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DIFFUSION TRANSFER RECEIVING SHEET CONTAINING CHINA CLAY AND AN ALIPHATIC AMINE

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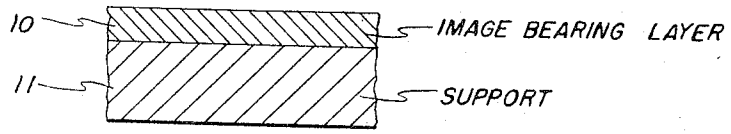


FIG. 1

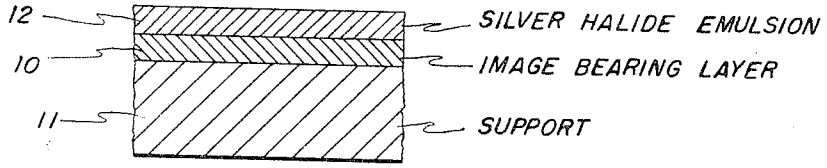


FIG. 2

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DIFFUSION TRANSFER RECEIVING SHEET CONTAINING CHINA CLAY AND AN ALIPHATIC AMINE

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This invention relates to processes of photographic reproduction particularly suitable for document copying, and to non-light-sensitive materials for use therein.

The silver salt diffusion process, sometimes called the solvent transfer process, of photographic reproductions is well known. In this process, a sensitive silver halide emulsion layer is exposed to a subject, usually a document or other line original, and developed to a silver image. During or after development, the emulsion layer is contacted in the presence of a silver halide solvent, with an image-receiving non-light-sensitive sheet material bearing on its face a layer containing a substance which will form a visible image of silver or a silver compound when contacted by a soluble silver complex. While the two layers are in contact, the unexposed silver halide from the emulsion layer is dissolved by the silver halide solvent to form a soluble silver complex which diffuses into the non-light-sensitive layer.

In commercial practice, the image-forming substance in this layer provides development nuclei for the diffusing silver complex which is then developed to a visible silver image by the developer. The image-forming substances employed are usually colloidal silver and colloidal silver sulfide, but numerous other substances have been suggested some of which form development nuclei by reaction with the soluble silver complex first diffusing into the layer, which nuclei are used to form the image, as described above. Typical of these compounds are zinc sulfide and various colloidal metals, colloidal metal sulfates and certain organic compounds. It is possible to employ an image-forming substance in such an amount that it forms an insoluble salt by double decomposition with the diffusing soluble silver complex. In this case, it is not necessary that developer be present in the image-receiving layer, and, if it is present, the final image will be formed partly by double decomposition and partly by physical development.

The usual commercial procedure is to form a single positive copy in the receiving sheet from the exposed sensitive material, but it has also been proposed to interrupt the transfer step with the receiving sheet first employed and continue the transfer with a second and sometimes a further receiving sheet. In this way, two copies can be made from the one exposed sensitive material. However, it has been found difficult to control the conditions so that more good copies can be made from the exposed sensitive material, although the negative material may contain enough silver halide to provide 6–8 copies of good density. One reason for this difficulty may be that the blue toners present in the positive contaminate the negative during the transfer operation, thus restricting the solubility of the silver halide and reducing the number of copies that can be obtained from a single negative.

It has been desired, therefore, to improve the receiving sheets used for multiple copies so that multiple copies can be obtained using a single exposed silver halide layer.

We have discovered a method of preparing an image receiving layer on the receiving sheet which makes it possible to obtain 6 to 12 good copies from a single exposed sensitive silver halide material.

One object of this invention is to provide an improved receiving sheet for use in the photographic diffusion transfer process. Another object is to provide a receiving sheet for use in the diffusion transfer system which enables 6 to 12 good copies to be made from a single exposed sensitive silver halide material. A further object is to provide a process for making multiple copies from a single exposed silver halide emulsion by the silver halide diffusion transfer process. A still further object is to provide a method of making an improved receiving sheet containing nuclei for use in obtaining a positive image in the diffusion transfer process.

The above objects are attained by precipitating the developed nuclei in the absence of a water-soluble colloid but in a suspension of china clay. After precipitation, a colloidal binder such as gelatin is added and the mixture coated on a support such as a paper sheet.

Although our preferred nuclei is zinc sulfide, it will be appreciated that other typical nucleating or silver precipitating agents which are known in the solvent transfer system may be used such as particles of silver, other metal sulfides, metal selenides, silver proteinate, etc. These nucleating agents include Carey Lea silver and the colloidal sulfides and selenides of the metals of Groups I–B, II–B, IV–B and VIII of the Periodic Table, e.g. zinc, cadmium, nickel, etc. These nuclei particles preferably have an average diameter of about 25 to 2,500 A. units.

