United States Patent

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[54] **UNITARY, PERMANENTLY COMPOSITE, PHOTOGRAPHIC LIGHT-SENSITIVE SHEET MATERIAL FOR USE IN THE SILVER COMPLEX DIFFUSION TRANSFER PROCESS FOR PRODUCING IMAGES**

15 Claims, No Drawings

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[50] Field of Search 96/28, 29, 76, 85

[56] **References Cited**

UNITED STATES PATENTS

2,878,121	3/1959	Gray	96/29
3,260,600	7/1966	de Haes et al.	96/29
3,347,674	10/1967	de Haes et al.	96/29
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3,433,634	3/1969	de Haes et al.	96/29

FOREIGN PATENTS

545,678	10/1959	Belgium	96/29

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ABSTRACT: A good quality reproduction can be obtained by the silver complex diffusion transfer process in a unitary permanently composite sheet material comprising of a nontransparent flexible sheet support, a light-sensitive silver halide emulsion layer and a layer containing an opaque white or colored pigment and a hydrophilic colloid binder, provided the pigment is present in amounts from 9–25 g. per sq.m. and the binder therefore in 0.5–3 g. per sq.m. and at least one photographic developing agent for the silver halide is contained in the material. Development nuclei for the complex silver halide can be supplied in an outer stratum of the pigmented layer or in a thin colloid layer superimposed thereon or can be incorporated in situ by means of a treatment bath containing the same which can be the alkaline processing liquid for forming the diffusion transfer image. Light-sensitive unitary composite materials useful for this purpose are also described.

UNITARY, PERMANENTLY COMPOSITE, PHOTOGRAPHIC LIGHT-SENSITIVE SHEET MATERIAL FOR USE IN THE SILVER COMPLEX DIFFUSION TRANSFER PROCESS FOR PRODUCING IMAGES

The present invention relates to a photographic light-sensitive composite sheet material and to a method of producing images according to the silver complex diffusion transfer process wherein such material is used.

In the U.S. Pat. No. 2,627,459 of E. H. Land issued Feb. 3, 1953 a photographic composite sheet material is described comprising in order a base layer, e.g. a cellulosic film base or a baryta paper, a light-sensitive silver halide emulsion layer and a transparent image-carrying layer such as a water-vapor-permeable cellophane sheet. Between the light-sensitive and the image-carrying layer a container is present filled with a liquid processing composition which also will form the image-receiving layer. This processing composition also contains opaque white pigment particles. After imagewise exposure through the transparent image-carrying layer, the composite film material is run through a pair of pressure rollers, the container end entering first. The pressure rollers rupture the container and spread the liquid composition uniformly between the light-sensitive layer and the image-carrying layer. From this liquid composition the image-receiving layer is formed. This layer shows the diffusion transfer image through the image-carrying layer and on a white background because of the opaque white pigment particles present in the image-receiving layer. The composition of the photographic sheet material for use in the method of the said United States specification is rather complex because of the presence of the said container and the image-carrying layer. Moreover, some mechanical help is needed in order to start the processing after the imagewise exposure and to form at the same time the combined image-receiving pigment layer. Also the diffusion transfer image density is rather low because the image has been formed over the full depth of the pigment layer and only for a minor part is situated at the surface of the pigment layer, which is in contact with the transparent image-carrying layer whereby the greater part of the diffusion transfer image is screened from the eye by the white pigment particles.

From the United Kingdom Pat. specification No. 746,948 filed Oct. 22, 1952 by Kodak a photographic light-sensitive composite sheet material is known for producing an image according to the silver complex diffusion transfer process, said material comprising in order a transparent support, a light-sensitive silver halide emulsion layer, a layer containing an opaque white or colored pigment, and an image-receiving layer containing well-defined chemical development nuclei. The light-sensitive silver halide emulsion layer is imagewise exposed through the transparent support and after processing a diffusion transfer image is produced in the image-receiving layer. On observing the transfer image thus produced, the negative image in the silver halide emulsion layer is screened from the eye by the pigment layer present between he image-receiving layer and the silver halide emulsion layer. A very important disadvantage of such a photographic composite material is that that exposure can only occur through the support. This support being transparent, the diffusion transfer copy obtained on its back side always will show the negative, which is highly disturbing and unpleasant. Finally, for said transparent support the manufacturer has to depend on hydrophobic film supports, which are unpleasant to the touch, cannot be folded easily and are not easy to write on.

