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LIGHT SENSITIVE SILVER HALIDE PHOTOGRAPHIC PRODUCT
FOR IMAGE TRANSFER AND PROCESS UTILIZING THE SAME
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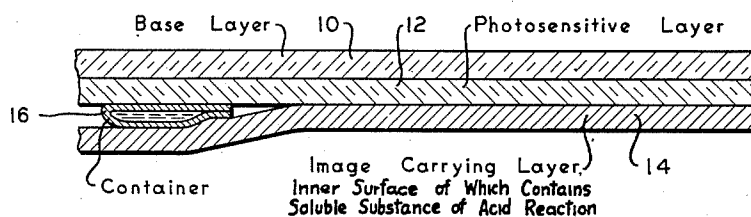


FIG. 1

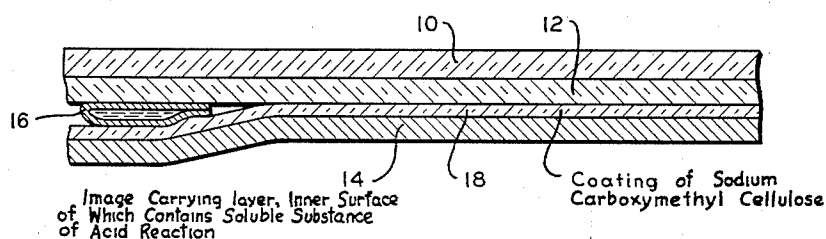


FIG. 2

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LIGHT SENSITIVE SILVER HALIDE PHOTOGRAPHIC PRODUCT FOR IMAGE TRANSFER AND PROCESS UTILIZING THE SAME

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45 Claims. (Cl. 95—8)

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This invention relates to photography, and to novel photographic processes and products in general and is a continuation-in-part of my co-pending application Serial No. 662,000, filed April 13, 1946, for Photographic Product and Process.

This invention relates more particularly to processes of the type wherein a positive image is formed from a latent negative image in a silver halide photosensitive layer by creating positive image-forming components under the selective control of the development of the latent image and by utilizing these image-forming components for creating the positive image. With such processes, staining of the highlights of the positive image is sometimes encountered due to the existence of unused developer in stain-forming condition in said highlights.

It is a principal object of the present invention to provide improved processes of the above type whereby staining of the highlights of the positive image is prevented and a stable positive image is obtained which requires no washing.

Still another object of the present invention is to provide novel composite photographic film units and products particularly suitable for use with such processes.

These and 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 drawing wherein:

Figure 1 is an exaggerated cross-sectional view of a preferred composite photographic film unit embodying the present invention; and

Fig. 2 is an exaggerated cross-sectional view of another composite photographic film unit embodying the present invention.

In the photographic processes with which this invention is particularly involved, a sheet of photosensitive material, preferably a silver halide, is exposed to actinic light to create therein a latent negative image. This latent image is developed and a positive image thereof is formed

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on an image-carrying layer, preferably by creating between the two layers a uniform film of a viscous alkaline developer solution containing a substance capable of forming positive image-forming components. This latter substance, in a preferred form of the invention, comprises a silver halide solvent such as sodium thiosulfate. With such a film of liquid composition between the exposed photosensitive layer and the image-carrying layer, the developer therein develops the exposed silver halide and the silver halide solvent simultaneously forms soluble complex ions with the unexposed silver halide. These complex ions are transported to the surface of the image-carrying layer where they are converted, by means of the developer, to particles comprising silver, these particles constituting a positive image of the latent negative image.

The creation of this layer of liquid, including the developer, is a mechanical process and subject to considerable variation as the result of different conditions of temperature, etc., during the spreading of the liquid. Therefore, it is desirable, in some cases, to include in the layer of liquid composition more developer per unit area than would ordinarily be required to fully cover and develop the negative image. Some of the excess developer may remain on the image-carrying layer containing the positive image.

It has been found that this excess developer, particularly in the highlights of the positive image, can be rendered incapable of staining the positive image if the alkalinity of this positive image is lowered, neutralized, or slightly acidified.

This is accomplished, in a preferred form of the invention, by including on the image-carrying layer a substance which slowly reacts with the liquid composition and slowly lowers the pH of the liquid composition, for example, to a pH of 7, 6 or lower. If the developer solution is too rapidly acidified by the material on the image-carrying layer, it may adversely affect the ability of the developer to develop a strong negative and also a strong positive image. Therefore, the acidification step is so adjusted that the lowering of the pH is not accomplished, at least to any substantial degree, until after the positive image has been formed. However, it does take place quite rapidly after the positive image has been formed.

