Dec. 28, 1954 E. H. LAND 2,698,238

PHOTOGRAPHIC PRODUCT AND PROCESS

Filed Feb. 8, 1947

FIG. 1

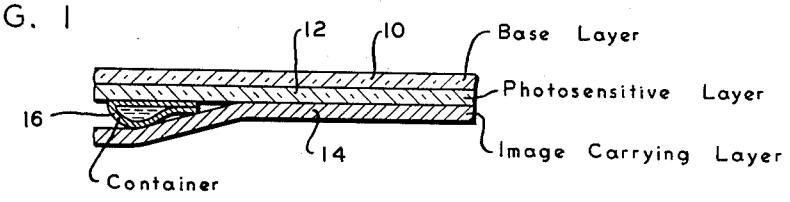


FIG. 2

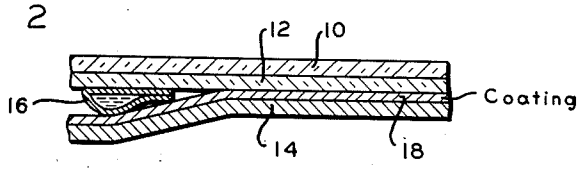
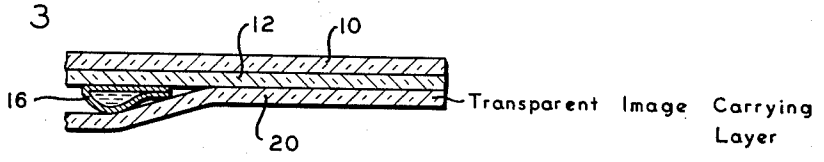


FIG. 3



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PHOTOGRAPHIC PRODUCT AND PROCESS

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23 Claims. (Cl. 95—8)

This invention relates to photography and more particularly to novel photographic processes and products for use therewith.

A principal object of the present invention is to provide a photographic process for obtaining an improved positive silver image from a latent negative image contained in a layer of a silver halide photosensitive material.

Another object of the present invention is to provide an improved photographic product for use with the above process.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components, and the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Figure 1 is an exaggerated diagrammatic cross-sectional view of a preferred modification of the product of the invention;

Fig. 2 is an exaggerated diagrammatic cross-sectional view of another modification of the product of the invention; and

Fig. 3 is an exaggerated diagrammatic cross-sectional view of still another modification of the product of the invention.

In general this application relates to improvements in image-forming reactions of the type wherein a latent negative image is formed in a silver halide photosensitive layer, the latent image is developed, and concurrently therewith soluble silver complexes are formed with undeveloped silver halide and these complexes are transferred to or within the surface of an image-carrying layer, or a layer supported by the image-carrying layer, where they are converted to particles of silver forming a positive image. In such processes, the above steps are preferably accomplished by spreading a viscous alkaline solution of a film-forming material, a developer and a silver halide solvent between the photosensitive layer and the image-carrying layer, to form a lamination having a dry exterior and within which said positive image-forming reaction may take place.

It has been found that the above positive image-forming reaction may be accelerated and improved to give a positive image having an increased gamma, density, and contrast by using lead sulfide in the conversion of the soluble silver complexes to the particles of silver. This effect is particularly noticeable where the silver halide photosensitive layer, such as the fast films, for example, Ansco "Triple S Pan" and Kodak "Verichrome," contains a relatively high percentage of silver iodide (or bromiodide), as compared with bromide and chloride "paper emulsions."

In addition to improving the quality of the positive image, the lead sulfide has definite utility in predetermining the particular stratum of the lamination in which the positive image is primarily formed.

In a preferred form of the invention the lead sulfide is included on the surface of the image-carrying layer, being formed either on that surface, or coated on that surface as a dispersion in a film-forming material or other coating medium.

Referring now to Fig. 1 there is shown one modification of a preferred type of film unit for use with the present invention. As shown in cross-section in Fig. 1 the film unit comprises a transparent base layer **10** carrying on one surface thereof a layer **12** of a silver halide photosensitive emulsion. There is also included an image-carrying layer **14**, which is preferably opaque. Positioned for discharge of its contained liquid between the photosensitive layer **12** and the image-carrying layer **14** is a container **16**. Preferably included in the container **16** is a viscous aqueous solution of a developer and a silver halide solvent.