In the Belgian Pat. specification No. 545,678 filed Mar. 1, 1956 by Gevaert Photo-Producten N.V. a photographic composite sheet material is described comprising in order a paper support, a light-sensitive silver halide emulsion layer, a pigment layer and an image-receiving layer. The pigment layer serves to screen the negative image developed in the silver halide emulsion layer to the naked eye. In the pigment layer the pigment particles and the binder are used in about the same amounts. In his way it is impossible to produce a high quality diffusion transfer image and at the same time to screen the negative image other words, when a thin pigment layer is used a high quality diffusion transfer image can be produced, but the background is dirty because the negative image is not screened by the pigment layer in a sufficient way. A sufficient screening of the negative can be attained indeed if a thicker pigment layer is used, but in that case the image formation by diffusion transfer is affected adversely because the diffusion of complexed silver halide is strongly hindered.

The new photographic light-sensitive composite sheet material according to the present invention and which is intended for the production of an image according to the silver complex diffusion transfer process in order comprises a nontransparent flexible support sheet, a light-sensitive silver halide emulsion layer, and a layer containing an opaque white or colored pigment and a hydrophilic colloid binder, wherein the pigment and the binder are present in amounts of from 9 to 25 g. and of from 0.5 to 3 g. per sq. m. respectively, and wherein the material comprises at least one developing agent.

This composite sheet material has a very simple composition and is especially suited in the production of an image according to the silver complex diffusion transfer process. The diffusion transfer image formation preferably occurs especially at the outer part of and/or on top of the pigment layer. The complexed silver halide can diffuse through the pigment layer without any difficulty. The diffusion transfer images produced are of high quality on a white or colored background dependent on the nature of the pigment applied, because the negative image produced in the silver halide emulsion layer is very well screened by the pigment particles. Also at the back side of the diffusion transfer copy obtained, the negative image is substantially invisible because a nontransparent support is used. The latter is preferably a paper support so that the diffusion transfer copy is very apt to be written on at its back side and to be folded and stored.

Notwithstanding the presence of a pigment layer comprising of from 9 to 25 g. of pigment per sq. m. in a weight ratio in respect of the binder between three and 50, the presence in the composite sheet material of developing agent(s) makes the development of the silver halide emulsion layer and the diffusion transfer image formation occurring so rapidly, that already very rapidly (about 5–10 seconds) after the wetting of the material with the alkaline processing liquid the diffusion transfer image becomes visible, and already after about 15–20 sec. reaches its full and high density.

The presence of a specific substance of specific substances (further on called development nuclei) in order to produce from the nonexposed complexed and diffusing silver halide a visible image is not essential. It has been stated that polysulfides, present in the ingredients applied and most of the pigments commonly used can act themselves as development nuclei to some extent, and that acceptable diffusion transfer copies can be obtained without using specific development nuclei. The diffusion transfer image obtained in this way, however, in general is rather faint. Improved results can be obtained by applying specific development nuclei. All the development nuclei generally known in the art, physical as well as chemical ones, may be used. As most suitable representatives may be cited the sulfides of heavy metals such as the sulfides of antimony, bismuth, cadmium, cobalt, lead, nickel, silver and zinc. Other suitable salts are the selenides, polysulfides, polyselenides, mercaptans and tin (II) halides. Heavy metals or their salts and fogged silver halides are suitable too. The complexed salts of lead and zinc sulfides are active alone as well as mixed with thioacetamide, dithiobiuret and dithiooxamide. Heavy metals, preferably silver, gold, platina, palladium, and mercury may be used in their colloidal form. From these metals the noble metals are the most active ones.

The development nuclei may be incorporated in the usual concentrations into the pigment layer, preferably in the outer part thereof (the inner part is the part at the side of the silver halide emulsion layer). The incorporation of the development nuclei into the outer part of the pigment layer can be realized by applying the pigment layer in two or more steps and to incorporate the development nuclei into the coating composition of the outer part. Preferably, however, the development nuclei are applied on top of the pigment layer. This embodiment is mostly realized by applying a separate nuclei-containing and preferably gelatin image-receiving layer on top of the pigment layer, and according to the most preferred embodiment by applying the nuclei without binder or with only a very small amount of binder, e.g. gelatin, on top of the pigment layer. The development nuclei can also be applied on top of the pigment layer by incorporating them into the processing liquid for carrying out the diffusion transfer image formation or into an additional liquid to be applied before or after the imagewise exposure, and in the latter case, preferably before applying the alkaline processing liquid for wetting the composite sheet material. From these liquid compositions the development nuclei deposit on the composite material, where the diffusion transfer image is then produced.

