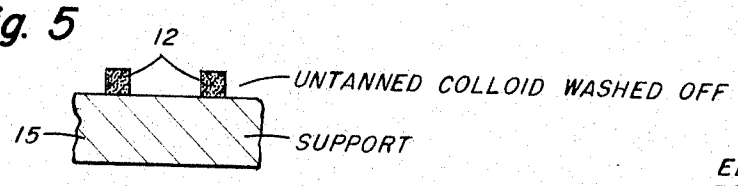


Fig. 5



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3,364,024

PHOTOGRAPHIC PROCESS

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This invention is concerned with a photographic process and more particularly with the use of certain colloid insolubilizing developing agents to make a photographic image or resist.

The use of certain developing agents to insolubilize gelatin and similar colloidal materials is well known. In a typical embodiment employing this hardening reaction, a tanning developer such as catechol is used to develop an exposed silver halide gelatino emulsion after which the unexposed areas are washed away using warm water to obtain a photographic image or resist. However, this mechanism has not been applicable to insolubilizing gelatin at very great distances from the site at which development takes place. For instance, catechol only insolubilizes gelatin at very short distances from the sites at which oxidation of the catechol takes place, probably less than 0.01 mm. It has been desirable to find a method of insolubilizing gelatin or similar colloids in a non-silver halide containing layer by using the oxidation products obtained by developing an exposed silver halide emulsion. The non-silver halide containing layer could be coated on the support on which the image or resist is desired thus avoiding contaminants on the support which could affect the silver halide. For instance, the resist might be provided on a metal plate to serve as a basis for etching the metal to obtain a relief printing plate or the like.

We have found a method of obtaining an image or resist in gelatin or similar pervious colloid by transfer of certain wandering gelatin-insolubilizing oxidized developing agents.

One object of this invention is to provide a photographic process for obtaining a photographic image or resist by the transfer of certain wandering gelatin-insolubilizing oxidized developing agents from a developing silver halide emulsion to a separate gelatin layer thereby insolubilizing the gelatin at distances of up to more than 0.10 mm. from the site at which oxidation of the developer takes place. Another object of this invention is to provide certain gelatin-solubilizing agents which insolubilize gelatin imagewise in a separate gelatin layer in contact with a developing silver halide emulsion. A further object is to provide a method of making a photographic resist on a support carrying a non-silver halide containing gelatin layer. A still further object is to provide a resist in a non-silver halide containing gelatin layer. Another object is to provide a hardened gelatin resist on a support which can be used in printing processes.

The above objects are attained by exposing a silver halide emulsion and then developing the emulsion with a developer whose oxidation products are capable of insolubilizing gelatin at distances removed from the site of oxidation of the developer. While the emulsion is developing, it is contacted against a gelatin layer on a separate support for a time sufficient for the oxidation products of the developer to harden the gelatin imagewise. The non-silver halide containing gelatin layer is then separated from the silver halide emulsion and washed in warm water to remove the unhardened areas to to reveal a resist image in the non-solver halide containing gelatin.

We have discovered that only certain tanning developers can be used in our process such as, for example, 1,4-dihydroxy benzene compounds such as, hydroquinone, chlorohydroquinone, bromohydroquinone, toluhydroquinone, morpholine methyl hydroquinone, etc. Among the

many gelatin tanning developers which are inoperative in our process are catechol, chlorocatechol, methylcatechol, phenylcatechol, morpholino methyl catechol, pyrogallol, gallic acid, etc.

It will be appreciated that this process which is particularly useful with a separate gelatin layer on another support can be used to obtain a thicker gelatin resist than is normally obtained by having a non-silver halide containing gelatin layer under the silver halide emulsion on the same support so that when the silver halide emulsion is developed and the unexposed portion is washed off, the gelatin undercoat would also be hardened imagewise.

In this embodiment there would be a reduction in the amount of silver halide needed to provide a thick gelatin resist as compared to the conventional resist in which silver halide would permeate the entire gelatin structure. However, it would be necessary in this embodiment for both layers to be composed of substantially unhardened gelatin.

The unhardened non-silver halide containing gelatin layer may be used as an overcoat over the silver halide emulsion for certain purposes. For instance, it might be used to provide a monochrome image from silver halide sensitized photographic material without using expensive color films. It often happens in graphic arts' applications that the line or half-tone images in color are desired without the costly or time-consuming conventional processing of color materials. The non-silver halide containing layer can be pigmented or can contain a mordant and dye. The wandering oxidation products from the silver halide layer harden the non-silver halid containing gel layer in the image areas so that when the unhardened areas are removed, a pigmented image remains.