The base layer **10** is preferably made of a suitable film base material such as a cellulosic ester or mixed ester, such as cellulose nitrate, cellulose acetate, cellulose acetate propionate, or other substance, such as paper or glass, capable of supporting a photosensitive emulsion. The photosensitive layer **12** is preferably an emulsion of a silver halide and in particular an emulsion which is high in silver iodide, or silver bromiodide content, such as that sold by the Eastman Kodak Company, under the trademark "Verichrome."

The image-carrying layer **14** in a preferred embodiment comprises a sheet of paper known in the art as baryta paper, which comprises a paper having thereon a gelatin coating including white particles of barium sulfate.

The image-carrying layer **14** may also be formed of many other materials. This layer is preferably permeable to a substance contained in the liquid composition, although this permeability is not absolutely essential, particularly if the surface thereof comprises a permeable coating. The image-carrying layer **14** may also be made of gelatin, regenerated cellulose, polyhydroxy alkanes, for instance, polyvinyl alcohol, sodium alginate, certain of the cellulose ethers such as methyl cellulose and their derivatives such as sodium carboxymethyl cellulose or hydroxyethyl cellulose, carbohydrates such as gum or starch and mixtures of these materials where the latter are compatible.

The image-carrying layer **14**, in one preferred embodiment of the invention has lead sulfide formed on its inner surface (i. e., that surface closest to the photosensitive layer) as set forth in the following nonlimiting example:

Example 1

A sheet of baryta paper is placed in a bath of water for 30 seconds to thoroughly wet the sheet. This sheet is then passed through a bath containing a $\frac{1}{10}\%$ water solution of neutral lead acetate, the sheet being in contact with this bath for 45 seconds. The sheet is then dipped for 30 seconds in a $\frac{1}{100}\%$ water solution of sodium sulfide, thus forming lead sulfide in and on the surface of the baryta paper.

When lead sulfide particles are formed by the above, and other methods, hereinafter discussed, there is in many cases a heterogeneous distribution of size of particles, depending upon the condition of formation of the particles, these particles ranging from .1 micron to several microns in diameter. Where the smallest particles exist on the image-carrying layer, they have been found to give, in some instances, objectionable yellow coloring to the intermediate tones of the positive image. It has been found that the smallest particles may be eliminated by treatment in acid solution either to dissolve these smallest particles or to convert them into more insoluble particles. Such an acid treatment may be accomplished by dipping in, or swabbing with, a solution of an acid or by use of an acid salt bath of the type described below.

A sheet prepared as above is preferably given a second bath for 30 seconds in a water solution containing by weight 10% cadmium acetate, 1% neutral lead acetate, and 30% zinc acetate. This second bath also has the desirable function of placing on the image-carrying layer a plurality of metal salts which are capable of forming relatively insoluble metal hydroxides with hydroxyl ions in the liquid composition.

The liquid composition in the container **16**, in its preferred embodiment, comprises a developer such as hydroquinone, a silver halide solvent such as sodium thiosulfate, and a film-forming substance such as sodium carboxymethyl cellulose which acts to form a dimensionally stable layer when spread between layers **12** and **14**. There are

also preferably included other substances to aid in the photographic reaction, such as preservatives, i. e., sodium sulfite, and an alkali, i. e., sodium hydroxide, plus water, to carry the above-mentioned elements in solution. A suitable liquid composition may be prepared by thoroughly mixing the materials shown in the following nonlimiting example:

Example 2

	Grams
Water	1860
Sodium carboxymethyl cellulose	93
Sodium sulfite	78
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	38.5
Hydroquinone	52.0

Various equivalents may be used in the above-mentioned liquid composition and it is equally possible to substitute for the film-forming sodium carboxymethyl cellulose, other film-forming materials such as other alkali-inert, water-soluble polymers, for example hydroxyethyl cellulose, the sodium salt of polymethacrylic acid, and aluminum carboxymethyl cellulose. Equally, other developers, preservatives, alkalies, and silver halide solvents may be used, and other substances such as restrainers may be added where desired.

The container **16** is preferably formed of a substance such as an oxygen and water vapor impervious material such, for example, as a sheet of wax impregnated metal-coated paper, wax-coated metal foil, or a metal foil coated with a resin such as polyvinyl butyral which is inert to alkalies.