One preferred method of obtaining acidification of at least the highlight portions of the positive image is to utilize a salt on the image-carrying layer which is slowly dissolved by the liquid composition, and which slowly forms insoluble

compounds with the alkali used to make the developer composition highly alkaline. In one preferred form of this modification of the invention, the alkali used in the liquid composition is sodium hydroxide and the material on the image-carrying layer is a metallic salt which, when dissolved in the liquid composition, slowly forms insoluble metallic hydroxides with the hydroxyl ions in the liquid composition. As the metallic hydroxides precipitate out of the solution they lower the pH thereof to about 5 or 6.

In general, the prevention of stain caused by excess developer in the positive image may be accomplished if the salt, used for preventing the stain, be one which, only slowly lowers the pH of the solution so as not to interfere with the development of the positive and negative images. It is desirable that the salt, when dissolved, be one which, in the concentrations used, does not appreciably destroy the latent negative image or at least does not have any such effect before the development of the latent image, in view of the rapid development of the negative. The salt should also be capable of combining slowly with hydroxyl ions in the liquid composition to precipitate these ions as insoluble or only slightly soluble hydroxides, these hydroxides being preferably white, or colorless, and stable, or having white or colorless end products. It is also desirable that any unreacted portions of the salt be white or colorless and relatively stable.

While many metallic salts satisfy the requirement of the formation of the relatively insoluble metal hydroxide, it is preferred that those metallic salts be used which do not decompose upon dissolution in water. Of these latter metal salts the acetates and nitrates are preferred. Preferred metal salts are the acetates and nitrates of lead, zinc, nickel and cadmium.

Another preferred method of obtaining acidification of at least the highlight portions of the positive image is to utilize, on the image-carrying layer, an acid or acid ester. This acid may be of the type which is slowly dissolved by the liquid composition and slowly lowers the pH thereof or it may be of the type which would ordinarily be rapidly dissolved, but is protected from rapid dissolution by positioning a slowly permeable layer between the locus of the acid and the liquid composition. In some cases the slowly permeable layer may itself be an acid or acid ester.

One preferred type of acid or acid ester is a high polymer having free carboxy or phenolic hydroxy groups along the chain. Preferred polymers of this type are modified cellulosic derivatives containing free carboxy groups along the chain, for example, a cellulosic acid, such as carboxymethyl cellulose, or a cellulosic acid ester, such as cellulose acetate hydrogen phthalate. These polymeric substances have a very low mobility in solution and ordinarily do not need to be protected from the liquid composition.

When the more soluble inorganic or lower molecular weight organic acids are utilized such, for example, as citric acid, they are preferably covered by a slowly permeable layer, for example, a slowly permeable high polymer which, in turn, may comprise one of the above-mentioned high polymers. When a solid acid, such as palmitic acid, is employed, it can, in some cases, be used without any protective coating.

Referring now to Fig. 1 there is shown a composite photographic film unit which embodies

within its confines all of the materials necessary to carry out a preferred type of process outlined above where a metallic salt is used on the image-carrying layer. This film unit is preferably so designed that it may be processed by the application of a mechanical stress thereto, thus making it particularly adaptable for use in a photographic apparatus such as a camera. As shown in Fig. 1, there is provided a base layer 10 adapted to carry, on one surface thereof, a photosensitive layer 12. There is also provided an image-carrying layer 14, which is adapted to carry on its surface the final positive image. Between the image-carrying layer 14 and the photosensitive layer 12 there is positioned a container 16 adapted to have therein a liquid composition. This container can be attached to either the photosensitive layer 12 or the image-carrying layer 14 or can be separate from either of these layers.

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 capable of supporting a photosensitive emulsion. This base can be made opaque, if desired, by addition of suitable dyes or pigments to the above-named substances or the base can be made of paper and other materials suitable for carrying a photosensitive emulsion. The photosensitive layer 12 is preferably of the type rendered developable by exposure to light, e. g., an emulsion of a noble metal halide, and in particular, an emulsion of a silver halide or of a mixture of silver halides, or of a mixed silver halide.

The image-carrying layer 14 in a preferred embodiment comprises a sheet of paper known in the art as baryta paper. The inner surface of this image-carrying layer, i. e., the surface nearest the photosensitive layer, is prepared, in one modification of the invention, in the following manner:

Example 1

A continuous strip of baryta paper is run through a bath comprising a water solution of 30% lead nitrate and 10% zinc nitrate, the speed being such that the baryta paper is in the bath for about one minute.

