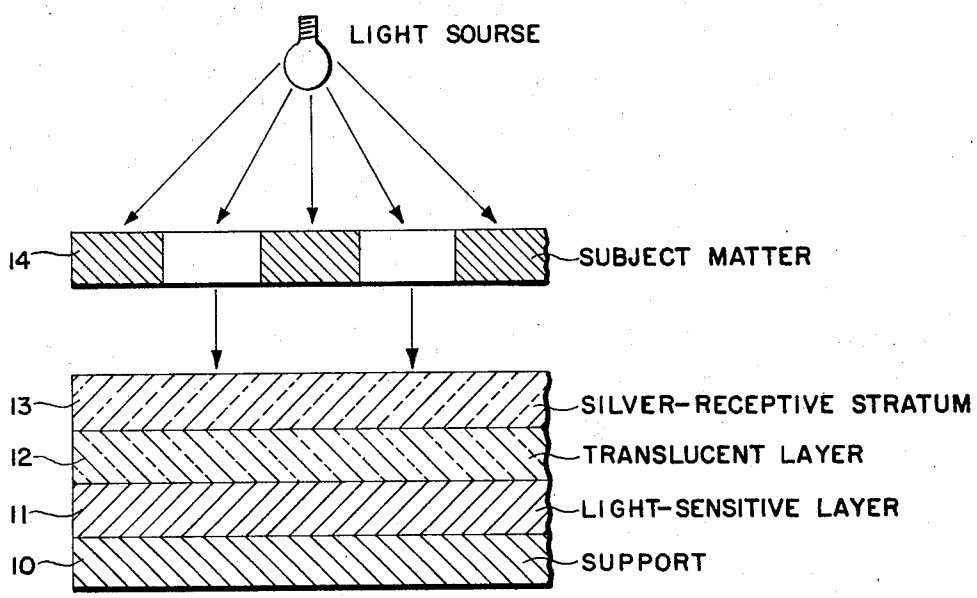
April 23, 1974 L. C. FARNEY ET AL 3,806,342

COMPOSITE DIFFUSION TRANSFER PHOTOGRAPHIC PRODUCT AND PROCESS

Filed Dec. 28, 1970



INVENTORS
LEONARD C. FARNEY
and
CAROLE L. GRONCKI
BY Brown and Mikulka
and
John P. Morley
ATTORNEYS

United States Patent Office 3,806,342
Patented Apr. 23, 1974

3,806,342

COMPOSITE DIFFUSION TRANSFER PHOTOGRAPHIC PRODUCT AND PROCESS

Leonard C. Farney, Melrose, and Carole L. Groncki, Lynnfield, Mass., assignors to Polaroid Corporation, Cambridge, Mass.

Filed Dec. 28, 1970, Ser. No. 101,902
Int. Cl. G03c 5/54
U.S. Cl. 96—29 R 28 Claims

ABSTRACT OF THE DISCLOSURE

Photographic products for providing diffusion transfer image patterns and having the capability of being developed by moisture preferably in the form of steam. Essential elements of the preferred products of the present invention are a moisture activatable processing system integrated with a diffusion transfer image pattern receiving layer, a layer comprising an opacification system which can provide a reflective background for viewing the diffusion transfer image pattern and at the same time effectively mask a developed image pattern in an underlying layer comprising a photosensitive system.

BACKGROUND OF THE INVENTION

Part 1.—The field of the invention

This invention relates to photography. More precisely, the invention disclosed herein relates to photographic products useful for producing diffusion transfer image patterns.

Part 2.—Description of the prior art

Photographic products for producing diffusion transfer image patterns which can be viewed without separation are also known to the art. U.S. Pat. 2,861,885, issued on Nov. 25, 1958 to Edwin H. Land discloses and claims photographic products having a silver halide system which when fully developed has a low maximum density; while forming a silver transfer pattern which has a very high covering power so that the composite print may be viewed as a positive reflection print without separation.

Recently other photographic products useful for providing diffusion transfer image patterns which can be viewed without separation have been presented to the art. This particular class of products is especially useful in the preparation of photocopies of printed matter and they are described in detail in commonly assigned U.S. patent application Ser. No. 519,884, filed as continuation-in-part of application Ser. No. 368,322, filed May 19, 1964 by Edwin H. Land and in commonly assigned U.S. patent application Ser. No. 519,995, filed as continuation-in-part of application Ser. No. 368,321, filed May 19, 1964 by Edwin H. Land and Leonard C. Farney.