In the use of the film unit of Fig. 1 the photosensitive layer **12** is exposed to a subject image by light passing through the base layer **10**. The processing of the film unit is next preferably accomplished by applying a mechanical stress to the film unit for the purpose of releasing the liquid composition from the container **16** and spreading it in a uniform thin layer between the image-carrying layer **14** and the photosensitive layer **12**. Such processing can be readily accomplished by passing the film unit through a pair of pressure rollers, the container end of the film unit passing through the rollers first. When the liquid composition is spread between the photosensitive layer **12** and the image-carrying layer **14**, the developer solution develops a visible negative image and the sodium thiosulfate, concurrently with the above development, dissolves the undeveloped, unexposed silver halide grains and forms therewith soluble silver complexes. The soluble silver complexes migrate to the image-carrying layer, while the strongly alkaline solution relatively slowly dissolves the lead sulfide grains in the image-carrying layer. As the sulfide ions are released they combine with the silver complex to form silver sulfide around which the remainder of the silver grains, constituting the positive image, are precipitated by the developer. In view of the slow dissolution of the lead sulfide, the positive image formation can be concentrated primarily in the stratum of the formed lamination containing the lead sulfide grains. This is true, even though the gelatin of the baryta image-carrying layer is a better protective colloid than the sodium carboxymethyl cellulose of the liquid layer. It is also believed that the lead ions released from the lead sulfide have the effect of forming a relatively insoluble lead thiosulfate complex, thereby assisting in breaking up the silver complex.

The other metal salts such as the cadmium, lead and zinc, applied in the after-bath of Example 1, are also slowly dissolved and slowly form relatively insoluble metal hydroxides with the hydroxyl ions to cause a lowering of the pH of the solution to 7 or lower.

After the above-described positive image-forming process is complete, the image-carrying layer is preferably separated from the photosensitive layer to reveal the positive image on the surface thereof. At the time of stripping, the pH of the surface of the image may be still quite high (about 8 or 9) but, due to the presence of the metallic salts (i. e., the lead, cadmium and zinc) deposited by the above second bath, the pH soon falls to 7 or lower.

Other suitable methods of treating an image-carrying layer in accordance with the present invention are set forth in the following nonlimiting examples:

Example 3

A sheet of baryta paper is thoroughly wetted with water and run through a 1/8% aqueous solution of neutral lead acetate for 45 seconds. The sheet is then squeegeed and run through a 1/12% aqueous solution of sodium sulfide solution for 3–4 seconds.

Example 4

A sheet of baryta paper is thoroughly wetted with water and run through a 1/10% aqueous solution of neutral lead acetate for 1 minute. The sheet is then run through a 1/100% aqueous solution of sodium sulfide for 30 seconds.

The sheets prepared by Examples 3 and 4 may be treated in an acid bath to remove the smallest particles of lead sulfide. A preferred type of bath is one which also makes available, for use in the processing, metal salts capable of forming relatively insoluble metal hydroxides. For the second bath there can be used an aqueous solution containing by weight 5% cadmium acetate, 30% neutral lead acetate, and 50% zinc nitrate, the sheet being in contact with this bath for about 30 seconds.

The process of preparing image-carrying layers as set forth in Examples 1, 3 and 4 may be considerably modified. For example, the sheet may be re-run through the neutral lead acetate and sodium sulfide baths several times. This re-running through these two baths is sometimes preferable since it seems to encourage the growth of uniform lead sulfide grains in the surface of the image-carrying layer. It generally seems preferable to run the baryta paper through the lead bath before running it through the sulfide bath. It is also sometimes desirable to pass the image-carrying layer, having lead sulfide on its surface, through suitable acid baths which may be prepared by using weak solutions of nitric, hydrochloric, citric, or maleic acids or the like. This acid bath is preferably used before a metal salt bath of the type described in Example 1, and the excess acid is preferably removed by washing in water.

In another form of the invention, the lead sulfide is formed in a solution before being applied to the image-carrying layer. In one modification of this form of the invention the lead sulfide is formed as single small crystals in a water solution of a film-forming material. In another form, the lead sulfide is formed in galaxies of extremely small particles, which are confined to the spaces between the surfaces of particles of an inert material dispersed in water. In both cases the lead sulfide so formed is preferably coated on the image-carrying layer.

This form of the invention is shown in Fig. 2 where like numbers correspond to like elements of Fig. 1. As shown in Fig. 2, there is provided a silver halide photosensitive layer **12** (preferably a fast emulsion such as Kodak "Verichrome") coated upon a usual cellulosic film base **10**. There is also provided a baryta image-carrying layer **14** and a container **16** having therein a liquid composition similar to that described in Example 2. On the surface of the image-carrying layer nearest the photosensitive layer there is preferably provided a coating **18** containing lead sulfide.