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 required, particularly if there is a permeable coating applied to the surface thereof. The image-carrying layer 14 may also be made of gelatin, regenerated cellulose, polyhydroxy alkanes, such for instance as polyvinyl alcohol, sodium alginate, certain of the cellulose ethers such as methyl cellulose and their derivatives such as sodium carboxy-methyl cellulose or hydroxyethyl cellulose, carbohydrates such as gum or starch and mixtures of these materials where the latter are compatible.

The liquid composition in the container 16, in its preferred embodiment, comprises a developer such as hydroquinone and a film-forming substance such as sodium carboxymethyl cellulose which acts to form a dimensionally stable image-receiving layer when spread between layers 12 and 14. There is also included a substance adapted to form positive image-forming components from a latent negative image. This latter substance, in a preferred form of the invention, is a silver halide solvent such as sodium

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thiosulfate. There are also preferably included other substances to aid in the photographic reaction, such as a preservative, 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 dissolving 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, perservatives, 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 most 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 develops the latent photographic image and the sodium thiosulfate simultaneously forms soluble silver complexes with the unexposed silver halide grains. These soluble silver complexes are transferred to the image-carrying layer and the layer created by the film-forming sodium carboxymethyl cellulose in the liquid composition where they are converted into insoluble visible particles constituting the positive image on the surface of the image-carrying layer as well as within the layer of sodium carboxymethyl cellulose.

While the above reactions are taking place, the lead nitrate and zinc nitrate are slowly dissolved by the liquid composition and release free lead, zinc and nitrate ions to the liquid composition. The decrease of alkalinity is primarily effected by the lead and zinc ions which slowly form relatively insoluble hydroxides, slowly crystallizing and precipitating these insoluble hydroxides from solution. This reaction progresses at a rate sufficiently slow to permit the positive image to be formed in an alkaline solution, and

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sufficiently fast so that the pH of the solution is lowered to a neutral or slightly acid condition within a short time.

In another method of preparing an image-carrying layer of the present invention the following steps are followed:

Example 3

A continuous strip of baryta paper is run through a coating bath comprising a 1% water solution of lead acetate, the speed of movement being such that the baryta paper is in the bath for about thirty seconds. The sheet is dried and then run through a bath comprising a 1/100% water solution of sodium sulfide, the speed being such that the baryta paper is in the bath for about fifteen seconds. It appears that the image-carrying layer prepared in the above manner contains lead sulfide and some lead acetate with no sodium sulfide as such. The sheet is then treated in accordance with the process of Example 1. The second bath, in addition to supplying zinc and lead salts to the sheet, also has the effect of dissolving the smallest lead sulfide grains. When such a sheet is used with a liquid composition of the type described in Example 2, the alkaline liquid composition slowly releases free sulfide ions from the coating of the image-carrying layer 14, which accelerate the positive image-forming reaction and increase the density, contrast and gamma of the positive image, particularly where the photosensitive layer contains a relatively high percentage of silver iodide.

In still other methods of preparing image-carrying layers in accordance with the present invention the following baths may be used:

Example 4

A water solution containing by weight 5% cadmium acetate, 10% lead acetate, and 50% zinc nitrate.

Example 5

A solution containing by weight 10% cadmium acetate, 30% lead acetate, and 30% zinc nitrate.

Example 6

A solution containing by weight 50% zinc nitrate.

Example 7

A water solution containing by weight 30% of manganous acetate.

Example 8

A water solution containing by weight 1% lead acetate, 10% cadmium acetate and 30% zinc nitrate.

The solutions given in the above examples are subject to considerable variation. As a general proposition it may be stated that, when a developer solution of the type described in Example 2 is used, i. e., one having a pH of about 11 or above, the image-carrying layer should be treated in the baths of Examples 1 and 4 through 8 for approximately 15 to 30 seconds. When the alkalinity of the developer solution is decreased, the time of dipping of the image-carrying layer in the above baths may be decreased. When the concentration of the bath is decreased, the time of dipping should be increased. The permeability of the image-carrying layer may also affect the time of dipping. As an example, with single-weight baryta paper procured from Eastman Kodak Company, the time of dipping or the concentration of the bath should appear-

ly be increased. For double-weight baryta, the time of dipping and concentrations should be as above. This difference appears to be due to the possibility that single-weight baryta is more impermeable than the double-weight baryta to solutions of these materials.