As disclosed in these applications, a photographic product including a layer containing an opacifying system may be exposed to a light source and then processed to form a negative image and a positive transfer image in a layer situated above the layer containing the opacifying system. The opacifying system is capable of effectively masking the negative image but does not prevent photoexposure of the light-sensitive material in the photographic product. Accordingly, the product provides a composite print which contains both a negative and a positive image pattern and the positive pattern is viewable by reflection as a positive reproduction of the original subject matter.

In application Ser. No. 519,995, the layer containing the opacifying system is situated over a layer containing a light-sensitive silver halide emulsion; while in application Ser. No. 519,884 the opacifying system is situated in the same layer as the light-sensitive silver halide emulsion and a second or additional layer containing an opacifying system may also be provided over the layer containing the silver halide emulsion.

Any of the aforementioned photographic products may contain an outer layer comprising a silver receptive layer, i.e., a layer containing at least one silver precipitating agent, or the silver precipitating agent may be present initially in the processing composition.

The photosensitive system of photographic products of the type mentioned above may contain a silver halide emulsion and preferably a mixed silver halide emulsion, having a relatively high film speed. Also, excellent results have been obtained employing emulsions containing a relatively small amount of silver. For example, application Ser. No. 519,995 discloses that the silver halide in the photographic products described and claimed therein may be present in an amount sufficient to provide a silver coverage on the order of from about 0.02 to about 0.1 g. per sq. ft. surface area. Moreover, application Ser. No. 519,884 discloses that the silver halide present in the single layer film units, ie., the film units containing no second or additional layer of opacity-providing material, may be present in an amount sufficient to provide a silver coverage with as little as 0.0018 g. per sq. ft., while in the two-layer film units, i.e., those containing a second layer of opacity-providing material, the silver halide is previously present in an amount sufficient to provide a silver coverage of at least 0.01 g. per sq. ft.

Development of exposed photographic products of the above described type usually involves a processing composition comprising an aqueous alkaline solution of a silver halide developing agent and a silver halide solvent. These ingredients may be present initially in the aqueous medium for the processing composition. Alternatively, any or all of the ingredients may be present initially in the film unit, e.g., by encapsulation, as discrete coatings, etc., in which case development is initiated by contacting the film unit with an aqueous medium to form the processing composition. Also, as described in commonly assigned copending application of Edwin H. Land, Ser. No. 519,885 filed Jan. 11, 1966, development of the exposed film unit may be effected by impregnation with a non-alkaline processing composition and the alkalinity required to initiate development may be generated in situ electrolytically at some time subsequent to impregnation. The processing composition may also contain other reagents such as a viscosity-increasing, film-forming material, for example, sodium carboxymethyl cellulose, hydroxyethyl cellulose, etc., preservatives, antifoggants, and the like.

In some instances, the processing composition may also contain silver precipitating nuclei. Such processing compositions are disclosed, for example, in U.S. Pat. No. 2,662,822 issued to Edwin H. Land. It is also contemplated that the silver precipitating nuclei may be generated in situ electrolytically according to the procedure described and claimed in the commonly assigned copending application of Ronald F. Cieciuch, Ser. No. 519,886, filed Jan. 11, 1966, or a soluble fogging agent may be contained in the processing composition according to the procedures described and claimed in the commonly assigned copending application of Leonard C. Farney, Ser. No. 519,967, filed Jan. 11, 1966.

Additional patent applications relating to photographic products of the type to which the present invention pertains include commonly assigned applications Ser. Nos. 519,955 and 526,673, both filed by Leonard C. Farney on Jan. 11, 1966. Application Ser. No. 519,955 relates to photographic products wherein a siliceous material preferably a finely granulated colloidal silica is incorporated in a layer containing the opacifying system. The presence of the siliceous material enhances the covering power of the opacifying system and increases the effectiveness of the silver in the transfer process by which

the positive image is obtained. Application Ser. No. 526,673 relates to photographic products which include an effective amount of a photographically innocuous humectant which materially lowers the processing time and/or the amount of processing composition necessary to form a silver image by diffusion transfer.

Also U.S. patent application Ser. No. 519,885, filed Jan. 11, 1966 by Edwin H. Land relates to modified photographic products of the aforedescribed type. Specifically, the application discloses and claims photographic product so structured that the resulting composite print may be viewed through a transparent support as a positive reeflctive print or from the opposite side, i.e., from the light sensitive layer side, as a negative image.

The present invention is directed to novel photographic products which present certain improvements over the photographic products heretofore known to the art such as those described and claimed in the above-mentioned patent applications.

