April 20, 1971 M. L. JUDD ET AL 3,575,703

# PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

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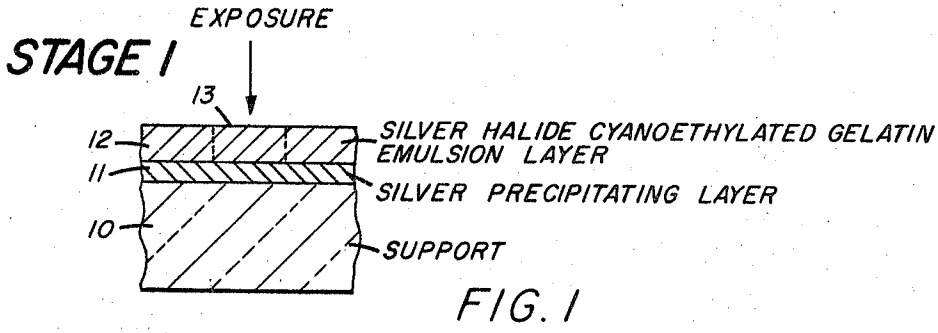



FIG. 1

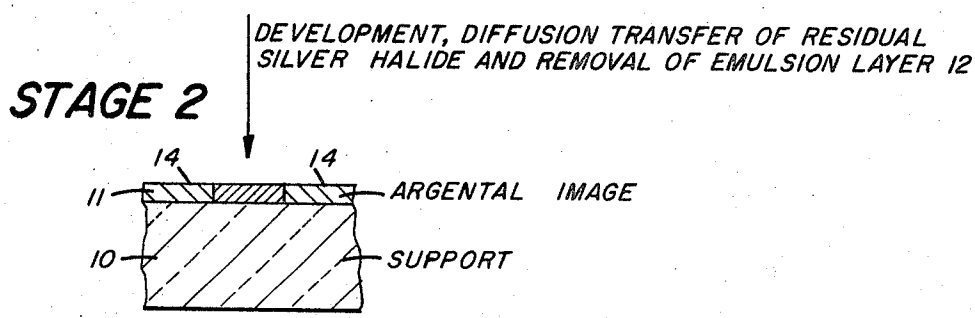



FIG. 2

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# PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

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U.S. Cl. 96—76 12 Claims

## ABSTRACT OF THE DISCLOSURE

A photographic element having a support carrying a hardened silver precipitating stratum containing silver precipitating nuclei and an overlying light sensitive silver halide stratum comprising cyanoethylated gelatin. A silver image is formed in the silver precipitating stratum by diffusion transfer. The overlying light sensitive layer is easily removed because the cyanoethylated gelatin is not hardened by hardner which may migrate thereto.

## BACKGROUND OF THE INVENTION

This invention relates to photographic diffusion transfer products and processes. More particularly, the invention relates to a diffusion transfer process of the type described in British Pat. 654,631 wherein undeveloped silver halide of an emulsion layer is transferred as a silver complex imagewise by imbibition to a silver precipitating or nucleating layer generally to form a positive image therein. The process is carried out utilizing a multilayer element such as one carrying on a support two gelatin layers of different solubility, for example, the layer next to the support containing a silver precipitating agent and being harder than the outer gelatin layer which is a gelatin emulsion layer containing silver halide. After exposure of the element, development is carried out with the silver halide solvent-containing developer to obtain a silver positive in the hardened gelatin silver precipitating layer, after which the emulsion layer containing the negative silver image is washed off, leaving the positive silver image on the support.

While the process described is quite successful, it has proven difficult, as a practical matter, to harden the underlying layer, particularly a gelatin layer of an element of this type without unduly hardening the outer gelatin emulsion layer and even then over a period of time the emulsion layer tends to harden and the silver precipitating layer tends to soften, which makes the differential removal in the final step of the process difficult or impossible.

This problem has been recognized in the art and various attempts have been made to overcome the problem as will be evident upon consideration of the following patent disclosures:

Yackel et al. U.S. Pat. No. 3,020,155 and British Pat. No. 868,241 describe the replacement of the gelatin of the emulsion layer wholly or for the greater part by other organic colloid vehicles having a decidedly different solubility than the organic colloid vehicle present in the silver precipitating layer, the most satisfactory of which are alkali-soluble acid-insoluble carboxylated cellulose derivatives such as the alkali-soluble acid-insoluble dibasic acid half-esters of cellulose ethyl ethers. However, in order to coat these light sensitive coatings using high speed machinery, it is necessary to utilize acids, such as citric acid, to quickly set the coating. It will be recognized that in some instances, the presence of this acid in the photographic element might be undesirable.