The support sheet of the photographic light-sensitive composite sheet material according to the present invention may be any usual flexible support sheet provided it is nontransparent. By nontransparent it is understood here that the nature of the support is such that the negative image produced in the light-sensitive silver halide emulsion layer is substantially invisible through the support. This may be achieved by using a support sheet, which is nontransparent by itself or which has been made nontransparent in the mass, or by applying one or more nontransparent layers, e.g. a baryta or other white or colored coating, to at least one side of the support. Although any usual flexible hydrophobic film support such as a support sheet of a cellulose ester (e.g. cellulose triacetate) or of polyethylene terephthalate can be used, a paper support is preferred. Such paper support can be made nontransparent by incorporating into the paper mass an opaque white or colored pigment during the preparation stage, and/or by applying a white or colored pigment coating such as a baryta coating to at least one of both sides of the paper sheet according to usual and generally known techniques in the art of papermaking. The advantages of the use of a paper support have already been described above. The nontransparent support sheet may be opaque or translucent. If it is translucent, the exposure of the emulsion layer through the support is still possible, but the silver image developed in same emulsion layer will be substantially and even completely invisible through the support.

The nontransparent flexible support sheet is coated with at least one silver halide emulsion layer, if necessary or advantageous after at least one suitable subbing layer and/or one or more other layer(s) has (have) first been applied to the support sheet.

Any silver halide emulsion layer, preferably a gelatino silver halide emulsion layer may be used, provided it is characterized by sufficiently rapid development of the exposed silver halide and sufficiently rapid complexing of the nonexposed silver halide to meet the requirements of the diffusion transfer process. The silver halide emulsion may be chemically and optically sensitized according to any usual and generally known technique. Preferably a relatively high-sensitive silver halide emulsion is used in order to carry out an episcopic exposure.

The present invention is also suited for radiography. According to this embodiment any silver halide emulsion layer for the direct or indirect registration of an X-ray or γ-ray pattern can be used. In the case of an indirect registration an intensifying screen may be incorporated in the photographic composite sheet material. Such a screen is generally known in the art and fluoresces or emits actinic light upon exposure to an imagewise-modulated X-ray or γ-ray beam. The intensifying screen may be built in one or more of the composing layers of the composite sheet material or may constitute a separate and additional layer. It is also possible to put a separate intensifying screen against the composite sheet material at the exposure stage and then to remove same before processing.

On top of the silver halide emulsion layer the pigment layer is applied. Preferably an opaque white pigment is used. A pigment that has proved to be particularly suited for the purpose of the invention is titanium dioxide. Further can be used zinc oxide, silica, calcium carbonate, barium sulfate, china clay and so on. Two or more pigments can be used together. The size of the pigment particles is of no special importance for the purpose of this invention; coarse as well as extremely fine grains are suited. Generally, the particle size lies between 0.05 and 0.5 μ. The pigment particles may be dispersed homogeneously in an aqueous solution of a hydrophilic collide, preferably gelatin, but other colloids i.e. carboxymethylcellulose, alginic acid, alginates, and mixtures of colloids are also suitable. In general, optimal results are obtained with an amount of 12 to 20 g. of pigment and of 1 to 2 g. of colloid per sq. m. In order to keep the great amount of pigment particles homogeneously dispersed in the aqueous solution of but a minor amount of hydrophilic colloid binder, great amounts of dispersing agent are often applied. So a great amount of titanium dioxide particles can be kept very well homogeneously dispersed in an aqueous solution of a minor amount of gelatin if saponine is used as dispersing agent in amounts ranging from about 0.5 to above 12 g. per 100 g. of titanium dioxide. All usual dispersing agents for pigment particles can be applied for replacing saponine or for being used in addition thereto. Further examples of especially appropriate dispersing agents are among others sodium hexametaphosphate, high molecular weight naphthalene sulfonate condensates, certain quaternary ammonium salts and certain polyphosphates. The pigments may also be formed in situ by a chemical interaction, e.g. at the coating stage or at the stage of the production of the diffusion transfer image. A water-soluble salt, e.g. a water-soluble barium salt, may be present in a layer on top of the silver halide emulsion layer as described above, and sulfate ions may be present in the alkaline processing liquid. In this way finely divided barium sulfate pigment particles are produced on top of the silver halide emulsion layer. It is also possible to produce the whole pigment layer in situ by applying a viscous processing paste comprising a hydrophilic colloid binder and opaque white or colored pigment particles.