SUMMARY OF THE INVENTION

In accordance with the practice of the present invention, there is presented to the art, novel photographic products which have the capability of being developed by moisture preferably in the form of steam. In accordance with the preferred embodiment of the present invention, novel photographic products are presented which can provide diffusion transfer image patterns viewable by reflection without separation and which have the additional capability wherein such image patterns can be developed by moisture.

The novel photographic products of the present invention as well as the essential elements thereof will be more fully understood by reference to the following description taken in connection with the accompanying drawing wherein:

The figure is a partially schematic, partially enlarged fragmentary sectional view illustrating a preferred film unit of this invention and the photoexposure thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the figure, a preferred film unit **1** of this invention comprises essentially, in order, a support **10**, which can be pellucid but is preferably opaque, having thereon a light-sensitive layer **11**, e.g., a light-sensitive silver halide emulsion and a pellucid layer, e.g., transparent or translucent layer **12** preferably comprising an opacifying material which is at least permeable to but substantially insoluble in a moisture activatable processing system to be described with more particularity hereinafter. The film unit **1** also includes an image-receiving layer **13** which is preferably substantially transparent.

Light-sensitive layer **11** preferably comprises a gelatine silver halide emulsion which upon development will form a negative silver image of relatively low density or covering power. Accordingly, the layer preferably contains a mixed halide emulsion, e.g., silver iodobromide emulsion. Additionally, light sensitive layer **11** usually has a pH between about 6.5 to about 8.5 and comprises a specific moisture activatable system including as essential components thereof, a silver halide developing agent and a silver halide transfer agent. The function of this moisture activatable system as well as the agents thereof and the manner in which the agents are integrated with photographic products of the present invention will be more apparent from the following detailed description. In the especially preferred embodiment of the present invention, layer **11** also includes an opacifying system, e.g., an opacifying material which will be described in more detail hereinafter in the description of layer **12**.

In the preefrred embodiment of the present invention, pellucid layer **12** comprises an opacifying system which may be an opacifying material such as finely divided titanium dioxide, calcium carbonate, magnesium oxide, barium sulfate, etc., or a mixture of such materials, dispersed in a suitable permeable colloidal carrier or matrix such as gelatin. The opacifying material is present in an amount sufficient to effectively mask the negative silver image formed after development in light-sensitive layer **11** but the amount of opacifying material is insufficient to preclude photoexposure of the light-sensitive layer from a light source on the same side of the support as the two layers (e.g., in the manner shown in the figure). Accordingly, the opacifying material further serves to provide a background, preferably a white background, for viewing the composite print, without separation, by reflected light as a positive silver image.

As used herein and in the appended claims, the term "effectively masking" denotes the ability of the opacifying material to sufficiently mask or obscure the negative image so that the composite print is viewable as a positive image.

It is to be understood that in some of the products embraced within the scope of the present invention, layer **12** need not contain an opacifying system and, in some products, an opacifying system need not be present. For example, as mentioned, the opacifying system can be included in light sensitive layer **11**. Also, a moisture activatable developer system of the type described in more detail hereinafter can be integrated in photographic structures such as those described in the aforementioned U.S. Pat. 2,861,885 in lieu of the processing compositions shown therein to provide photographic products for producing diffusion transfer image patterns developable by moisture and which can be viewed without separation.

Pellucid, image-receiving layer **13** comprises one of the known vigorous silver precipitating environments containing silver-precipitating nuclei, e.g., at least one silver-precipitating agent dispersed in a microscopically continuous vehicle. A dispersion of such nuclei in a colloidal material such as colloidal silica or gelatin can provide suitable pellucid image-receiving layers for products of the present invention. Additionally, pellucid, image-receving layer **13** preferably comprises an ingredient which can selectively prevent diffusion thereto or deposition therein of any substantial amount of visible sliver from the exposed and developed portions of light sensitive layer **11**.

Referring again to the figure, the subject matter **14**, e.g., a document having areas which are opaque, e.g., printing and areas which will transmit visible light, is shown positioned between a suitable light source **15** and silver receptive layer **13** of the photographic product. It is to be understood that if support **10** is transparent, light sensitive layer **11** can be exposed therethrough to provide an image pattern in layer **13** which can be viewed by projection. It will also be appreciated that the photographic product is confined in a camera or other suitable device so that light-sensitive layer **11** is photoexposed for the requisite time only to light transmitted through or reflected from subject matter **14**, thereby to form a developable image in terms of the light-transmittant areas of the subject matter.