In the above solutions, the acetates and the nitrates of the various metal salts may generally be used interchangeably. The nitrates, being salts of a stronger acid, may usually be employed in slightly smaller quantities than the acetates. With highly alkaline developer solutions of the type set forth in Example 2, and with dipping times of between 15 seconds and one minute, the total weight of the lead and/or zinc salts in the bath should be in the neighborhood of 30% or more to get complete neutralization of excess developer solution, where such neutralization is desired.

Other metallic salts that may be used are: calcium acetate, chromic acetate, zirconyl nitrate, cobaltous chloride, cupric acetate, beryllium nitrate, cadmium nitrate, aluminum acetate, and stannic chloride, these salts being somewhat less preferred than those listed previously.

An image-carrying layer prepared by use of the bath of Example 8 is particularly adapted for use in photocopy work where the photosensitive layer comprises a contrasty negative such as that sold by Eastman Kodak under the trade name of Kodabromide 4025 and the image-carrying layer comprises a sheet of ordinary bond paper.

In still another method of providing the metallic salt on the image-carrying layer there is provided a film unit of the type shown in Fig. 2, where like numbers correspond to like elements of Fig. 1. In this case the salt is absorbed by the image-carrying layer 14 of Fig. 2 and then covered by a coating 18 of a film-forming material. Such a method is set forth in the following nonlimiting example:

Example 9

A sheet of single-weight baryta paper is run through a 50% water solution of lead acetate, being in contact with the solution for about 1 minute. The sheet is then dried and there is applied to the surface thereof a coating 18 approximately .015 inch thick of a 5% water solution of sodium carboxymethyl cellulose. With such a coating technique, the lead partially insolubilizes the sodium carboxymethyl cellulose, by cross-linking therewith, and thus increases its insolubility. The lead sodium carboxymethyl cellulose, due to its increased insolubility, seems to slow down the dissolution of the lead ions. Thus, this type of image-carrying layer may be used in processes where high concentrations of water-soluble lead salts might otherwise be undesirable due for example to their possible effect of decreasing the gamma of the positive image, with some emulsions.

In the use of the modification of the invention of Fig. 2, the metallic salt, or salts, are slowly released from the image-carrying layer 14 and serve the same function as previously described, the permeability of coating 18 controlling the speed of dissolution of the salt or salts from layer 14.

The above description of the invention is concerned with preferred modifications and is subject to considerable variation without departing from the scope thereof. For example, the metallic salt, or salts, used for forming the relative-

ly insoluble metallic hydroxide may be applied to the image-carrying layer in a number of ways other than by dipping the image-carrying layer in a water solution thereof. As an example of such a modification of the invention, the salt, or salts, may be incorporated in solid or dissolved form in a suitable film-forming material and then coated on the image-carrying layer.

When an acid or acid ester is used on the image-carrying layer, a preferred type is a high polymer, as mentioned previously. A particular advantage of this type of acid resides in its relative immobility and its "enteric solubility" characteristics, i. e., its insolubility in an acid solution and its solubility in an alkaline solution. These characteristics make this substance particularly useful where the polymeric acid or acid ester is used as a base coat on the image-carrying layer, on top of which there is placed a coating of a colloidal precipitant, such as lead sulfide. When the colloidal precipitant is coated over the polymer it is preferably applied in a slightly acid or neutral medium. Thus it does not appreciably dissolve the undercoat of the polymer. During the processing reaction, the alkalinity of the liquid composition is slowly lowered by the polymer as the hydroxyl ions diffuse down to the relatively immobile polymer, thus causing neutralization.

Several preferred types of polymeric acid substances may be incorporated on the surface of the image-carrying layer, for example, by providing a coating 18 thereof in a modification of the invention of the type shown in Fig. 2. This type of coating may be formed as described in the following nonlimiting examples:

Example 10

A baryta image-carrying layer is coated with a thin layer of a 5% water solution of sodium carboxymethyl cellulose. This coating is then converted to the acid polymer, carboxymethyl cellulose, by dipping for 1 minute in a 15% water solution of hydrochloric acid, followed by a washing in plain water. This acid polymer can also be prepared by adding an acid, such as citric, to the water solution of the sodium salt of the polymer.