In the embodiment in which the non-silver halide containing gelatin is coated on a separate support, this gelatin would be substantially unhardened gelatin. The gelatin of the silver halide emulsion should also be substantially unhardened gelatin to avoid transfer of hardener to the non-silver halide containing gelatin. The silver halide carrying colloid could be any of the well-known alkali-permeable colloids used for photographic purposes as carriers for silver halide. The coverage of the silver halide emulsion is not critical and can be varied depending upon the use intended. A useful range is about 50 to 500 mg./ft.^{2} gelatin and about 100 to 300 mg./ft.^{2} silver.

The silver halide emulsion can be any of the well known silver halide emulsions including silver chloride, silver bromide, silver chloroiodide, silver chlorobromide, silver chlorobromoiodide, silver bromoiodide, etc. It will be appreciated that unhardened, direct positive emulsions of the type described in P. J. Hillson, U.S. Patent 3,062,651, may be utilized to obtain direct positive images. In emulsions of this type, a non-hardening fogging agent such as stannous chloride, formamidine sulfinic acid, or the like may be used.

The developing agent may be incorporated in the silver halide emulsion or the non-silver halide containing layer and development attained by using an alkaline activator, or development may be carried out by immersing the exposed photographic emulsion in a conventional alkaline developing bath provided the oxidized developing agent is one of those identified above as a wandering insolubilizing developing agent.

Typical activator baths for the photographic emulsion containing the developing agent comprise, for example, an aqueous solution of an alkaline material, such as sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, mixtures of sodium hydroxide and sodium sulfite, etc. Suitable baths can comprise, for example, an aqueous solution containing about 1 percent sodium hydroxide and 5 percent sodium sulfite.

A particularly advantageous method for carrying out

the invention is to incorporate an alkaline material in the non-silver halide containing layer and the wandering developing agent in the silver halide emulsion. A useful amount of alkali metal salt or similar alkaline material incorporated in the non-silver halide containing layer is 3–5 mols/mole of silver in the emulsion. In this way, the layers may be moistened and contacted together to provide the alkaline material necessary to oxidize the developing agent contained in the silver halide layer which results in development of the exposed emulsion and hardening of the non-silver halide containing layer.

Typical of the activator solutions which can be used in our process are those disclosed in U.S. Patents 2,596,754, 2,596,756, 2,725,298, 2,739,890, 2,763,553, 2,835,575, 2,852,371, and 2,865,745.

It will be appreciated that any of the known hydroquinone compounds which have alkali splittable groups thereon to stabilize the hydroquinone during storage may be incorporated in the emulsion. These compounds release hydroquinone in the presence of alkali and may be used in whole or in part to replace the hydroquinone or hydroquinone derivative incorporated in the silver halide emulsion in the non-silver halide containing layer or in the processing solution.

It will also be appreciated that an auxiliary developing agent can be used along with a hydroquinone developing agent in order to improve the speed without affecting the operation of our invention. Typical auxiliary developing agents include 3-pyrazolidone developing agents known in the art as well as Elon (N-methyl-p-aminophenol sulfate) and the like. Useful auxiliary agents are 1-phenyl-3-pyrazolidone and 1-phenyl-4,4-dimethyl-3-pyrazolidone.

Suitable supports for the photographic emulsion comprise any of the well known supports such as cellulose ester film base (e.g., cellulose acetate butyrate, cellulose nitrate, cellulose acetate, cellulose acetate propionate, etc.), polyethylene, polypropylene, polystyrene, polyethylene terephthalate and other polyesters, paper, polyethylene coated glassine paper, glass, metal, polycarbonates, etc.

The non-silver halide containing colloid layer can be coated on any of the above supports or may be coated on any support on which it is desirable to obtain a photographic image or resist. For instance, it could be coated on a metallic sheet such as copper, zinc, aluminum or the like, or on some other surface for use as a template, etc. A particular advantage of this process is the ability to coat the gelatin or similar colloid on many surfaces which might contain contaminants which would be detrimental to the sensitivity, fog level, etc., of a silver halide emulsion. In addition, the gelatin could be coated on a curved surface such as a cylinder, and the developing silver halide emulsion wrapped around the cylinder to obtain the resist image on a curved support.

Photographic developing out silver halide emulsions in our invention can also contain such addenda as chemical sensitizers, speed-increasing compounds, reducing agents, sensitizing dyes, etc., which are known to those skilled in the art. They may be blue sensitive, orthochromatic, panchromatic, infrared sensitive, etc., emulsions.