After exposure, photographic products of the present invention can be developed by moisture preferably in the form of steam. This development is achieved by integrating a moisture activatable system including a silver halide developing agent and a silver halide transfer agent with the elements of the photographic products. The integration is such that in the presence of moisture, e.g., steam, the silver halide developing agent can reduce exposed silver halide while at least part of the imagewise distribution of soluble silver complex formed from unreduced silver halide can be transferred to layer **13** by the silver halide transfer agent.

The manners in which the moisture activatable system is integrated with the essential elements of the photographic products of the present invention can vary. For example, the silver halide developing agent and/or the

silver halide transfer agent can be included separately or together in any of the layers mentioned before. However, in the preferred embodiment of the present invention, at least the developing agent is included in light sensitive layer **11** and in the especially preferred embodiment, both the developing agent and the transfer agent are included in light sensitive layer **11**.

Silver halide developing agents are known to the art and include among others, hydroquinone and derivatives of hydroquinones such as 4'-methylphenyl hydroquinone etc., catechol and derivatives of catechol, such as 4-phenyl catechol etc., derivatives of naphthol, such as 4-methoxy-1-naphthol, derivatives of phenol such as methyl para-aminophenol etc., the 3-pyrazolidones, such as 1-phenyl-3 - pyrazolidone. The especially preferred silver halide developing agents in the practice of the present invention are metol, phenidone, pyrocatechol, methyl hydroquinone and toluyl hydroquinone.

The compounds which function as silver halide transfer agents of the present invention are succinimide, the alkali metal sulfites or combinations thereof. The transfer agents of the present invention are surprisingly compatable with silver halide developing agents and they can be included in silver halide emulsion layers in combination with such developing agents. As those skilled in the art know, silver halide transfer agents, e.g., silver halide solvents or silver halide complexing agents heretofore employed in the diffusion transfer art are not conveniently included in silver halide emulsion layers containing silver halide developing agents. For example, the inclusion of transfer agents such as thiocyanates, thioureas, thiosulfates and mercapto containing compounds in emulsion layers containing developing agents can desensitize, fog, spot or otherwise adversely affect the quality of the diffusion transfer image pattern obtained on exposure and development of such emulsions. Moreover, it should be mentioned that succinimide and alkali metal sulfites have not been regarded in the art as effective transfer agents in silver halide diffusion transfer systems.

The particular amounts of developing agent and transfer agent employed and the ratio of one to the other can vary. For example, the silver halide developing agent can be employed in amounts between about .01 to about .1 g./ft.^{2} and the silver halide transfer agent can be employed in amounts between about 0.04 to about 0.4 g./ft.^{2}.

In addition to the above-mentioned essential ingredients of the moisture activatable system, auxiliary materials may be included in the photographic products at the present invention to provide predescribed properties such as stability, image density, processing time and/or related considerations. Such auxiliary ingredients include water and/or alkali precursors, e.g., materials which in the presence of moisture produce, liberate or otherwise provide water or alkali. Water precursors are known to the art and representative species include, among others, sugars, β-nitroethanol, and hydrated salts, e.g., acetates, silicates and phosphates. Alkali precursors are also well known to the art and a particularly preferred class of such precursors include compounds which in the presence of moisture release ammonia or amines. Representative species of alkali precursors include urea, N-methylurea, formamide, sulfamide, glutarimide and the like.

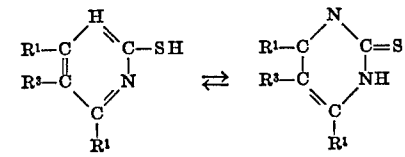
As mentioned, in the preferred embodiment of the present invention, the silver halide developing agent as well as the silver halide transfer agent are included in light sensitive layer **11**. Also in the preferred embodiment, layer **11** contains an opacifying material which can be the same material providing the opacifying system of translucent layer **12**. An especially suitable opacifying material for inclusion in layer **11** is titanium dioxide with the preferred amount involved being sufficient to provide between about 800 to about 2000 mgms./ft.^{2} of titanium dioxide in layer **11**.

After exposure, the photographic product of the figure is contacted with moisture, preferably steam to activate the aforementioned processing system. In the presence of moisture, the system reduces exposed silver halide in layer **11** while substantially simultaneously forming an imagewise distribution of soluble silver complex from unreduced silver halide. At least part of the complex is transferred through pellucid layer **12** to image-receiving layer **13** where it is reduced to image silver to provide a positive silver transfer image pattern.