British Pat. No. 1,000,116 describes adding polystyrene sulfonic acid to the light sensitive gelatin silver halide layer. While this increases the initial solubility of the layer, migration of hardener from the silver precipitating layer will eventually take place and this is presumably why an intermediate starch scavenger layer is mentioned.

British Pats. No. 1,006,292, No. 1,042,009 and No. 1,053,074 each describe the use of scavengers for gelatin hardeners such that, if hardener, such as formaldehyde, migrates from the hardened layer into the emulsion layer which is to be eventually removed, the hardener is tied up by reaction with the scavenger and is thus prevented from hardening gelatin in the emulsion layer. It should be readily apparent, however, that with time a scavenger greatly reduces the aldehyde content of the silver precipitating layer since aldehyde which is tied up by the scavenger cannot return to the hardened layer.



## SUMMARY OF THE INVENTION

According to the present invention, the mentioned difficulties in connection with providing layers having sufficiently disparate hardness to permit facile wash-off after providing a silver image in the lower layer by diffusion transfer processing are overcome by utilizing a cyanoethylated gelatin binder in the light sensitive silver halide layer. Cyanoethylated gelatin is gelatin wherein the amine groups have been cyanoethylated. This gelatin derivative can be conveniently prepared as described in U.S. Pat. No. 2,518,666 by reacting gelatin and acrylonitrile in an inert solvent. Cyanoethylated gelatin is unaffected by aldehyde protein hardeners such as formaldehyde. Accordingly, it is contemplated that a protein hardener may migrate from the hardened silver precipitating layer into the light sensitive layer. However, according to the present invention, hardener which wanders out of the lower layer does not react in the upper layer. This system is free from changes in the solubility relationship between layers with time as the unreactive water soluble layer is unaffected by any wandering hardener or cross-linker.

## BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing is illustrated in greatly enlarged cross-sectional view a sensitive element comprising a part of our invention, as well as the general method for obtaining photographic reproductions by our silver halide diffusion transfer process. As shown therein, in Stage **1** a representative sensitive element includes a support **10** such as paper, cellulose ester or synthetic resin, if desired carrying a subbing layer not shown, and on the support the silver precipitating layer **11**, for example, a gelatin layer containing a colloidal heavy metal or heavy metal sulfide and thereon the emulsion layer **12** containing silver halide grains dispersed in the cyanoethylated gelatin binder. As shown in Stage **1**, the element is exposed to a line halftone or continuous-tone subject in a suitable manner, preferably so as to obtain a "right-reading" reproduction, the exposure being shown as taking place in area **13** of emulsion layer **12**.

In carrying out the process of our invention, the exposed element is then developed with a silver halide developing solution containing a silver halide solvent such as sodium thiosulphate with the result that a silver image is developed in area **13**, and shortly thereafter the residual undeveloped silver halide is transformed to a soluble silver complex a portion of which diffuses imagewise to the silver precipitating layer **11** where an argental image is formed by reaction of the silver complex with the silver precipitating agent of the silver precipitating layer. The emulsion layer **12** containing the negative silver image is then merely washed from the support with an excess of water to obtain the reproduction shown in Stage **2** of the drawing wherein the argental positive image occupies areas **14** of the silver precipitating layer **11**.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The silver precipitating layer or stratum referred to herein is a hardened gelatin layer containing a silver precipitating agent, that is an agent capable of yielding with silver ion a dark-colored argental or silver-containing substance, when dissolved silver salts from the emulsion layer come into contact with it. The silver precipitating agent may comprise either physical development nuclei or a chemical precipitant for silver ions.

Suitable silver precipitating agents for use in the silver precipitating layer for forming the argental image include sulfides, selenides, polysulfides, polyselenides, thiourea, mecaptans, stannous halides, heavy metals and heavy metal salts, and fogged silver halide. Heavy metal sulfides such as lead, silver, zinc, antimony, cadmium, nickel, cobalt and bismuth sulfides are useful, particularly the sulfides of lead and zinc alone or in admixture, or complex salts of these with thio-acetamide, dithio-oxamide, or dithiobiuret. The heavy metals include silver, gold, platinum, palladium and mercury preferably in the colloidal form. The noble metals are particularly efficacious.

In a particularly useful embodiment, silver precipitating agents are provided in a binder of hardened colloid. The colloid must be hardened sufficiently so that it will not be removed by rubbing gently under warm water, i.e. have a melting point above about 100° F. Any of the known hardening agents, such as those disclosed by Mees The Theory of the Photographic Process, Revised edition, pages 75–84, most commonly formaldehyde, may be used. The binder may be applied to a support such as paper, a cellulose derivative support such as cellulose acetate, or to any suitable supports, such as synthetic resin supports. Of course, if the element is used for a lithographic support, suitable supports include aluminum, polyesters, etc. If used for movie film, or the like, a transparent base is preferred.