Although gelatin is the preferred colloid for the non-silver halide containing layer, other alkali-permeable colloidal resins may be used which have the property of being imagewise hardened with tanning silver halide oxidized developers, for example, other proteins, such as casein, zein, etc.

In addition to preparing photographic resists on conventional supports, our process can be used for making plates by means of stencils. The non-silver halide containing layer is coated on a porous support such as cloth, silk or highly porous paper and, after being hardened by contacting against the developing exposed silver halide emulsion, the unhardened areas are removed by washing in warm water leaving the support pervious to a printing ink in the areas wherein the gelatin has been removed. Prints are then made from the resulting stencil in the usual manner using a low viscosity ink with a result that a large number of positive prints can be made.

Although we prefer to use carbon black as the pigment in the non-silver halide containing layer, any other pigment or dye may be used including those which might not be normally compatible with a silver halide emulsion because of their effect on the silver halide. When the term "pigment" is used herein and in the appended claims, it is to be understood to include, for example, any insoluble organic and inorganic materials of nature such that they impart density to the copy.

By substantially unhardened gelatin, is meant gelatin which is not harder than would be the case with gelatin containing 0.25 ounce of formaldehyde (40 percent diluted 1:3 with water) or 0.7 gram dry formaldehyde per pound when freshly coated; or 0.1 ounce of the solution per pound for a sample aged 3 to 6 months. It will also be appreciated that the resist image can be treated with hardeners or other known materials in order to make the image more resistant to abrasion or the like, if it is used for printing or to aid in protecting it against chemical action of an etching solvent or solution in the event that the support on which the resist is formed is to be etched.

The drawing shows a preferred embodiment of our invention.

FIG. 1 discloses a support 10 having thereon an exposed silver halide photographic emulsion 11 showing a latent image 14.

FIG. 2 shows the same photographic element of FIG. 1 after development with a wandering insolubilizing developer in which the exposed areas 14 have been developed.

FIG. 3 illustrates the transfer of the oxidized developer from developed image areas 14 to corresponding areas 12 of the colloid layer 13 on the support 15.

FIG. 4 shows the support 15 carrying the colloid layer 13 with the image areas 12 in tanned colloid after the non-silver halide containing layer 13 has been stripped from the emulsion layer 11.

FIG. 5 shows the image areas 12 in tanned colloid remaining after the untanned colloid layer 13 in the non-image area has been washed off.

The following examples are intended to illustrate our invention but not to limit it in any way.

EXAMPLE I

A suitable film support was coated with a silver chloride emulsion having an unhardened gelatin vehicle, so that the support carried 100 mg. of silver chloride and 400 mg. of gelatin/ft.^{2} when dry.

A suitable film support was also coated with a dispersion of fine particles of carbon in unhardened gelatin to the extent of 1,000 mg. of gelatin/ft.^{2} and sufficient carbon to give an optical density of 2.0 when dry.

The exposed (to a line negative) silver chloride sensitized coating was placed in an aqueous solution of hydroquinone 1 percent, sodium sulfate (to prevent excessive softening of the gelatin) 3 percent at 74–76° F. for 60 seconds at which time 3.6 g./sq. ft. of the solution was absorbed. Excess solution was removed by squeegeeing. Simultaneously, the carbon gelatin coating was placed in an aqueous solution of sodium carbonate 5 percent at 74–76° F. for 60 seconds at which time 5.3 g./sq. ft.. of the solution was absorbed. The excess was removed by squeegeeing. The two sheets were then placed face to face in intimate contact by pressure (mild) rollers.

Development of the line image occurred immediately and contact was maintained for 60 seconds at 74–76° F. after which the two coatings were separated, rinsed with tap water, placed in an acid stop bath for 15 seconds and washed in tap water at 110° F. The gelatin in the image areas was very insoluble, the reminder washed away. A

mirror image in insoluble gelatin containing carbon was also obtained on the gelatin carbon coating.

EXAMPLE II

The following layers were prepared:

Layer I

Carbon black-gel:

3.1% Molacco black carbon } 4.8% gelatin }	aqueous solution	--g-- 100.0
6.7% Triton X-200 (p-tert. octyl phenoxy-ethoxy ethyl sodium sulfonte)	--ml--	2.0
	g.	102.0

This solution was coated on cellulose acetate film support at 10.2 ml./ft.^{2} to yield a gelatin coverage of 480 mg./ft.^{2} and 310 mg. of carbon/ft.^{2}.