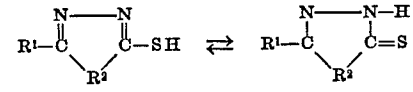
The composite print comprising the positive silver image superimposed upon the negative image therebeneath may be viewed as a positive reflection print having an acceptable low $D_{min.}$, due to the opacity of layer **12** effectively masking or substantially obscuring the negative image therebeneath.

As previously mentioned, transparent image-receiving layer **13** preferably comprises an ingredient which can selectively prevent diffusion thereto or deposition therein of any substantial amounts of visible silver from the exposed and developed portions of light sensitive layer **11**. In the absence of such an ingredient, the soluble complex providing the positive image pattern is transferred to layer **13** initially but apparently silver from exposed portions of layer **11** can also be transferred to or deposited in layer **13**. This transfer of silver from exposed portions of layer **11** can ultimately prevent effective discrimination between the positive and negative patterns. The effect of this unwanted visible silver in layer **13** is not especially apparent when succinimide is employed as a transfer agent but is especially apparent when the alkali metal sulfites alone are so employed. Accordingly, in the especially preferred embodiments of the present invention, layer **13** comprises an ingredient which can effectively prevent this unwanted silver from being diffused thereto or otherwise deposited therein.

Ingredients which can function in the above described manner and which are preferred in the practice of the present invention are compounds conforming to the following tautomeric formulae:

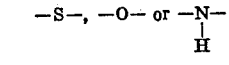


Formula 1



Formula 2

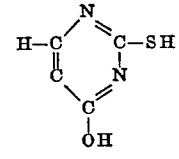
wherein R^1 can be hydrogen, hydroxyl, amino, lower alkyl of from 1–4 carbon atoms, lower alkoxy of from 1–4 carbon atoms, an aryl radical, e.g., phenyl, tolyl or a heterocyclic radical, e.g., pyridyl, provided that only one R^1 of Formula 1 can be hydrogen and the other is as defined; R^2 is



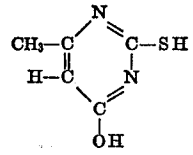
R^3 can be hydrogen, halogen, lower alkyl, aryl or lower alkoxy group.

Representative compounds of Formula 1 include the following:

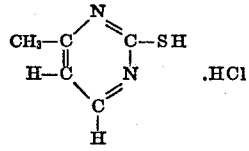
(A)



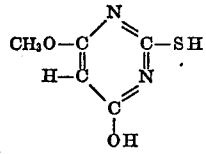
(B)



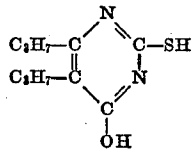
(C)



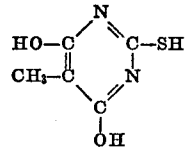
(D)



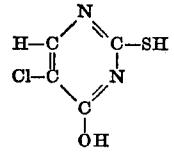
(E)



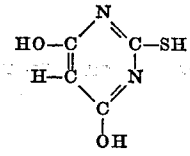
(F)



(G)

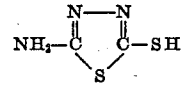


(H)

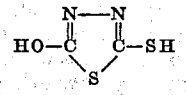


Representative compounds of Formula 2 include the following:

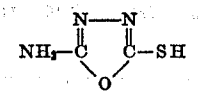
(I)



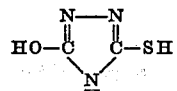
(J)



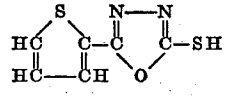
(K)



(L)



(M)



Of the above compounds 2 - thiouracil (Formula A) and 2-thiobarbituric acid (Formula H) are especially preferred.

The amount of the above described compounds employed in products of the present invention can vary and amounts between about 0.5 to about 3.0 mg. per sq. ft. are suitable.

For optimum results, it has been found that the silver halide in layer **11** should be present in an amount sufficient to provide a silver coverage on the order of from about 0.02 to about 0.1 gm. per sq. ft. of surface area, although good results have been obtained with as little as 0.006 gm. per sq. ft. The ratio of colloidal binder, e.g., gelatin, to silver is preferably from about 5:1 to about 10:1

It has also been found that the presence in layer **11** of a photographically innocuous humectant such as α-methyl glucoside materially lowers the processing time and/or the amount of processing composition necessary. This is apparently due to the ability of the humectant to retain water in the emulsion matrix which in turn minimizes shrinkage or, stated another way, minimizes the swelling needed for processing, thus lowering the induction time and/or the time required for the soluble silver complex to transfer to the layer where it is reduced to image silver. This concept of providing a humectant in the emulsion layer is described with more particularity, and claimed in the aforementioned copending application of Leonard C. Farney. Ser. No. 526,673.