In one form of the invention this coating **18** is formed as set forth in the following nonlimiting example:

Example 5

To 50 cc. of an aqueous 1% hydroxyethyl cellulose solution is added 5 cc. of an aqueous 20% neutral lead acetate solution. To another 50 cc. of an aqueous 1% hydroxyethyl cellulose solution is added 5 cc. of an aqueous 20% sodium sulfide solution. Each of these solutions is thoroughly mixed and then the second solution is slowly added to the first solution, while stirring constantly, until the first solution turns a rich gray-brown. A baryta image-carrying layer is prepared for receiving the above mixture by dipping for 2 minutes in a water solution containing 1% neutral lead acetate, 10% cadmium acetate and 30% zinc nitrate, and subsequently dried. The hydroxyethyl cellulose containing lead sulfide is then rubbed on the baryta sheet in a coating **18** thick enough to give a very pale brown color to the baryta paper.

When an image-carrying layer, prepared as in Example 5, is used in the film unit of Fig. 2, the processing thereof is the same as mentioned in connection with the discussion of Fig. 1 above. The positive image obtained as the result of this processing has neutral colored tones.

In another method of preparing a lead sulfide coating for application to an image-carrying layer, the procedure set forth in the following nonlimiting example may be used:

Example 6

15 grams of silica aerogel is added to 192 cc. of a 20% neutral lead acetate water solution, and is then mixed mechanically. To the above mix is added 50 cc. of a .1% water solution of sodium sulfide. After this, 25 cc. of a 1% water solution of sodium sulfide is added. The above is thoroughly mixed and then 1 part of a 1% water solution of copper acetate may be added to 4 parts of the above mix. It is believed that the copper acetate added to the silica aerogel-lead sulfide mix bleaches out the smallest aggregates of lead sulfiide which might otherwise dominate the positive image, tending to give yellow-brown middle tones. It also has the function of toning the positive image. This mix is applied to a sheet of baryta paper. A preferred method of applying the above silica aerogel, containing lead sulfide, is to apply a small quantity of the mix to the surface of the baryta paper, to work this into the surface of the baryta paper, and to remove excess of the mix by means such as a resiliently mounted chamois buffer.

An image-carrying layer of the above type may be used advantageously to obtain excellent positive images. Where these images have a tendency to be unstable with time, due to oxidation of excess developer, their stability may be improved by washing in plain water, painting with a weak acid or incorporating a substance of acid reaction in the surface of the image-carrying layer. Such a substance of acid reaction may comprise a plastic acid such as carboxymethyl cellulose or an acid ester such as cellulose acetate hydrogen phthalate.

Another type of baryta paper having an acidifying substance contained on its surface may be prepared by dipping a sheet of baryta paper for 30 seconds in a ¼% water solution of neutral lead acetate, followed by a dipping for 1½ seconds in a $\frac{1}{40}$% water solution of sodium sulfide, followed by a dipping for 30 seconds in an aqueous solution containing 1% neutral lead acetate, 10% cadmium acetate, 30% zinc nitrate. In some cases the image-carrying layer, which has been treated as described immediately above, has superior characteristics for receiving the dispersion of silica aerogel and lead sulfide, since the sulfide in the metallic sulfides already on the layer seems to keep the metal salts from reacting with much more sulfide in the lead sulfide-silica aerogel dispersion.

The quantity of silica aerogel mentioned above may be varied quite widely, for instance between 1 gram to 30 grams. The ratio of volume of mix to the volume of 1% copper acetate solution may be varied between, for example, 2 to 1, and 30 to 1.

Other lead sulfide-silica aerogel mixes may be prepared in accordance with the method outlined in Example 6 using the ingredients set forth in the following examples.