The clay which is useful in our invention is preferably china clay of at least as pure a grade as normally employed in the preparation of art papers. China clay is well known as a clay having great purity, also identified as kaolin. Kaolin normally contains a mixture of silica and alumina such that the total of this mixture is at least 80 percent with about 13 percent organic matter with a minimum of other compounds such as iron iodides, titania, lime, maganese, soda and potash.

Other forms of clay such as bentonite and fuller's earth are not preferred since they do not give as high a standard of background whiteness as is normally desired in photographic copying paper.

The nuclei are normally prepared by carrying out a reaction which results in precipitating finally divided insoluble particles of the desired nuclei. For instance, sodium sulfide can be reacted with zinc nitrate to form zinc sulfide. According to our invention, the precipitation of the nuclei such as zinc sulfide is carried out in an aqueous suspension containing 30%–70% china clay. To this reaction mixture containing the precipitated nuclei and china clay is added at least sufficient colloidal binder, such as gelatin, to cause the clay and nuclei to adhere to the support. However, clay to binder ratios may be used of 15:1 to about 1:1. A useful coverage range for the nuclei is 0.1 to 100 mg./ft.^{2}, and for gelatin 0.2 to 3.0 g./ft.^{2}.

Image receiving papers having a layer of development nuclei prepared in situ in a dispersion of china clay may give images which are not of the normally desired neutral tone. Therefore, it is preferred to perform the transfer of the soluble silver complex from the unexposed regions of the exposed layer to the image-receiving sheet in the presence of a long chain aliphatic amine or salt, such as the acetate, thereof, such as an aliphatic amine having from 14 to 18 carbon atoms in the chain thereof. The aliphatic amine or salt thereof is preferably incorporated in the suspension of development nuclei before coating. An aliphatic amine which is particularly useful is octadecylamine in the form of its acetate. The amine is preferably employed in a concentration of from 5 to 30 mgs./square meter when incorporated in the receiving layer, or from 0.05 to 0.5 gram/liter when incorporated in the developing solution. Suitable amines are sold by

the Armour Industrial Chemical Co. under the trade name "Armeen," and are water soluble.

The silver halide emulsion may comprise any of the conventional gelatino-silver halide developing out emulsions, e.g. gelatino-silver chloride, -chlorobromide, -chloroiodide, -chlorobromoiodide, -bromide, -bromoiodide developing out emulsions. The emulsions for use in the invention include emulsions having a silver halide carrier other than gelatin, for example, collodion, albumin, synthetic resins and the like. These emulsions can be coated in the usual manner on a suitable support, e.g. glass, cellulose nitrate film, cellulose ester film, paper or metal, etc.

The silver halide developing solution used for initiating development of the exposed sensitive element is not especially critical. It can be of the conventional type used for developing films or papers with the exception that a silver halide solvent such as sodium thiosulfate, sodium thiocyanate or ammonia is present in the quantity required to form a soluble silver complex which diffuses imagewise to the receiving support. Silver halide developing agents useful in the developing solution include hydroquinone, monomethyl-p-aminophenol sulfate, aminophenols, halogenated hydroquinones, toluenequinone, p-hydroxyphenyl, aminoacetic acid, 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and mixtures of these developing agents. Useful developer compositions cotnaining combinations of 3-pyrazolidone silver halide developing agents with weak developing agents such as ascorbic acid are disclosed in U.S. Patents 2,685,515, 2,685,516, 2,688,548, 2,688,549, 2,691,589 and 2,751,300.

It will be appreciated that common emulsion addenda such as chemical and spectral sensitizing agents which are known in the art can be added to the photographic emulsion.

In our preferred embodiment it is intended that the receiving sheet be used to contact the silver halide emulsion, but other layer arrangements can be used employing the nucleated surface obtained according to our invention. For instance, a support having thereon the nucleated layer of this invention can be overcoated with a removable silver halide emulsion. After exposure and development using a silver halide solvent containing developer, the emulsion can be removed leaving a positive print in the nucleated layer. The nucleated layer can also be used as an overcoat by pigmenting the nucleated layer with a material such as titanium dioxide so that the positive silver image will be visible against a white background when the silver halide which has been exposed from the reverse side through the support is developed and processed with a silver halide solvent containing developer. This nucleated layer is also suitable for use in place of other nucleated layers known in the art used in connection with the solvent transfer process.

In the accompanying drawing;

FIG. 1 illustrates one embodiment of our invention wherein a support **11** has thereon the image receiving layer **10** containing a binder having therein silver precipitating nuclei formed in situ in an aqueous dispersion of china clay.