As was mentioned previously, in the preferred embodiment the opacifying material in pellucid layer **12** is present in an amount sufficient to mask effectively the negative image formed in layer **11** and to provide the background for viewing the composite print as a positive reflection print. Also, the amount of opacifying material is insufficient to preclude photoexposure, and most preferably, insufficient to effect adversely, i.e., to lower the film speed of the product, at least to any appreciable extent. For optimum results, ranges on the order of at least 0.1, e.g., from about 0.1 to about 2.0 gm. of opacifying material per sq. ft. of surface area have been found to be desirable with from about 0.8 to about 1.5 gm. per sq. ft. providing particularly satisfactory results in terms of density, contrast and stability.

The ratio of opacifying material per sq. ft. in layer **12** to silver per sq. ft. in layer **11** is preferably on the order of from about 30:1 to about 50:1.

With amounts of opacifying material on the order to that described above, it has been found that the film speed is approximately the same as would be obtained if no opacifying material were present. In other words, with substantially same quantum or level of exposure, one may obtain an image having a density comparable to that obtainable from a similar photographic product having no opacifying material.

The present invention thus makes it possible for one to obtain positive silver transfer images of good density and resolution from photographic products containing a relatively small amount of silver.

The following examples show by way of illustration and not by way of limitation the practice of this invention.

EXAMPLE 1

Prepare a silver halide emulsion by mixing the following ingredients:

Urea	gms.	2.4
Hydroquinone	gms.	0.4
Sodium sulfite	gms.	0.4
AgIBr emulsion (6.5% Ag).	mls.	5.8

Coat the above emulsion on paper, preferably on the coated surface of a paper coated with cellulose triacetate to render the surfafce water impermeable, at a rate of 4.8 cc./ft.^{2} to provide an emulsion coating containing 0.04 gm. silver halide/ft.^{2}.

Prepare a silver diffusion transfer receptive layer by mixing the following ingredients and coating the mixture on the emulsion layer at a rate of 1.04 cc./ft.^{2}.

Ludox (30% soln.)	mls.	50
Water	mls.	50
$AgNO_3$ (0.5 N)	ml.	1
Sodium sulfide (1 N)	mls.	0.5
2 thiouracil	gm.	0.05
Succinimide	gms.	8
Wetting agent (25% Triton X–100)	cc.	.5

In the practice of the present invention the pH of the diffusion transfer layer is basic, e.g., above 7.5 and preferably between about 7.5 to about 9.5.

After the receptive layer is dry, expose to an image pattern under 9000 meters candle seconds and thereafter place the so exposed product in steam for 30 seconds to obtain a positive image pattern with a $D_{max.}$ of 0.68 and a $D_{min.}$ of 0.45.

EXAMPLE 2

Prepare a titanium dioxide slurry by mixing together the following ingredients:

TiO_2 (pigment grade)	gms.	612
10% gelatin soln	mls.	750
Methyl glucoside	gms.	37.5
Wetting agent (Daxad 30)	mls.	3
Water	mls.	900

Make a photosensitive coating mixture by taking 54 grams of the above TiO_2 slurry and mixing the slurry with the following ingredients:

Urea	gms.	2.4
Hydroquinone	gm.	0.4
Sodium sulfite	gm.	0.4
AgIBr emulsion (6.5% Ag).	mls.	5.8

Coat the above emulsion on paper preferably on the coated surface of a paper coated with cellulose triacetate to render the surface water impermeable at a rate of 4.8 cc./ft.^{2} to provide an emulsion coating containing 0.04 gm. silver halide/ft.^{2}.

After the emulsion layer is dry, coat on the above prepared titanium dioxide slurry at a rate of 4.8 cc./ft.^{2}.

Prepare a silver diffusion transfer receptive layer by mixing the following ingredients and coating the mixture on the titanium dioxide containing layer at a rate of 1.04 cc./ft.^{2}.

Ludox (30% soln.)	mls.	50
Water	mls.	50
$AgNO_3$ (0.5 N)	ml.	1
Sodium sulfide (1 N)	ml.	0.5
2 thiouracil	gm.	0.05
Succinimide	gms.	8
Wetting agent (25% Triton X–100)	cc.	.5

After the receptive layer is dry, expose to an image pattern under 9000 meters candle seconds and thereafter place the so exposed product in steam for 30 seconds to obtain a positive image pattern with a $D_{max.}$ of 1.05 and a $D_{min.}$ of 0.02.