Example 11

A solution containing 20 grams of cellulose acetate hydrogen phthalate dissolved in 50 cc. of acetone is doctored, or roll-coated, on a baryta image-carrying layer. This is next preferably covered with a dispersion of lead sulfide and silica aerogel in water.

Other acid cellulose derivatives that may be used are cellulose hydrogen phthalate, carboxyethyl cellulose, and carboxy cellulose. Equally, other acid polymers, such as polymethacrylic acid, may be used.

When readily soluble inorganic or readily soluble low molecular weight organic acids are employed, it is desirable to slow down the dissolution of these acids by the liquid composition. This is preferably accomplished by the formation of a slowly permeable layer over the acid which has been imbibed onto the surface of the image-carrying layer. It is possible, however, to include such an acid in solid or dissolved form in a film-forming material which is slowly permeable, or to coat the acid on the back of the image-carrying layer, i. e., that side thereof which is farthest from the photosensitive layer. When solid acids are used, particularly those which are only slowly soluble in an alkaline solu-

tion, they can be used without any protective coating. Various specific methods of incorporating an acid in film units of the type shown particularly in Figs. 1 and 2 above are set forth in the following nonlimiting examples:

Example 12

2 grams of diphenyl disulfonic acid are added to 30 grams of a 2% water solution of sodium carboxymethyl cellulose and spread on a baryta image-carrying layer.

Example 13

2 grams of succinic acid are added to 30 grams of a 2% water solution of sodium carboxymethyl cellulose and coated on a baryta image-carrying layer. Over this coating there is applied another coating of a water solution of sodium carboxymethyl cellulose.

Example 14

1½ grams of malic acid are added to 30 grams of a 2% water solution of sodium carboxymethyl cellulose and coated on a baryta image-carrying layer.

Example 15

1½ grams of O-phthalic acid dissolved in methanol are added to 30 grams of a 2% water solution of sodium carboxymethyl cellulose and coated on a baryta image-carrying layer.

Example 16

A 20% water solution of maleic acid is painted on the back of a single-weight baryta image-carrying layer.

Example 17

A 5% water solution of palmitic acid is painted on the back of a single-weight baryta image-carrying layer.

Example 18

5 grams of molybdic acid are added to 15 cc. of a 10% water solution of sodium hydroxide. The image-carrying layer is dipped in this solution for 5 minutes and dried. Then it is dipped in a 5% hydrochloric acid solution to obtain molybdic acid and sodium chloride.

Example 19

A 5% solution of salicylic acid in water and methanol is applied to a baryta image-carrying layer by dipping for about 5 minutes.

Other solid acids that may be applied to the image-carrying layer by imbibing from water, or other solutions thereof, are as follows: oxalic acid, sebacic acid, hydrocinnamic acid, metanilic acid, palmitic acid, paratoluene sulfonic acid, and benzenedisulfonic acid. These acids may be added in solutions of organic solvents, or water, and a film-forming material, depending upon their solubility.

With respect to the acids which are included in, on, or under the image-carrying layer it may be stated generally that their concentration should be adjusted to their solubility and the permeability of any protecting medium in which, or under which, they are located. Thus when the acids are coated on the front of the image-carrying layer they must, unless relatively slowly soluble, be incorporated in smaller quantities than they would be if protected by a slowly permeable layer.

It is generally preferred to utilize such acids under, or in, a protective medium which slows down their rate of dissolution so that, even

though a great excess of acid may be present, the acid does not lower the pH of the developer solution to any substantial degree until the image-forming reaction is complete.

The invention described above may be considerably modified such as by combining certain of the above treatments, for example by using an acid polymer layer of the type described in Example 11 over a metallic salt layer of the type described in Example 5, or an acid layer of the type described in Example 12.

While the acidifying substance is preferably included on or associated with the image-carrying layer, this is not essential and it might, for example, be positioned between the photosensitive layer and the base carrying this photosensitive layer, or on the back side of the base for the photosensitive layer, in those cases where this base is at least slowly permeable to the liquid composition. It is preferred, however, that this acidifying substance, whether acid, polymer or salt, be associated with the image-carrying layer, since in most cases it is desirable to be able to separate the positive image from the negative image at a predetermined time during the processing thereof. It is also desirable in most cases to have the acidification or neutralization of the positive image take place after the positive image has been completely formed. Thus, when the acid substance is associated with the image-carrying layer, this layer, having on its surface the positive image, may be separated from the negative photosensitive layer at any predetermined time and the acidification or neutralization of the positive image may continue after this positive image has been separated from the photosensitive layer.