FIG. 2 illustrates an embodiment of our invention wherein the element of FIG. 1 has a photographic silver halide emulsion overcoat **12** which can be removed after processing. The silver halide emulsion is exposed and processed using a silver halide developer containing a silver halide solvent which causes the unexposed silver halide to diffuse into the image receiving layer **10** where a positive image is formed. The silver halide emulsion **12** is then removed from the surface.

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

Example 1

A sensitive silver chloride emulsion layer is exposed by reflux to the original to be copied. A photographic silver halide developing solution is prepared to which 1 to 2 grams per liter of crystalline sodium thiosulfate is added.

An image-receiving sheet is prepared by coating on a paper support such as a 90 gram document copying base, a layer of the following coating composition prepared by mixing in the order given.

China clay	grams	30
Distilled water	mils	80
.01 N $AgNO_3$	do	20
.01 N Na_2S	do	20
10% Hide gelatin	do	50

The mixture is homogenized, and any desired wetting agents, dyes or other addenda added and the volume made up to 200 mls. with distilled water. The mixture is coated at 40°–45° C. at a coverage of 50–80 mls./square meter.

When this first layer has been coated, a second layer is supplied thereover, which is formed from

	Mls.
0.25% Capogel 400/500 (carboxymethyl cellulose)	98
7.5% Saponin solution	2

The coating weight is 70 mls./square meter in the second layer.

The exposed sensitive material and the image-receiving sheet are passed together through a processing machine of the type employed for the solvent transfer process, which contains the developing solution. The sandwich is left in contact for 10 to 20 seconds after which the negative emulsion layer is peeled off. The wet negative layer is laid emulsion down on a second piece of the image-receiving paper, the leading edges separated slightly and the sandwich fed through the slots of the machine. After 20 seconds contact, the negative is peeled off and the cycle repeated. 8 to 12 copies having a brown tone are made by this procedure. The negative should not be fogged during the procedure or the number of copies obtainable will be considerably fewer than the maximum. It is found that the density of the copies is uniform throughout the process and they are free from curl when dry.

Example 2

The procedure of Example 1 was followed except that the nuclei were precipitated in a dispersion of clay in gelatin. A similar number of copies were obtained except that the density is less than that obtained in Example 1 and the brown tone was lighter.

Example 3

The procedure of Example 1 was repeated except that the nuclei were precipitated in the gelatin solution prior to mixing with clay in water. Five copies were obtained having a tan tone and slightly less density than that obtained using the receiving sheets of Example 2.

Example 4

The procedure of Example 1 was repeated employing the same negative material, the same developing solution and the same processing steps.

The image-receiving sheet is prepared in a similar manner to that of Example 1, except that the coating composition contains 2 grams of Armac 18D which is commercial octadecylamine acetate supplied by Hess Armour Chemicals Ltd. When this first layer has been coated, a second layer is coated thereover as in Example 1. By proceeding in the manner of this example, six to twelve uniform density, neutral-toned copies are obtained.

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

We claim:

1. A nucleated layer for use in the silver salt diffusion transfer process comprising china clay having dispersed

therein silver precipitating agents having an average diameter of about 25 A. to about 2500 A. and containing an aliphatic amine having 14 to 18 carbon atoms selected from the class consisting of the amine and salts thereof.

2. A nucleated layer of claim 1 containing a colloidal binder.

3. A nucleated layer of claim 1 in which the silver precipitating agents are formed in situ in an aqueous dispersion of china clay.

4. A nucleated layer of claim 3 containing a colloidal binder.

5. A nucleated layer of claim 1 in which the silver precipitating agents are formed in situ in an aqueous dispersion of china clay, substantially in the absence of a water soluble colloid.

6. A nucleated layer of claim 5 containing a colloidal binder.

7. A process of forming images by the diffusion transfer process which comprises developing an exposed silver halide emulsion, transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer in contiguity with a silver halide solvent to an image receiving layer containing a nucleating composition, said composition comprising china clay having dispersed therein silver precipitating agents having an average diameter of about 25 A. to about 2500 A. and an aliphatic amine having 14 to 18 carbon atoms selected from the class consisting of the amine and salts thereof.

8. A process of claim 7 in which the said image receiving layer comprises a colloid binder containing the said composition.

9. A process of claim 7 in which the said composition is formed by precipitating the silver precipitating agent in situ in an aqueous dispersion of china clay.

10. A process of claim 7 in which the said composition is formed by precipitating the silver precipitating agent in situ in an aqueous dispersion of china clay, substantially in the absence of a water soluble colloid.

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