The silver precipitating layer, or stratum, may be applied directly to the support or may be anchored thereto by one or more subbing layers known to be suitable for that purpose, applied by vacuum deposition, etc. When a binder is employed for the precipitating layer, it is not necessarily all hardened colloid, as other compatible colloids can be added thereto. If desired, of course, the binder may be any alkali permeable binder. However, due to the generally desirable qualities of gelatin, it is preferred that the major proportion of the binder of the silver precipitating layer is hardened gelatin and it is more preferable that the binder is essentially all hardened gelatin.

The cyanoethylated gelatin which is provided in the overlying light sensitive emulsion layer is gelatin contain-in cyanoethyl groups which may be produced by reacting gelatin with acrylonitrile as disclosed in U.S. Pat. No. 2,518,666. It is preferred that a major proportion of the amine groups of the gelatin are rendered inactive by cyanoethylation. However, it is more preferred to essentially completely cyanoethylate the gelatin which is readily accomplished by using a stoichiometric excess of acrylonitrile in the mentioned process. It is also preferred that a major proportion of the binder in the light sensitive layer is cyanoethylated gelatin. Furthermore, while other compatible binder may be utilized, such as non-cyanoethylated gelatin, it is more preferred that substantially all of the binder is of the cyanoethylated type.

The cyanoethylated gelatin may be deaminated prior to cyanoethylation as disclosed in British Pat. No. 628,757. By this process, a portion of the amino groups are destroyed thus lowering the isoelectric point. The deaminated gelatin is then reacted with acrylonitrile according to the method of U.S. Pat. No. 2,518,666.

The silver halide component of the emulsion can include various silver halides and mixtures of silver halides such as silver bromoiodide, silver chloride or silver bromide spectrally sensitized in the usual manner. The emulsions may be developing-out emulsions designed for development to negative images in which case the image obtained in the silver precipitating layer is a positive with respect to the original subject. If desired, the emulsion can be of the direct positive type with the result that the silver image developed in the emulsion is a positive and the image in the silver precipitating layer a negative in respect to the original subject. The procedures of Leermakers U.S. Pat. 2,184,013 and Kendall et al. U.S. Pat. 2,541,472 are useful in conferring the direct positive characteristics to the emulsions.



The silver halide developing solution used for initiating development of the exposed sensitive element described can be of the conventional type used for developing films or papers with the exception that a silver halide solvent such as sodium thiosulphate, sodium thiocyanate or ammonia is present in the quantity required to form the soluble silver complex which diffuses imagewise to the silver precipitating layer. Silver halide developing agents useful in the developing solution include hydroquinone, monomethyl-p-aminophenol sulfate, aminophenols, halogenated hydroquinones, toluquinone, p-hydroxyphenyl aminoacetic acid, 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and mixtures of these developing agents. Useful developer compositions containing combinations of 3-pyrazolidone silver halide developing agents with weak developing agents such as ascorbic acid are disclosed in U.S. Pats. 2,688,549, 2,691,589, 2,688,548, 2,685,515, 2,685,516 and in the James et al. U.S. Pat. 2,751,300.

The image tone and tonal range of the reproductions obtained in our process are measurably improved if development of the sensitive element and the image-wise diffusion of the silver complex takes place in the presence of certain toning compounds, as disclosed in U.S. Pat. No. 3,020,155.

When the direct-positive emulsions are used in the process of the invention it is sometimes advantageous to dispense with or reduce the concentration of these toning compounds when it is actually desired to obtain sepia or warm-toned reproductions. When our invention is practiced in this manner the portrait photographer can readily prepare photographs having the desired tone.

In this process and the processes of the examples hereinafter, the silver halide developing agent may be present in either the developing solution or the emulsion itself. In the latter case it is perferable to use a substantially non-diffusing developing agent such as an alkyl or aryl substituted polyhydroxybenzene developing agent in the emulsion layer or other layer in the photographic element.

Our invention will now be illustrated in more detail by the following example.

## EXAMPLE 1

A one percent gelatin solution containing nickel sulfide nuclei is applied to film support to give 100 mg. of gelatin per square foot. Over this is coated a 0.5 percent gelatin solution containing antihalation dyes, spreading agent and sufficient formaldehyde to equal 0.7 percent of the total gelatin weight in the bottom two layers. These layers are allowed to stand three days to allow adequate hardening before applying subsequent layers.

A suspension containing 42 grams of cyanoethylated gelatin and .31 mole of silver bromoiodide per liter (plus other normal photographic addenda) is coated over the aged underlayers to give a coverage of 450 mg. of silver and 610 mg. of cyanoethylated gelatin per square foot.