Layer II

Gelatin-silver chloride emulsion (3800 g./Ag mole) containing:

170 g. gelatin	--g--	633.0
6.7% Triton X-200	--ml--	17.0
1% chlorohydroquinone aqueous solution	--ml--	1100.0
	ml.	1750.0

This solution was coated over Layer I at 5.0 ml./ft.^{2} to yield a silver coverage of 54 mg./ft.^{2}, a gelatin coverage of 85 mg./ft.^{2}, and a chlorohydroquinone coverage of 30 mg./ft.^{2}.

The element is exposed, activated and transferred as described below:

(1) *Contact exposure.*—1 second to a reflector photoflood with a high contrast line positive.

(2) *Activation.*—20 seconds in 4% potassium carbonate, 2% urea solution at 87% F.

(3) *Transfer.*— Multiple transfers to regular colloid transfer receiver sheets in a Regent Verifax machine.

About 20 copies were made by this technique. The copies had dense black images against a clean background. This is 3 to 4 times the number of copies which can be obtained by the process described in U.S. Patent 2,596,756.

EXAMPLE III

The process of Example I was repeated with a variety of developing agents. In all cases where hydroquinone or its derivatives were used, a mirror image of insolubilized gelatin containing carbon was formed. The oxidation product of the developing agent had wandered and insolubilized the gelatin in the gelatin carbon layer. In all cases where catchol or its derivatives were used, insolubilization of the gelatin occurred only in the image areas of the silver halide sensitized coating. There was no insolubilization of the gelatin in the gelatin carbon layer; no mirror image was formed. The oxidation product had not wandered.

Inasmuch as a mirror image is obtained according to our process, it may be desirable to coat the non-silver halide containing gelatin on a tranparent support so that it can be viewed as either a normal or mirror image depending upon whether it is viewed through the base or above it. Our process has particular utility in obtaining images of almost any density or color or in any particular medium, if the medium can be dispersed in gelatin or other polymeric material that can be insolubilized by wandering oxidation products of developing agents.

EXAMPLE IV

A transparent film base was coated with an unhardened gelatino-silver halide emulsion so that 400 mg. of gel and 100 mg. of silver as silver halide covered the area of one square foot of base. Over this was coated a finely divided TiO_2 pigment dispersed in unhardened gel (500 mg. TiO_2, 400 mg. gel/ft.^{2}). The photosensitive element was exposed through the base to a line image film negative and developed in an aqueous alkaline solution (5 percent Na_2CO_3) containing 0.4 percent of hydroquinone. Development was carried out for 20 seconds at 75–76° F. followed by a 3-second rinse, a 10-second immersion in a 5 percent acetic acid stop bath and "washoff" in water at 110° F. for 10–20 seconds, and dried. When viewed through the film base the image is the typical black silver; when viewed from the face of the image is the brilliant white of TiO_2.

It may be desirable in some cases to remove the black silver. If so, this is easily done by a quick bleach in dilute ferricyanide and halide followed by fixing and washing.

EXAMPLE V

A direct positive image is obtained by employing a fogged silver chloride emulsion as follows:

Fogged silver chloride emulsion

Fogging operation.—The pH of a gelatino-silver chloride emplusion is adjusted to 8.5 by the addition of sodium hydroxide, and 10 mg. of $SnCl_2 \cdot 2H_2O$ dissolved in 5 cc. of methyl alcohol is added to a portion of the emulsion containing 1 mole of silver halide. The emulsion is heated to 80° C. and held for 7 minutes and then cooled to 40° C. and the pH adjusted to 6.0 with surfuric acid.

Preparation and coating.—The following ingredients are added to the fogged silver chloride emulsion containing 1 mole of silver halide:

(1) 2-(p-nitrostyryl)-6-ethoxy quinoline metho p-toluene sulfonte	--g--	[1] 0.75
(2) 10% solution of gelatin	--g--	650.0
(3) 15% aqueous solution of Saponin	--cc--	100.0
(4) .34% solution of bromohydroquinone	--g--	680.0
(5) Distilled water	--cc--	2075.0

[1] In 75 cc. of methyl alcohol.

The emulsion is coated on a cellulose acetate support at a coverage of 250 mg. of silver and 445 mg. of gelatin per square foot.

A suitable film support is also coated with a dispersion of fine particles of carbon in unhardened gelatin to the extent of 1,000 mg. of gelatin/ft.^{2} and sufficient carbon to give an optical density of 2.0 when dry.