Example 7

192 cc. of a 40% neutral lead acetate solution
30 grams of silica aerogel
50 cc. of a ⅛% sodium sulfide solution
25 cc. of a 2% sodium sulfide solution
66 cc. of a 1% copper acetate solution
36 cc. of a 15% ascorbic acid solution

Example 8

96 cc. of a 40% neutral lead acetate solution
15 grams of silica aerogel
30 cc. of a ½% sodium sulfide solution
18 cc. of a 15% ascorbic acid solution

Example 9

96 cc. of a 40% neutral lead acetate solution
15 grams of silica aerogel
30 cc. of 1% sodium sulfide solution
10 cc. of a 10% nitric acid solution

Other inert powdered materials which may be used in the same general portions as the silica aerogel are finely powdered glass, bentonite, fuller's earth, talc, or diatomaceous earth such as kieselguhr, and those filter aids such as "Celite," "Super Floss," etc. These powdered materials preferably have a size from about 7 to 75 microns, are preferably transparent and preferably have indices of refraction of the same order as the plastic used in the liquid composition. A preferred silica aerogel is that sold by Monsanto Chemical Company under the designation "Santocel" (micropulverized).

In some cases, it is desirable to wash the silica aerogel-lead sulfide dispersion in plain water to remove any lead acetate or sodium sulfide, this washing being accomplished prior to the coating of the mix on the image-carrying layer.

In still another form of the invention, the lead sulfide is formed in a weak solution of a protective colloid such as gelatin. One method of practicing this modification of the invention is set forth in the following nonlimiting example:

Example 10

Solution A is prepared by adding, to 1000 cc. of water, 200 grams of neutral lead acetate and 10 grams of gelatin. Solution B is prepared by adding, to 1000 cc. of water, 10 grams of sodium sulfide and 10 grams of gelatin. Then 200 cc. of A are added to 100 cc. of B and mixed. To this mixture is added 400 cc. of a 1% water solution of gelatin and then mixed thoroughly. A baryta image-carrying layer is then dipped in this solution. An image-carrying layer so prepared may be further treated by dipping, for example, in an acid solution such as a water solution of nitric acid.

While the specific examples given above are preferred and give the most satisfactory results, they are subject to considerable variations thereof. For instance, where no particular importance is placed upon the production of gray intermediate tones, excellent sepia pictures can be obtained with good blacks and clear whites over a considerable range of dipping baths. One method of getting such a sepia image is to prepare an image-carrying layer in accordance with the following nonlimiting example:

Example 11

A continuous strip of baryta paper is run through a coating bath so that only one surface thereof contacts the bath and at such a speed that the surface is in contact with the bath for approximately two minutes. This first bath contains, for example, a water solution of a ⅛% lead acetate. The lead acetate coating is then squeegeed to remove excess water or permitted to dry by allowing the water to evaporate. The sheet is next passed in contact with the surface of a second liquid composition which contains a ⅛% solution of sodium sulfide. The sheet is run in contact with the bath at such a speed that the surface of the sheet is in contact with this bath for about two seconds. This sheet is then dried by allowing the water to evaporate. It appears that the image-carrying layer, prepared in the above manner, contains some lead acetate and a smaller amount of lead sulfide, while no sodium sulfide exists as such.

It has been found that the most satisfactory results have been obtained with a coating technique of the above type when the percentages of lead acetate and sodium sulfiide vary between $\frac{1}{100}$% and 2%. These ranges give the best pictorial quality with some of the usual emulsions but they are by no means limitations on the amounts usable to obtain good positive images. Lead concentrations in the coating bath have been used as high as 75% while sulfiide concentrations in the coating bath have run as high as 2%. When the higher percentage of lead and sulfide solutions are used some of the lead sulfide forms as incrustations which may be brushed off the surface of the image-carrying layer. On the low side, concentrations of solutions having one part in 50,000 have given satisfactory images.

In general, it seems that the best results for black, gray and white pictures are obtained when the concentration of the lead bath is higher than the concentration of the sulfide bath and in particular when there is a ratio of about 2 to 1 for lead to sulfide concentration in the two baths.

In the preferred methods of forming lead sulfide in the surface of an image-carrying layer, as exemplified by the processes of Examples 1, 3 through 10, the resultant black, white and gray positives obtained are believed to be due to the size of the silver grains, constituting the positive image, the individual grains being large enough to have a high optical absorption. This large grain size is determined, it is believed, in Examples 1, 3, and 4, by the fact that the lead sulfide grains on the surface of the image-carrying layer, although substantially smaller than the final silver grains, expand to the size of the desired silver grains as the result of the slow dissolution thereof by the strongly alkaline liquid composition. Thus, the sul-

fide ions have a slow radial diffusion from their point of release (i. e., the lead sulfiide grain). As the silver complex reaches the locus of the diffusing sulfiide ions, the sphere defining their outward diffusion is approximately the size (about ½ micron) of the desired silver grain, and the immediate precipitation of the silver sulfiide prevents further diffusion.