With the use of substances of acid reaction on the image-carrying layer, some quite remarkable conditions are encountered. This is particularly true when the substance is an acid salt since the pH of the layer of liquid, a moment after spreading, seems to be much lower at the surface of the image-carrying layer than at the surface of the photosensitive layer. As permeation of the two layers continues the pH of the liquid layer reaches a value which is lower than the pH of the liquid initially but which may be higher (particularly in the shadows) than the initial pH of the liquid at the surface of the image-carrying layer when it first contacted the image-carrying layer. This variation of pH through the depth of the layer may be used in some cases to aid in preventing the initial precipitation of silver in the positive image, thereby giving a momentary time delay between development of the negative and positive images, which is sometimes of assistance in maintaining clear highlights.

It is also contemplated by the present invention that the above processes of acidification of the positive image may be carried out by dipping the image-carrying layer, having thereon the final positive image, in a bath containing a solution of an acid salt. In certain industrial applications it is possible to acidify or neutralize the positive image by subjecting it to acid fumes. However, these modifications of the invention are much less preferred for use with a hand camera. It is preferred that the film unit contain all of the materials necessary to produce a final stable positive image from a latent negative image, with no addition of any materials, and with a substantially dry process requiring no washing or baths.

The symbol pH as used throughout the above specification and the attached claims represents

the logarithm of the reciprocal of the hydrogen ion concentration.

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 drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic process for forming, by transfer, a positive print of a latent image contained in the silver halide emulsion of a photosensitive element wherein a single application of liquid to said element is effective to give a finished print sufficiently stable to require no subsequent liquid stabilizing treatments, which process comprises the steps of bringing a relatively uniform layerwise distribution of a processing liquid into contact with the photosensitive element so as to permeate said emulsion with said liquid, said layerwise distribution of processing liquid providing the entire mass of liquid for performing said process; providing a print-receiving element in superposed relation with the photosensitive element, said print-receiving element being at least partially permeable to the processing liquid and the layerwise distribution of the processing liquid being confined between the outer surfaces of said superposed elements throughout the processing, said processing liquid containing, after permeation of said silver halide layer, all of the reagents, including a silver halide developer and an alkali, for developing the latent image in the silver halide emulsion and for forming a positive print of the subject matter of said latent image upon said print-receiving element, said developer being characterized by its propensity for oxidizing in an alkaline environment to form stains; and introducing into the alkaline processing liquid, subsequent to its contact with the photosensitive element, a substance of acid reaction in sufficient concentration to reduce the alkalinity of said processing liquid to a pH at which the unused developer therein is substantially incapable of oxidation to form a stain in said positive print, said substance of acid reaction being dissolved from a permeated portion of one of said elements and being present in said processing liquid in addition to all of the reagents for forming the transfer print.

2. The process of claim 1 wherein the liquid is spread in a layer between the photosensitive element and the print-receiving element.

3. The process of claim 2 wherein the liquid as spread contains, in solution, the alkali and the developer, and also contains a silver halide solvent.

4. The process of claim 1 wherein the substance of acid reaction comprises at least one neutralizing metal salt carried adjacent the inner surface of one of said elements, said neutralizing metal salt being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal salt.

5. The process of claim 1 wherein the substance of acid reaction comprises a plurality of neutralizing metal salts carried adjacent the inner surface of one of said elements, said neutralizing metal salts being soluble in the processing liquid and the metal ions thereof forming metallic hydroxides which are substantially more

insoluble in the processing liquid than are said neutralizing metal salts.

6. The process of claim 1 wherein the substance of acid reaction is an acidic high polymer located adjacent the inner surface of said print-receiving element.

7. The process of claim 6 wherein the acidic high polymer is a cellulosic compound and has free carboxy groups along its chain.

8. The process of claim 1 wherein the substance of acid reaction is provided by the print-receiving element and comprises an acid located beneath the inner surface of the print-receiving element, said acid being overlaid with a layer of solid material slowly permeable to the processing liquid.

9. The process of claim 1 wherein the substance of acid reaction is an acid dispersed depthwise throughout at least a substantial portion of the thickness of the print-receiving element.