The cyanoethylated gelatin is prepared by swelling 1 kg. of dried gelatin in 7 liters of distilled water overnight. The swollen gelatin is melted at 60° C. The pH is raised to 10 with sodium hydroxide, and, with good stirring, 100 g. of acrylonitrile is slowly added. The melt is stirred 4 hours at 40–45° C. and subsequently acidified to pH 6 with sulfuric acid. The melt is strained, chilled, noodled, washed 4 hours in running cold tap water, and dried.

The emulsion layer is overcoated with a 2 percent gelatin solution to give a coverage of 90 mg. of gelatin per square foot.

This coating is exposed for 1/100 of a second to 500 watt tungsten illumination and developed for 20 seconds at 90° F. in a diffusion transfer developer. The film is rinsed with 90° F. water which readily dissolves away the emulsion and overcoat layer leaving the positive containing nuclei layer and gelatin interlayer intact. This difference in solublity can be demonstrated even after prolonged ageing of the material, e.g. 6 months.

While it has been found, according to the invention, that the mentioned problem in the art has been met by the use of cyanoethylated gelatin according to the present invention, it has also been discovered that these results are not obtained by the use of certain other gelatin derivatives as is apparent from the examples which follow.

## EXAMPLE 2

One hundred grams of dried gelatin is swollen in 900 ml. of water and subsequently melted at 40° C. After adjusting the pH to 5.7, 10 g. of N-ethylmaleimide in 60 ml. of acetone is added slowly with good stirring. When addition is completed, the gelatin solution is allowed to set in a cold store for 1 week. It is then sliced, washed 6 hours in running water and dried.

One hundred grams of dried gelatin is swollen in 900 ml. of water and subsequently melted at 40° C. After adjusting the pH to 10, 7 g. of phthalic anhydride in 50 ml. of acetone is added slowly with good stirring. Alkali is added simultaneously to maintain a pH of 10. The melt is stirred 10 minutes after reagent addition is completed. It is subsequently chill-set, sliced, and dried.

The resulting gelatin derivatives and also cyanoethylated gelatin are melted, and 0.5 percent formaldehyde is added, and the melts are coated on a polyester (polyethylene-terephthalate) film support.

A sample of each film coating is tested for hardness before and after 3 days' incubation at 120° F./50% RH (equivalent to about 6 months' shelf life), by immersing in Kodak DK–50 Developer at 25° C. for 3 minutes and calculating percent swell of the emulsion. The following results show that cyanoethylated gelatin is unique in maintaining the same amount of hardening with time.

| Reagent | Percent swell | |
|---|---|---|
| | Fresh | 3 days' incubation |
| N-ethylmaleimide | 730 | 460 |
| Phthalic anhydride | 950 | 480 |
| Acrylonitrile | 1,150 | 1,000 |

In addition to the gelatin derivatives mentioned in Example 2, it has been found that benzene sulfonyl chloride gelatin derivatives and phenyl isocyanate gelatin derivatives are ineffective in maintaining resistance to hardening over long periods of time.

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 set forth in the appended claims.



We claim:

1. A light sensitive photographic element comprising a support carrying a silver precipitating stratum comprising hardened colloid and a silver precipitating agent, said colloid being hardened by a protein hardener, and an overlying light sensitive stratum comprising silver halide dispersed in a binder comprising cyanoethylated gelatin.

2. A light sensitive photographic element according to claim 1 wherein at least a major proportion of the amine groups of said cyanoethylated gelatin are cyanoethylated.

3. A light sensitive photographic element according to claim 2 wherein said cyanoethylated gelatin is essentially completely cyanoethylated.

4. A light sensitive photographic element according to claim 1 wherein at least a major proportion of said binder is cyanoethylated gelatin.

5. A light sensitive photographic element according to claim 4 wherein at least a major proportion of the amine groups of said cyanoethylated gelatin are cyanoethylated.

6. A light sensitive photographic element according to claim 4 wherein said cyanoethylated gelatin is essentially completely cyanoethylated.

7. A light sensitive photographic element according to claim 1 wherein said binder consists essentially of cyanoethylated gelatin.

8. A light sensitive photographic element according to claim 7 wherein at least a major proportion of the amine groups of said cyanoethylated gelatin are cyanoethylated.

9. A light sensitive photographic element according to claim 7 wherein said cyanoethylated gelatin is essentially completely cyanoethylated.

10. A photographic element of claim 1 in which said silver precipitating stratum comprises a colloid binder containing a colloid hardener.

11. A photographic element of claim 1 in which said silver precipitating stratum comprises a gelatin binder containing a gelatin hardener.

12. A photographic element of claim 1 in which said silver precipitating stratum comprises a gelatin binder containing a formaldehyde hardener.


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