In Examples 5 through 10 the lead sulfide is in the form of galaxies having a diameter of about ½ micron. Although these galaxies are made up of lead sulfide crystals having a high optical absorption coefficient, the mass density of the galaxy is so low that little or no optical density is apparent on the image-carrying layer. When the silver complex ions arrive at these galaxies, silver sulfide is formed at each of the sulfide ions and is covered immediately by a mass of metallic silver reduced from the other ions in solution. The silver aggregates act as if there were metallic conduction between the particles early in the course of deposition of the silver on the galaxy, so, from the start, the galaxy acts like a large particle, with respect to hue.

The inert particles of material, such as silica aerogel seem to have the desirable function of maintaining the galaxies of small lead sulfide particles during the spreading of the mix on the surface of the image-carrying layer, thereby permitting the achievement of more uniform color through the various tone gradations.

In Example 11 the sepia middle tones are achieved by the presence of slightly smaller lead sulfide particles which form smaller particles of silver.

The polysulfides may generally be used in place of the sulfides in the same order of magnitude. One nonlimiting example is set forth below, where a polysulfide is used in addition to a sulfide in preparing an image-carrying layer of the type described in previous examples:

Example 12

The following materials are placed in a mechanical mixer and thoroughly mixed:

192 cc. of a 60% neutral lead acetate solution
30 grams of silica aerogel
180 cc. of a 75% solution of sodium sulfide to which "liver of sulfur" was added to saturation.

The resulting mix may be diluted with equal parts of water and then spread on the image-carrying layer in a thin coat.

While the liquid composition of Example 2 is preferred, it is subject to considerable variations. One further nonlimiting example of a liquid composition is set forth below:

Example 13

5% water solution of sodium carboxymethyl cellulose	grams	17.6
Sodium sulfite	do	.78
Paraphenylenediamine (diethyl hydrochloride)	grams	.52
Citric acid	do	.385
Ammonium hydroxide	to a pH of 8	

The above liquid composition has certain unique properties in that the silver halide solvent is also the developer and that the alkali is volatile thereby giving neutralization by evaporation.

In still another modification of the invention, the ability of the lead sulfide to control the stratum of the lamination in which the positive image is formed is utilized to provide a film unit in which no layers need be separated for either exposure of the photosensitive or for viewing the final positive image. This form of the invention is shown in Fig. 3 where like numbers correspond to like elements of Figs. 1 and 2. The film unit of Fig. 3 preferably comprises a cellulosic film base **10**, carrying a silver halide photosensitive layer **12**. There is also provided a transparent image- carrying layer **20** and a container **16**, being therein a liquid composition similar to that described in Example 2. This liquid composition has added thereto a sufficient quantity of colloidal titanium dioxide to give to the liquid the ability of forming a dense white layer when spread between the photosensitive and image-carrying layers. The image-carrying layer **20** preferably comprises a sheet of unhardened gelatin which is treated in accordance with any of Examples 1 and 3 through 12 to provide lead sulfide on and in its surface.

With a film unit of the type described above, the photosensitive layer may be exposed to actinic light passing through the base layer **10**. When the film unit is processed, the positive image is formed on and in the surface of the transparent gelatin image-carrying layer. The liquid composition, due to the contained titanium dioxide, forms an opaque white background between the image-carrying layer and the photosensitive layer, against which the positive image may be viewed.

As explained above, the use of lead sulfide on the surface of the image-carrying layer causes the principal amount of image formation to occur in the stratum of the lead sulfide. This permits the film-forming layer to act as a reservoir for the unreacted portions of the developer, for example, and also for some of the reaction products. Therefore this film-forming layer may be stripped from the image-carrying layer to remove a great many of the elements of the liquid which might otherwise stain the positive image. This stripping preferably is accomplished as the result of separating the image-carrying layer from the photosensitive layer and may be effectuated by so forming the inner surfaces of these layers that the formed film has a greater affinity for the photosensitive layer than it has for the image-carrying layer. This feature of the invention is particularly useful in the modifications of the invention shown in Figs. 1 and 2 and is of considerable assistance in producing a positive image of excellent resistance to staining. When such a modification of the invention is utilized the surface of the image-carrying layer prepared in accordance with the preceding examples may be further treated with a substance which decreases the affinity of the film-forming material for the surface of the image-carrying layer. Such a substance may be a soap solution which can be conveniently applied by coating or dipping. It is also desirable in some forms of this modification of the invention to increase the impermeability of the strata of the image-carrying layer below the lead sulfide layer. This may be accomplished by providing an impermeable coating thereunder or by hardening the underlying strata of the image-carrying layer during or after the coating operations. Such increased impermeability has the advantage of preventing absorption by the image-carrying layer of substantial quantities of potential stain-forming components and assists in assuring that the majority of the stain-forming components are removed from the positive image when the formed film is stripped therefrom.