10. A photographic process for forming, by transfer, a positive print of a latent image contained in the silver halide emulsion of a photosensitive element wherein a single application of liquid to said element is effective to give a finished print sufficiently stable to require no subsequent stabilizing treatments, which process comprises the steps of spreading, in a layer between the photosensitive element and a print-receiving element, all of the processing liquid for performing said process, which liquid includes, in solution, a silver halide developer, a silver halide solvent and an alkali and which, when spread, permeates the silver halide emulsion, said liquid developing a latent image in said emulsion and forming a positive print in silver upon said print-receiving element, the developer being characterized by its propensity for oxidizing in an alkaline environment to produce stains; after formation of the positive print, separating said print-receiving element from said photosensitive element; and at some stage of the process, subsequent to the spreading of the liquid, introducing into the processing liquid a substance of acid reaction, by dissolving the same from said print-receiving element, said substance being carried in solid form by said print-receiving element in a sufficient amount to reduce the alkalinity of the processing liquid of said print-receiving element to a pH at which the unused developer in said liquid is substantially incapable of oxidation to form a stain in said positive print.

11. The process of claim 10 wherein the substance of acid reaction comprises at least one neutralizing metal salt carried adjacent the inner surface of said print-receiving element, said neutralizing metal salt being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal salt.

12. The process of claim 10 wherein the substance of acid reaction comprises at least one neutralizing metal acetate carried adjacent the inner surface of one of said elements, said neutralizing metal acetate being soluble in the processing liquid and the metal ions thereof forming a metal hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal acetate.

13. The process of claim 10 wherein the substance of acid reaction comprises zinc acetate and is carried adjacent the inner surface of said print-receiving element.

14. The process of claim 10 wherein the substance of acid reaction comprises cadmium acetate and is carried adjacent the inner surface of said print-receiving element.

15. The process of claim 10 wherein the substance of acid reaction comprises at least one neutralizing metal nitrate carried adjacent the inner surface of one of said elements; said neutralizing metal nitrate being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal nitrate.

16. The process of claim 10 wherein the substance of acid reaction comprises a plurality of neutralizing metal salts carried adjacent the inner surface of one of said print-receiving elements, said neutralizing metal salts being soluble in the processing liquid and the metal ions thereof forming metallic hydroxides which are substantially more insoluble in the processing liquid than are said neutralizing metal salts.

17. The process of claim 16 wherein the said neutralizing salts are a mixture of lead, cadmium and zinc salts.

18. The process of claim 10 wherein the substance of acid reaction is an acidic cellulosic high polymer having free carboxy groups along its chain and is located adjacent the inner surface of said print-receiving element.

19. The process of claim 10 wherein the substance of acid reaction is a layer of carboxymethyl cellulose and is located adjacent the inner surface of said print-receiving element.

20. The process of claim 10 wherein the substance of acid reaction is a layer of cellulose acetate hydrogen phthalate and is located adjacent the inner surface of said print-receiving element.

21. The process of claim 10 wherein the substance of acid reaction is an acid, substantially all of which is located beneath the surface of said print-receiving element so as to be only slowly accessible to the processing liquid spread over said print-receiving element.

22. The process of claim 10 wherein the substance of acid reaction is a palmitic acid, substantially all of which is located beneath the surface of said print-receiving element so as to be only slowly accessible to the processing liquid spread over said print-receiving element.

23. The process of claim 10 wherein the substance of acid reaction is a maleic acid, substantially all of which is located beneath the surface of said print-receiving element so as to be only slowly accessible to the processing liquid spread over said print-receiving element.

24. A photographic product comprising a liquid-confining layer, including at least a photosensitive portion, said photosensitive portion comprising silver halide as the photosensitive material thereof, another liquid-confining layer and a rupturable container holding a liquid, said layers and said container being associated together so as to permit said layers to be superposed with said liquid held by said container so as not to wet said layers and with said container positioned for releasing said liquid between said layers, said product containing all of the reagents, including a silver halide developer and an alkali, in sufficient quantity to develop a latent image in said photosensitive portion and to provide a layer of said product, other than said photosensitive layer, with a positive transfer print of the subject matter of said latent image, said re-

agents being rendered effective upon the release of said liquid from the rupturable container, said silver halide developer tending to oxidize and form stains in an alkaline environment, said product containing, in addition to all of said reagents for forming a transfer print, a substance of acid reaction which is carried by one of the layers of said product in a position to be dissolved in said liquid upon the release thereof, said substance of acid reaction being operative to reduce the alkalinity of the liquid at a rate substantially slower than the rate at which the developing reaction takes place and being sufficient in quantity to reduce the alkalinity of the processing liquid to a pH at which the developer is substantially incapable of oxidizing to form stains in said positive transfer print.