EXAMPLE 3

Repeat the procedure of Example 2 but substitute 0.5 gm. of 2-thiobarbituric acid for the 0.05 gm. of 2-thiouracil in the mixture for preparing the receptive layer.

EXAMPLE 4

Repeat the procedure of Example 2 but use 0.8 gm. of sodium sulfite in the emulsion mixture rather than the 0.4 gm. used in Example 2 and leave out the 8 gms. of succinimide in the mixture for preparing the receiving layer of Example 2. A positive image pattern having a $D_{max.}$ of 0.86 and a $D_{min.}$ of 0.1 is obtained after the exposed product is processed in steam for 60 seconds. If the product is processed in steam for 3 minutes, a positive image pattern having a $D_{max.}$ of 1.38 and a $D_{min.}$ of 0.08 is obtained.

EXAMPLE 5

Repeat the procedure of Example 2 but use 0.8 gm. of sodium sulfite in the emulsion mixture rather than the 0.4 gm. of sodium sulfite used in Example 2. Also leave out the 2.4 gms. of urea in the emulsion mixture of Example 2 and leave out the 8 gms. of succinimide in the mixture for preparing the receiving layer of Example 2.

EXAMPLE 6

Repeat the procedure of Example 2 but add 1.2 gms. succinimide to the emulsion mixture and leave out the 8 gms. of succinimide in the mixture for preparing the receptive layer.

EXAMPLE 7

Repeat the procedure of Example 2 but substitute 1 ml. 0.5 N $Ni(NO_3)_2$ for the $AgNO_3$ in the diffusion transfer layer of Example 2.

EXAMPLE 8

Repeat the procedure of Example 2 but do not coat the titanium dioxide slurry on the silver halide emulsion layer and instead coat the diffusion transfer layer mixture directly on the emulsion layer to provide a product having the opacifying system distributed in the emulsion layer.

EXAMPLE 9

Repeat the procedure of Example 1 but coat the slurry of Example 2 on the emulsion layer of Example 1 to provide a product having the opacifying system interposed between the emulsion layer and receptive layer.

As will be apparent from the foregoing description and illustrative examples of the preferred embodiment, the present invention provides novel film products comprising a layer of opacifying material superposed on a light-sensitive layer, which film product is exposed through the translucent layer and then processed by moisture, preferably steam, to form a composite print containing a visible transfer image which may be viewed by reflection or projection as a positive image.

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 diffusion transfer photographic product for forming a composite print wherein a positive image is formed in an image-receiving layer arranged in combination with a light sensitive layer containing a negative image so that said positive image is viewable by reflection or projection without separation; said product comprising as essential elements thereof a light sensitive silver halide emulsion layer, a receiving layer which can receive a diffusion transfer positive image pattern and comprises an ingredient which can selectively prevent diffusion thereto of any substantial amounts of silver from exposed portions of the light sensitive layer and a moisture activatable system comprising a silver halide developing agent and a silver halide transfer agent chosen from the group consisting of succinimide, an alkali metal sulfite or mixtures thereof integrated with said elements so that the product can be developed by moisture.

2. A photographic product of claim **1** further including an opacifying system.

3. A photographic product of claim **1** wherein said light sensitive layer comprises an opacifying system.

4. A photographic product of claim **1** including a layer comprising an opacifying system interposed between said receptive layer and said light sensitive layer.

5. A photographic product for forming a composite print wherein a positive image is formed over a negative image and said positive image is viewable by reflection or projection without separation and said product comprising as essential elements thereof a support, a first layer on the support containing a light sensitive silver halide emulsion, a second layer on said first layer containing an opacifying system which can effectively mask a developed negative image pattern in the first layer and a silver receptive layer which can receive a positive diffusion transfer image pattern from the light sensitive layer and comprising a material which can selectively prevent diffusion thereto of any substantial amounts of silver from exposed and developed portions of the light sensitive layer and a moisture activatable processing system comprising a silver halide transfer agent chosen from the group consisting of succinimide, an alkali metal sulfite or mixtures thereof integrated with said elements so that the product can be developed by moisture.

6. A product of claim 5 wherein said support is substantially opaque to visible light.

7. A product of claim 5 wherein the light sensitive layer contains the silver halide developing agent or the silver halide transfer agent.

8. A product of claim 5 wherein the light sensitive layer contains an opacifying system.

9. A product of claim 8 wherein said transfer agent comprises sodium sulfite.

10. A product of claim 5 wherein said transfer agent is succinimide.

11. A product of claim 5 wherein the light sensitive layer contains the silver halide developing agent and the silver halide transfer agent.