The expression "image-carrying layer," as used in the specification and the claims, refers to a layer adapted to receive a positive image in or on its surface or to support a layer which contains an image in or on its surface. When the image-carrying layer has the lead sulfide formed on and in its surface as a result, for example, of sequential dipping in lead acetate and sodium sulfide baths, the image is formed primarily on and in the surface of the image-carrying layer. When the lead sulfide is incorporated in a film-forming material and coated on the image-carrying layer, the positive image is formed primarily in the layer of film-forming material. The same is true when the lead sulfide is incorporated in a water suspension of an inert substance such as silica aerogel and coated on the surface of the image-carrying layer. In the above cases some of the shadow density may form in the layer of liquid composition.

While the preferred liquid composition has been described as containing the developer, the silver halide solvent, the film-forming material, the alkali etc., various of these materials may be included in the film unit in position to be dissolved by the liquid composition as it is spread through the film unit. For example, all or part of the silver halide solvent may be on the image-carrying layer. Likewise, all or part of the developer may be included in the photosensitive emulsion, and in this case the alkali can be included on the image-carrying layer. Various other modifications are equally feasible and within the scope of the present invention.

The expression "sulfide" as used in the attached claims is intended to indicate a binary compound of bivalent sulfur or a binary compound of sulfur which contains more sulfur than is required by the normal valency of the metal.

The expression "relatively slowly" should be interpreted in the light of the speed of the process involved, which

may vary from as little as 5 seconds to as much as 1 to 2 minutes.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic product comprising a photo-sensitive element which includes a silver halide layer, a print-receiving element for receiving, by transfer, a positive print, and a rupturable containing means holding a liquid, said product having positioned therein photographic reagents including a silver halide developer and a silver halide solvent, said containing means and said elements being so held together that said containing means is capable, upon rupture, of releasing at least part of its contents to permeate superposed portions of said elements including said silver halide layer, the portion of said print-receiving element adapted to be permeated by said liquid including a dispersion of lead sulfide, said liquid, upon release, rendering said silver halide developer and said silver halide solvent effective to develop a latent negative image in said silver halide layer and to form soluble silver complexes with the undeveloped silver halide in said silver halide layer, said lead sulfide initiating and so controlling the precipitation of the silver from said soluble silver complex as to form a transfer image of improved color and density characteristics adjacent the surface of the print-receiving element.

2. A photographic product comprising a photo-sensitive element which includes a silver halide layer, a print-receiving element for receiving, by transfer, a positive print, and a rupturable containing means holding a liquid, said product having positioned therein photographic reagents including a silver halide developer and a silver halide solvent, said containing means and said elements being so held together that said containing means is capable, upon rupture, of releasing at least part of its contents to permeate superposed portions of said elements including said silver halide layer, the portion of said print-receiving element adapted to be permeated by said liquid including lead sulfide dispersed among particles of an inert, water-insoluble substance, said liquid, upon release, rendering said silver halide developer and said silver halide solvent effective to develop a latent negative image in said silver halide layer and to form soluble silver complexes with the undeveloped silver halide in said silver halide layer, said lead sulfide initiating and so controlling the precipitation of the silver from said soluble silver complex as to form a transfer image of improved color and density characteristics adjacent the surface of the print-receiving element.

3. The product of claim 2 wherein the inert, water-insoluble substance is silica aerogel.

4. The product of claim 2 wherein the inert, water-insoluble substance is powdered glass.

5. The product of claim 2 wherein a mixture of lead sulfide and lead polysulfide is dispersed among the particles of the inert, water-insoluble substance.

6. The product of claim 1 wherein the lead sulfide is dispersed in a solid polymeric film permeable to the liquid in the containing means.

7. The product of claim 1 wherein the print-receiving element is a sheet of baryta paper and the lead sulfide is dispersed on and within the surface portions of said baryta paper.