The light-sensitive silver halide emulsion layer, the pigment layer and the separate image-receiving and nuclei-containing layer occasionally applied may at least partially be hardened. The erasureproof character of the diffusion transfer image produced becomes mostly improved by hardening the outer layer at least partially. Of course, the hardening agent has to be choosen according to the hydrophilic colloid to be hardened. Suitable and generally known hardening agents for gelatin and similar colloids, which are often used as binders for the layers to be hardened, are formaldehyde, glyoxal, monochloric acid, potassium alum and chrome alum. The hardener need not to be incorporated into the layer to be hardened during the preparation stage but can be applied in any other layer which is in water-permeable relationship with the layer to be hardened, said hardening taking place after diffusion of the hardener into the latter layer. The hardener may also be incorporated into the alkaline processing liquid for carrying out the diffusion transfer process or in another processing liquid. Also latent hardeners can be incorporated into the photographic composite material according to the present invention. Such latent hardeners are active only in a well-defined *pH* range, mostly the *pH* range of the usual alkaline processing liquids for carrying out the diffusion transfer image formation. For suitable latent hardeners reference can be made to the United Kingdom Pat. specification No. 962,483 filed Jan. 1, 1962 by Agfa A.G. and to the published German Pat. specification No. 1,203,604 filed Jan. 15, 1964 by Agfa A.G.

In addition to the layers already referred to above, the photographic light-sensitive composite sheet material according to the present invention may comprise one or more occasionally hardened layers such as a subbing layer, an antihalation layer, an intermediate layer, a hydrophilic colloid top layer, e.g. a preferably hardened gelatin top layer, an antistatic layer, a layer for improving the adhesion of two other layers etc.

The photographic composite material according to the invention further contains at least one developing agent. This (these) developing agent(s) has (have) to be present in water-permeable relationship with the emulsion layer and consequently also with the place where the diffusion transfer image will be formed. The developing agent(s) has (have) to be present in a substantial amount, i.e. preferably in an amount of at least about 100 mg. per sq. m. of the composite sheet material, so that it (they) contribute(s) substantially to make the process of image formation by transfer proceed quickly. Developing agents which are especially suited for being incorporated into the material are, e.g. hydroquinone, 3-pyrazolidone developing agents, ascorbic acid, p-aminophenols and derivatives. Often combinations of two or more developing agents are applied. Preferably a mixture of hydroquinone and 1-phenyl-3-pyrazolidone preferably in amounts of above 200 mg. and about 50 mg. respectively is applied. The alkaline processing liquid too may contain a part of the developing agent(s) e.g. up to 17 g. per liter, but according to a preferred embodiment, the total amount of developing agent(s) is present in the composite sheet material (mostly from about 100 to 500 mg. per sq. m. of the composite sheet material) whereby the processing liquid becomes reduced to a mere alkaline aqueous liquid that is substantially free from developing substances and possesses optimal keeping qualities. Such a liquid is also called an activator liquid.

The photographic composite sheet material may also comprise one or more other substances necessary or advantageous in carrying out the silver complex diffusion transfer process as well as other usual additives such as preservatives for developing agents, toning agents, antisludge agents, agents counteracting yellowing, optical brighteners, anticurling agents, stabilizing agents, plasticizers, hardening agents, especially latent hardening agents, pigments, lattices, dispersing agents, antihalation dyes, etc. All these substances are mostly applied in the usual concentrations as is generally known from the literature. Agents counteracting yellowing which are suited for being incorporated into the composite sheet material, preferably into the pigment layer, are 3-hydroxypropylene sulfite pentaerythritol disulphite, triethanolamine sulfite hydrochloride, heaethyl tetraphosphate, potassium ascorbic borate, hypophosphorous acid and benzoic acid.