25. The product of claim 24 wherein the container is mounted so as to spread its contents in a layer between the photosensitive layer and the print-receiving layer.

26. The product of claim 25 wherein the liquid in the container contains, in solution, the alkali and the developer, and also contains a silver halide solvent.

27. The product of claim 24 wherein the substance of acid reaction comprises at least one neutralizing metal salt, said neutralizing metal salt being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal salt.

28. The product of claim 24 wherein the substance of acid reaction comprises a plurality of neutralizing metal salts, said neutralizing metal salts being soluble in the processing liquid and the metal ions thereof forming metallic hydroxides which are substantially more insoluble in the processing liquid than are said neutralizing metal salts.

29. The product of claim 24 wherein the substance of acid reaction is a film of an acidic high polymer located adjacent the inner surface of the print-receiving layer.

30. The product of claim 29 wherein the acidic high polymer is a cellulosic compound and has free carboxy groups along its chain.

31. The product of claim 24 wherein the substance of acid reaction is an acid, substantially all of which is located beneath the surface of one of said layers between which the liquid is released so as to be only slowly accessible to said liquid.

32. A photographic product capable of forming transfer prints in conjunction with a photosensitive silver halide element, said product comprising a rupturable container 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 and onto which said liquid is spreadable in a thin layer directly from said containing means, said product carrying all of the reagents, including a stain-forming silver halide developer and an alkali, for forming a transfer print of a latent image in a silver halide emulsion, said reagents and said liquid being sufficient in amount and being so located in relation to said image-receiving area that the spreading of said liquid over said area disperses the silver halide developer and the other reagents throughout said area in adequate quantity to form a transfer print of a latent image in an area of a contiguous silver halide element equivalent to

said image-receiving area, said support carrying, distributed over said image-receiving layer and in addition to said reagents, a substance of acid reaction in sufficient quantity to substantially neutralize said liquid when spread on said support from said containing means, said substance consuming alkali at a substantially slower rate than the rate at which said reagents form a transfer print.

33. The product of claim 32 wherein the liquid in the containing means contains, in solution, the alkali and the developer, and also contains a silver halide solvent.

34. The product of claim 32 wherein the substance of acid reaction comprises at least one neutralizing metal salt carried adjacent the surface of said support upon which said liquid is spread, said neutralizing metal salt being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal salt.

35. The product of claim 32 wherein the substance of acid reaction comprises a plurality of neutralizing metal salts carried adjacent the surface of said support upon which said liquid is spread, said neutralizing metal salts being soluble in the processing liquid and the metal ions thereof forming metallic hydroxides which are substantially more insoluble in the processing liquid than are said neutralizing metal salts.

36. The product of claim 32 wherein the substance of acid reaction is an acidic high polymer located adjacent the surface of said support upon which said liquid is spread.

37. The product of claim 36 wherein the acidic high polymer is a cellulosic compound and has free carboxy groups along its chain.

38. The product of claim 32 wherein the substance of acid reaction is an acid, substantially all of which is located beneath the surface of the support on which the liquid is spread so as to be only slowly accessible to said liquid.

39. The product of claim 32 wherein the substance of acid reaction comprises at least one metal acetate carried adjacent the surface of said support upon which said liquid is spread, said neutralizing metal acetate being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal acetate.

40. The product of claim 32 wherein the substance of acid reaction comprises at least one metal nitrate carried adjacent the surface of said support upon which said liquid is spread, said neutralizing metal nitrate being soluble in the processing liquid and the metal ions thereof forming a metallic hydroxide which is substantially more insoluble in the processing liquid than is said neutralizing metal nitrate.

41. The product of claim 32 wherein the substance of acid reaction comprises a plurality of neutralizing metal salts carried adjacent the surface of said support upon which said liquid is spread, said metal salts including salts of cadmium, zinc and lead, and being soluble in the processing liquid, the metal ions of said salts forming metallic hydroxides which are substantially more insoluble in the processing liquid than are said neutralizing metal salts.

42. The product of claim 32 wherein the substance of acid reaction is cadmium acetate.

43. The product of claim 32 wherein the substance of acid reaction is zinc acetate.

44. The product of claim 32 wherein the substance of acid reaction is a layer of carboxymethyl cellulose and is located adjacent the surface of said support upon which said liquid is spread.

45. The product of claim 32 wherein the substance of acid reaction is a layer of cellulose acetate hydrogen phthalate and is located adjacent the surface of said support upon which said liquid is spread.

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