8. The product of claim 2 wherein the liquid in the rupturable containing means includes a film-forming colloid and, upon release, forms a film of said colloid between said superposed portions of said elements, said inert, water-insoluble substance being colorless and having an index of refraction of the same order as the index of refraction of said film-forming colloid.

9. A photographic product capable of forming transfer prints in conjunction with a silver halide element, said product comprising a rupturable containing means holding a liquid, and a sheet support upon which said containing means is mounted, said sheet support providing an image-receiving area adjacent said containing means onto which said liquid is spreadable in a thin layer directly from said containing means, said product carrying a silver halide developer and a silver halide solvent, said image-receiving area of said support including a dispersion of lead sulfide, said liquid and said other reagents being sufficient in amount and being rendered effective by the spreading of said liquid on the image-receiving area to form a transfer print on said image-receiving area of a latent image contained in an area of a silver halide element equivalent to said image-receiving area.

10. A photographic product capable of forming transfer prints in conjunction with a silver halide element, said product comprising a rupturable containing means holding a liquid, and a sheet support upon which said containing means is mounted, said sheet support providing an image-receiving area adjacent said containing means onto which said liquid is spreadable in a thin layer directly from said containing means, said product carrying a silver halide developer and a silver halide solvent, said image-receiving area of said support including lead sulfide dispersed among particles of an inert, water-insoluble substance, said liquid and said other reagents being sufficient in amount and being rendered effective by the spreading of said liquid on the image-receiving area to form a transfer print on said image-receiving area of a latent image contained in an area of a silver halide element equivalent to said image-receiving area.

11. The product of claim 10 wherein the inert, water-insoluble substance is silica aerogel.

12. The product of claim 10 wherein the inert, water-insoluble substance is powdered glass.

13. The product of claim 10 wherein a mixture of lead sulfide and lead polysulfide is dispersed among the particles of the inert, water-insoluble substance.

14. The product of claim 9 wherein the lead sulfide is dispersed in a solid polymeric film permeable to the liquid in the containing means.

15. The product of claim 9 wherein the sheet support is a sheet of baryta paper and the lead sulfide is dispersed on and within the surface portions of the baryta paper.

16. The product of claim 10 wherein the liquid in the rupturable containing means includes a film-forming colloid and, upon release, forms a solid film of said colloid upon the surface of said sheet support, said inert, water-insoluble substance being colorless and having an index of refraction of the same order as the index of refraction of said film-forming colloid.

17. A print-receiving element for having transfer prints formed thereon by precipitating the silver of a soluble silver complex brought into contact therewith, said element comprising a support and a silver precipitation layer provided as a discrete coating on one surface of said support, one surface portion of said element, including said layer, being permeable to an aqueous solution of a soluble silver complex, said layer being principally constituted of particles of a powdered, water-insoluble substance having a particle size not greater than approximately 75 microns and having dispersed therethrough a substantially lesser concentration of lead sulfide particles, said lead sulfide particles being aggregated into galaxies of low optical density by said substance, the latter being chemically inert to the soluble silver complexes and the lead sulfide.

18. The product of claim 17 wherein the inert, water-insoluble substance is silica aerogel.

19. The product of claim 17 wherein the inert, water-insoluble substance is powdered glass.

20. The product of claim 17 wherein a mixture of lead sulfide and lead polysulfide is dispersed among the particles of the inert, water-insoluble substance.

21. The process of forming positive images in silver which comprises developing a latent negative image in a silver halide layer, reacting a silver halide solvent with part at least of the undeveloped silver halide of said layer to form an imagewise distribution of soluble silver complex in said layer, transferring, in solution, at least part of said imagewise distribution of said soluble silver complex to an image-receiving material so located in relation to said silver halide layer as to receive the solution of said complex without appreciably disturbing the imagewise distribution thereof, and reducing to silver the silver ions of said soluble silver complex in the presence of lead sulfide which is dispersed in said print-receiving material.

22. The process of claim 21 wherein the lead sulfide is dispersed among particles of a powdered, water-insoluble substance and said lead sulfide is aggregated by said particles into separate galaxies, the lead sulfide being present in a substantially lesser concentration than said

water-insoluble substance and the latter being chemically inert to the silver halide solvent, the silver halide developer and the lead sulfide.

23. The process of claim 22 wherein the water-insoluble, chemically inert substance has a particle size not greater than approximately 75 microns.

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