The present invention also relates to a method of producing an image according to the silver complex diffusion transfer process wherein a photographic light-sensitive composite sheet material according to the invention substantially as described above is used. This method comprises the steps of imagewise exposing the silver halide emulsion layer of the composite material and treating the material with an aqueous alkaline processing liquid in the presence of a developing compound and a complexing agent for silver halide, while development nuclei are present in the pigment layer and/or on top thereof.

The imagewise exposure of the silver halide emulsion layer can take place in different ways. It can occur in contact and according to the transmitted light method through an original printed on one side, by placing the image side of the original in contact with the support side of the composite material, and by subsequent exposure through the original. Preferably, however, an episcopic exposure is carried out, which results in a considerable sharpness of the diffusion transfer image. When an episcopic exposure is applied, originals printed on both sides can be used too, and when a suitable optical system is used true-sided images can be produced. The composite material can face the original either with its support side or with its front side.

After the imagewise exposure the photographic composite material may be wetted with the alkaline processing liquid.

This wetting may occur in any way, e.g. by dipping the composite sheet material in the alkaline processing liquid, by one-side wetting by means of a roller, by contacting with a subject soaked with the alkaline processing liquid, by spraying and by spreading a viscous or nonviscous liquid, e.g. contained in a pod. This technique is generally known in the art. This pod may be situated on top of the composite material or may be embodied, e.g. between the nontransparent support sheet and the silver halide emulsion layer, or between this emulsion layer and the pigment layer.

The alkaline processing liquid may contain part of the developing agent(s) and preferably comprises the complexing agent for the unexposed silver halide. An especially suitable alkaline substance, by means of which a processing liquid can be obtained that does not give specks of crystallization on the composite material is diethanolamine, occasionally buffered with trisodium phosphate.

The alkaline processing liquid may also contain the development nuclei as already said hereinbefore. At the wetting stage of the photographic composite sheet material, the development nuclei settle substantially at the surface of the pigment layer or of a hydrophilic colloid layer applied on top thereof, where the diffusion transfer image is then produced. The development nuclei may also be applied from another liquid composition by means of which the photographic composite material may be wetted before or after exposure, but preferably after exposure, and in that case preferably before the treatment with the alkaline processing liquid for carrying out the silver complex diffusion transfer image formation. Such another liquid composition may contain the developing agent(s) that according to the present invention have to be present in the composite sheet material.

Shortly after wetting the photographic composite material with the alkaline processing liquid, a high quality diffusion transfer image appears at the side of the pigment layer opposite the support side, i.e. on a white or colored background through which the negative image in the silver halide emulsion layer can not be seen or at most can be seen only faintly. Further, the copy obtained is practically immediately dry after the diffusion transfer image has been produced, so that it can be used or stored immediately. Especially when a paper support is used, the copy can be folded easily and the backside is easily written on.

The following examples illustrate the photographic composite sheet material as well as the method of the present invention.

Example 1

A nontransparent paper sheet of 90 g. per sq. m. was coated with a high-sensitive ortho-sensitized gelatino silver chloride emulsion containing hydroquinone and 1-phenyl-3-pyrazolidone in such a way, that a silver halide emulsion layer was obtained comprising per square meter an amount of silver chloride equivalent to 0.5 g. of silver nitrate, 0.2 g. of hydroquinone and 0.05 g. of 1-phenyl-3-pyrazolidone.

The light-sensitive silver halide emulsion layer was provided with a pigment layer by applying the following coating composition for each 12 sq. m.

water	764.4 ccs.
gelatin	15 g.
titanium dioxide	150 g.
20 percent aqueous solution of formaldehyde	4 ccs.
3-hydroxypropylene sulfite	6.6 ccs.
sorbitol	50 g.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	10 ccs.

On top of the pigment layer thus obtained the following composition containing development nuclei was applied pro rata of 1 liter per 45 sq. m.

water	980 ccs.
aqueous dispersion comprising 0.60 percent of nickel sulfide and 1.90 percent of gelatin	10 ccs.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	10 ccs.