Both the exposed (to a line negative) silver chloride and the carbon gelatin coating are placed in an aqueous solution of sodium carbonate 5 percent at 74–76° F. for 36–60 seconds. The excess is removed by squeegeeing The two sheets are then placed face to face in intimate contact by pressure (mild) rollers.

Development of a direct positive line image occurs immediately and contact is maintained for 60 seconds at 74–76° F. after which the two coatings are separated, rinsed with tap water, placed in an acid stop bath for 15 seconds and washed in tap water at 110° F. The gelatin in the direct positive image areas is very insoluble, the remainder washes away. A mirror image in insoluble gelatin containing carbon is also obtained on the gelatin carbon coating.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A process of preparing a photographic resist comprising:

(a) developing with a composition substantially free of a silver halide complexing agent, containing a 1,4-dihydroxy benzene silver halide tanning developer selected from the class consisting of hydroquinone, chlorohydroquinone, bromohydroquinone, toluhydroquinone and morpholine methyl hydroquinone, a photographic element exposed to a light image, said element comprising a support having thereon a light sensitive substantially unhardened silver halide gela-

tin emulsion, and having integral therewith, a pigmented, non-silver halide containing colloid layer capable of being insolubilized imagewise by the diffusible oxidation products of the said 1,4-dihydroxy benzene tanning silver halide developer to form an image negative to said light image, said colloid layer and said gelatin emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated,

(b) transferring the oxidized developer to the colloid layer integral with the silver halide emulsion layer to harden said colloid layer imagewise to form an image negative to said light image, and

(c) removing the unhardened areas from said unhardened colloid layer.

2. A process of claim 1 in which the colloid layer is contiguous to the silver halide emulsion.

3. A process of claim 1 in which the colloid layer is a gelatin layer.

4. A process of claim 1 in which the developer is hydroquinone.

5. A process of claim 1 in which the developer is chlorohydroquinone.

6. A process of claim 1 in which the developer is bromohydroquinone.

7. A process of claim 1 in which the developer is toluhydroquinone.

8. A process of claim 1 in which the developer is morpholine methyl hydroquinone.

9. A process of claim 1 in which the colloid layer is a gelatin layer which is contiguous to the silver halide emulsion.

10. A process of preparing a photographic resist comprising:

(a) developing with a composition substantially free of silver halide complexing agent, containing a 1,4-dihydroxy benzene silver halide tanning developer selected from the class consisting of hydroquinone, toluhydroquinone, chlorohydroquinone, bromohydroquinone and morpholine methyl hydroquinone, a photographic element exposed to a light image, said element comprising a support having thereon a light sensitive substantially unhardened silver halide gelatin emulsion,

(b) contacting the emulsion while developing against a non-silver halide containing colloid layer capable of being insolubilized imagewise by the diffusible oxidation products of the said 1,4-dihydroxy benzene tanning silver halide developer to form an image negative to said light image, said colloid layer coated on a separate support, said colloid layer and said gelatin emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated,

(c) transferring the oxidized developer to the colloid layer to harden said colloid layer imagewise to form an image negative to said light image,

(d) stripping the colloid layer from the silver halide emulsion, and

(e) removing the unhardened areas from said unhardened colloid layer.

11. A process of claim 10 in which the colloid layer is a gelatin layer.

12. A process of claim 10 in which the developer is hydroquinone.

13. A process of claim 10 in which the developer is chlorohydroquinone.

14. A process of claim 10 in which the developer is bromohydroquinone.

15. A process of claim 10 in which the developer is toluhydroquinone.

16. A process of claim 10 in which the developer is morpholine methyl hydroquinone.

17. A process of preparing a photographic resist comprising:

(a) developing with a composition substantially free of a silver halide complexing agent, containing a 1,4-dihydroxy benzene silver halide tanning developer selected from the class consisting of hydroquinone, chlorohydroquinone, bromohydroquinone, toluhydroquinone and morpholine methyl hydroquinone, a photographic element exposed to a light image, said element comprising a support having thereon a light sensitive silver halide emulsion and having over the emulsion, a pigmented, non-silver halide containing colloid layer capable of being insolubilized imagewise by the diffusible oxidation products of the said 1,4-dihydroxy benzene tanning silver halide developer to form an image negative to said light image, said colloid layer and said gelatin emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated,

(b) transferring the oxidized developer to the colloid layer over the silver halide emulsion layer to harden said colloid layer imagewise to form an image negative to said light image, and

(c) removing the unhardened areas from said unhardened colloid layer.

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