12. A product of claim 11 wherein said transfer agent comprises sodium sulfite.

13. A product of claim 5 wherein said opacifying system comprises a white pigment as an opacifying material.

14. A product of claim 5 wherein said opacifying system comprises titanium dioxide as an opacifying material.

15. A product of claim 5 wherein said silver-precipitating agent is dispersed in a colloidal carrier.

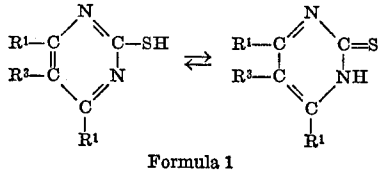
16. A product of claim 5 wherein the silver halide in said first layer is present in an amount sufficient to provide a silver coverage of from about 0.02 to about 0.1 gm. per sq. ft. of surface area.

17. A product of claim 5 wherein said emulsion comprises a mixed silver halide emulsion and said opacifying system is present in an amount insufficient to lower, at least to any appreciable extent, the film speed of said product.

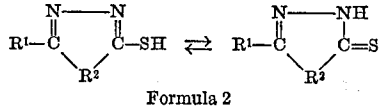
18. A product of claim 5 wherein said opacifying system comprises a white pigment material in an amount sufficient to provide from about 0.1 to about 2.0 gm. of opacifying material per sq. ft. of surface area.

19. A product of claim 5 wherein said opacifying system comprises a white pigment material in an amount sufficient to provide a ratio of opacifying material per square foot in said second layer to silver per square foot in said first layer of from about 30:1 to about 50:1.

20. A product of claim 5 wherein the silver receptive layer comprises a compound conforming to the following tautomeric formulae:

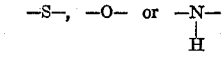


Formula 1



Formula 2

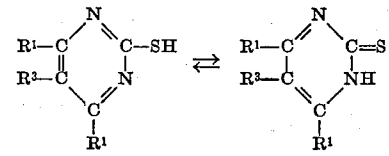
wherein each R^1 can be hydrogen, hydroxyl, amino, lower alkyl, lower alkoxy, an aryl radical or a heterocyclic radical provided that if one R^1 of Formula 1 is hydrogen, the other is as defined above, R^2 is



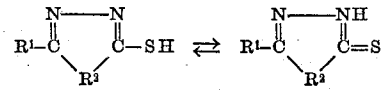
and R^3 can be hydrogen, halogen, alkyl, aryl or alkoxy.

21. A product of claim 5 wherein the receptive layer comprises a compound selected from the group consisting of 2-thiouracil, 2-thiobarbituric acid or mixtures of these.

22. A product of claim 5 wherein the light sensitive layer contains the silver halide developing agent and silver halide transfer agent chosen from the group consisting of succinimide, sodium sulfite or mixtures theerof and the silver receptive layer comprises a compound conforming to the following tautomeric formulae:

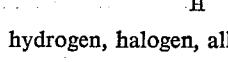


Formula 1



Formula 2

wherein each R^1 can be hydrogen, hydroxyl, amino, lower alkyl, lower alkoxy, an aryl radical or a heterocyclic radical providing that if one R^2 of Formula 1 is hydrogen, the other is as defined above, R^2 is



and R^3 can be a hydrogen, halogen, alkyl, aryl or alkoxy group.

23. A product of claim 22 wherein said transfer agent comprises sodium sulfite.

24. A product of claim 5 wherein the silver receptive layer comprises a compound chosen from the group consisting of 2-thiouracil, 2-thiobarbituric acid and mixtures of these and the light sensitive layer contains hydroquinone and sodium sulfite.

25. A photographic process comprising the steps of exposing a photographic product of claim 1 to a source of activating radiation and contacting the exposed produce with moisture.

26. A photographic process of claim 25 wherein said product is contacted with steam after exposure.

27. A photographic process of claim 25 wherein a product of claim 20 is exposed to a source of activating radiation and said product is contacted with steam after exposure.

28. A photographic process of claim 25 wherein a product of claim 22 is exposed to a source of activating radiation and said product is contacted with steam after exposure.

References Cited

UNITED STATES PATENTS

2,861,885	11/1958	Land	96—29
2,692,830	10/1954	Land	96—29
3,362,826	1/1968	Weyde	96—109 X
3,457,072	7/1969	Ditzer	96—109
3,615,510	10/1971	Yudelson	96—109
2,410,644	11/1946	Fierke	96—66

RONALD H. SMITH, Primary Examiner

J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

96—60 R, 76 R