The light-sensitive composite sheet material thus produced was episcopically exposed to an original and through the pigment layer and then at a rate of 2.5 cm./sec. conducted through a usual apparatus for the production of diffusion transfer copies and containing an activator liquid of the following composition:

water	800 ccs.
trisodium phosphate-12-water	75 g.
anhydrous sodium sulfite	40 g.
anhydrous sodium thiosulfate	10 g.
potassium bromide	0.5 g.
1 percent solution of 1-phenyl-2-tetrazoline-5-thione in ethanol	4 ccs.
water to make	1,000 ccs.

A positive true-sided diffusion transfer image of the original was obtained on a white background. Even through the side of the supporting paper the negative produced in the silver halide emulsion layer was substantially invisible. Already a few seconds after the composite sheet material had left the apparatus, the diffusion transfer image reached its optimal value. The keeping qualities of the diffusion transfer copy on ageing were excellent.

Example 2

Example 1 was repeated with the difference that the pigment coating composition was replaced by the following one:

water	829 ccs.
gelatin	3.7 g.
propylene glycol ester of alginic acid	3.3 g.
calcium carbonate	150 g.
20 percent aqueous solution of formaldehyde	4 ccs.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	10 ccs.

About the same results as those described in example 1 were obtained.

Example 3

Example 1 was repeated with the difference that the pigment coating composition was replaced by the following one:

water	829 ccs.
gelatin	3.7 g.
carboxymethylcellulose	3.3 g.
china clay	150 g.
20 percent aqueous solution of formaldehyde	4 ccs.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	10 ccs.

About the same results as those described in example 1 were obtained.

Example 4

Example 1 was repeated with the difference that the pigment coating composition was replaced by the following one:

water	821 ccs.
gelatin	15 g.
silica powder	150 g.
20 percent aqueous solution of formaldehyde	4 ccs.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	10 ccs.

About the same results as those described in example 1 were obtained.

Example 5

Example 1 was repeated with the difference that no composition containing development nuclei was applied on top of the pigment layer and that the pigment coating composition described in example 1 was replaced by the following one:

water	817.4 ccs.
gelatin	3.7 g.
carboxymethylcellulose	3.3 g.
titanium dioxide	150 g.
20 percent aqueous solution of formaldehyde	4 ccs.
3-hydroxypropylene sulfite	6.6 ccs.
aqueous dispersion comprising 0.60 percent of nickel sulfide and 1.90 percent of gelatin	5 ccs.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	10 ccs.

About the same results as those described in example 1 were obtained. Only the optical density of the diffusion transfer image was somewhat lower.

Example 6

A nontransparent paper sheet was coated with a silver chloride emulsion as described in example 1. The light-sensitive silver halide emulsion layer was provided with a pigment layer by applying the following coating composition in a proportion of 1 liter per 10 sq. m.

water	308 ccs.
dispersion of 150 g. of titanium dioxide in 150 ccs. of ethanol and 300 ccs. of water	
gelatin	15 g.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	20 ccs.
20 percent aqueous solution of formaldehyde	5 ccs.
solution of 2 g. of 1-phenyl-3-pyrazolidone in 50 ccs. of ethanol	

The light-sensitive composite sheet material thus produced was substantially free from specific development nuclei. It was episcopically exposed to an original and through the pigment layer and then conducted through a usual apparatus containing the activator liquid described in example 1.

About the same results as those described in example 5 were obtained.

Example 7

Example 6 was repeated with the difference that the pigment coating composition was replaced by the following one:

water	303 ccs.
dispersion of 150 g. of titanium dioxide in 150 ccs. of ethanol and 300 ccs. of water	
gelatin	15 g.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	20 ccs.
20 percent aqueous solution of formaldehyde	5 ccs.
solution of 2 g. of 1-phenyl-3-pyrazolidone in 50 ccs. of ethanol	
aqueous dispersion comprising 0.60 percent of nickel sulfide and 1.90 percent of gelatin	5 ccs.

About the same results as those described as in example 5 were obtained.

Example 8

A nontransparent paper sheet was coated with a silver chloride emulsion layer as described in example 1.

The silver chloride emulsion layer was provided with a pigment layer by application of the following coating composition in a proportion of 1 liter per 10 sq. m.

water	402 ccs.
dispersion of 75 g. of titanium dioxide in 75 ccs. of ethanol and 150 ccs. of water	
dispersion of 50 g. of china clay in 50 ccs. of ethanol and 100 ccs. of water	
gelatin	15 g.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	20 ccs.
20 percent solution of formaldehyde	5 ccs.
solution of 2 g. of 1-phenyl-3-pyrazolidone in 50 ccs. of ethanol	
3-hydroxypropylene sulfite	6 ccs.

On top of the pigment layer thus obtained a coating composition containing development nuclei was applied as described in example 1.

The light-sensitive composite sheet material thus obtained is episcopically exposed to an original and through the pigment layer and then conducted through a usual apparatus for the production of diffusion transfer copies and containing an activator liquid of the following composition:

water	800 ccs.
trisodium phosphate-12-water	35 g.
anhydrous sodium sulfite	20 g.
anhydrous sodium thiosulfate	5 g.
potassium bromide	0.5 g.
1 percent solution of 1-phenyl-2-tetrazoline-5-thione in ethanol	4 ccs.
diethanolamine	25 ccs.
water to make	1,000 ccs.

About the same results as those described in example 1 were obtained. The diffusion transfer copy produced, after drying did not show any specks as a consequence of the crystallization on its surface of compounds present in the activator liquid.

Example 9

Example 1 was repeated with the difference that the pigment coating composition was replaced by the following one:

water	764.4 ccs.
gelatin	15 g.
titanium dioxide	150 g.
20 percent aqueous solution of formaldehyde	4 ccs.
3-hydroxypropylene sulfite	6.6 ccs.
sorbitol	50 g.
12.5 percent solution of saponine in a mixture of ethanol and water (20/80)	120 ccs.

This pigment coating composition is very stable.

About the same results as those described in example 1 were obtained.

We claim:

1. Photographic light-sensitive unitary composite sheet material for the production of an image according to the silver complex diffusion transfer process comprising in order a nontransparent flexible support sheet, a light-sensitive silver halide emulsion layer and a layer containing an opaque white or colored pigment and a hydrophilic colloid binder, wherein the pigment and the binder of the pigment particles are present in amounts of from 9 to 25 g. per sq. m. and of from 0.5 to 3 g. per sq. m. respectively, said material containing at least one photographic developing agent for silver halide.

2. Photographic material according to claim 1, wherein at least a stratum of said colloid binder adjacent the surface of said pigmented layer has therein development nuclei for complexed silver halide.

3. Photographic material according to claim 2, wherein said nuclei are present in a this hydrophilic colloid layer.

4. Photographic material according to claim 2, wherein the development nuclei are applied to such stratum with not more than a very small amount of binder.

5. Photographic material according to claim 1, comprising hydroquinone and a 1-phenyl-3-pyrazolidone as developing agents.

6. Photographic material according to claim 1, wherein the developing agent is present in an amount of from about 100 to about 500 mg. per sq. m.

7. Photographic material according to claim 1, wherein the pigment at least partially consists of titanium dioxide particles.

8. Photographic material according to claim 1, wherein the particle size of the pigment particles lies between 0.05 and 0.5 μ.

9. Photographic material according to claim 1, wherein the pigment particles are homogeneously dispersed in the binder by the presence of a large amount of at least one dispersing agent.

10. Photographic material according to claim 1, wherein at least one layer is at least partially hardened.

11. Photographic material according to claim 3, wherein the outermost layer is at least partially hardened.

12. Photographic material according to claim 10, wherein the hardening occurs by means of a latent hardener present in the photographic material in effective contact with the layer to be hardened.

13. Photographic material according to claim 1, wherein the silver halide emulsion layer is a high-sensitive silver halide emulsion layer.

14. Photographic material according to claim 1, wherein the silver halide emulsion layer is a silver halide emulsion layer for the recording of an X-ray or γ-ray pattern.

15. Photographic material according to claim 1, wherein the silver halide emulsion layer halide emulsion layer for the recording of an X-ray or γ-ray pattern and an intensifying screen is incorporated in the material.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,607,270 Dated September 21, 1971

Inventor(s) Louis de Haes et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, claim 3, line 2, change "this" to -- thin --.

line 2, after "layer" but before the period, insert -- applied to the remote surface of the pigment layer --.

Column 10, claim 15, line 2, after "layer" (first occurrence), insert -- is a silver --.

Signed and sealed this 18th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents