

June 20, 1967

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DIFFUSION TRANSFER PHOTOGRAPHIC PROCESS  
USING 4, 6-DIAMINO-ORTHO CRESOL  
Filed Sept. 27, 1962

3,326,683

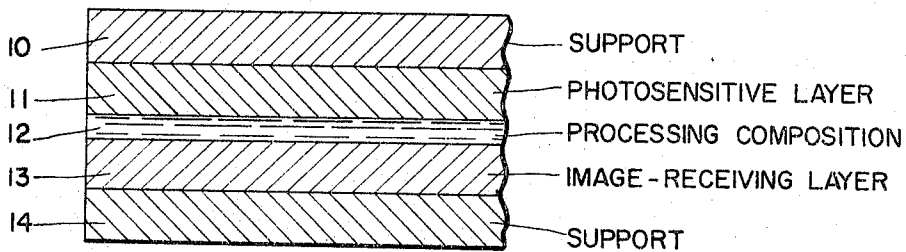


FIG. 1

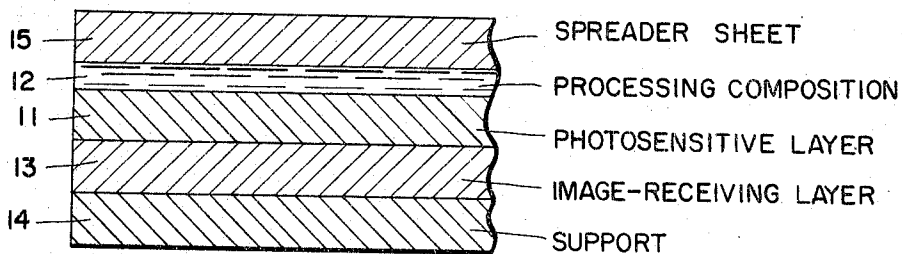


FIG. 2

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## DIFFUSION TRANSFER PHOTOGRAPHIC PROCESS USING 4,6-DIAMINO-ORTHO CRESOL

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Filed Sept. 27, 1962, Ser. No. 226,547

8 Claims. (Cl. 96—29)

This application is a continuation-in-part of our copending U.S. application Ser. No. 564,492, filed Feb. 9, 1956 (now abandoned).

The present invention relates to photography and more particularly to high speed diffusion processes wherein a silver halide photosensitive emulsion has been underexposed in relation to its A.S.A. Exposure Index, that is, to processes for deriving useful photographic transfer prints from latent images formed at low exposure levels.

In diffusion transfer processes, for the formation of positive silver images, a latent image contained in a selectively photoexposed photosensitive silver halide emulsion is developed. Almost concurrently therewith, a soluble silver complex is obtained by reaction of a silver halide solvent with the unexposed and undeveloped silver halide of said emulsion. Preferably, the photosensitive silver halide emulsion is developed with a processing composition in a viscous condition, which is spread between the photosensitive element comprising the silver halide emulsion and a print-receiving element comprising, preferably, a suitable silver precipitating layer. The processing composition effects development of the latent image in the emulsion and substantially contemporaneous therewith forms a soluble silver complex, for example, a thiosulfate or thiocyanate complex, with undeveloped silver halide. This soluble silver complex is, at least in part, transported in the direction of the print-receiving element and the silver thereof is largely precipitated in the silver precipitating layer of said element to form the desired positive image therein.

High speed diffusion transfer processes of the present invention are generally of the type in which, for example, a silver halide stratum containing a latent image formed at a low exposure level and an image-receiving stratum, in superposition, are subjected to a processing composition containing a highly energetic silver halide developing agent set forth hereinafter and a silver halide solvent in order to form a silver transfer print in and/or on the image-receiving stratum. The silver halide developing agent serves to reduce photoexposed silver halide to silver in the photosensitive emulsion stratum. The silver halide solvent reacts with unreduced silver halide to form the aforementioned soluble silver complex which, in turn, is reduced in the presence of the image-receiving stratum to form the desired positive print. The photosensitive stratum may be subsequently dissociated from the image-receiving stratum. In accordance with the present invention, the silver halide stratum may be underexposed in relation to its rated A.S.A. Exposure Index and the silver halide developing agent is specifically selected from the class hereinafter set forth.

Preferably, the image-receiving stratum is in such condition as to cause silver reduced there, in comparison with silver reduced in the photosensitive silver halide stratum, to possess very high covering power, that is, opacity per given mass of reduced silver. This high covering power is achieved by accumulating the silver deposited in the silver-receptive stratum in unusually dense masses, for example, by minimizing the thickness of the stratum in which the silver-receptive material is contained.

The high speed diffusion transfer processes set forth herein provide readily available and uniquely simple processes for producing satisfactory high quality prints of good resolution and trivial granularity at low illumination levels, for example, at overall exposures that are equivalent to A.S.A. Exposure Indices of 800 and up.

Accordingly, objects of the present invention are to provide novel high speed diffusion transfer processes wherein a selectively photoexposed silver halide emulsion has been substantially underexposed to relation to its A.S.A. Exposure Index, and to employ, in processes of the aforementioned type, as a silver halide developing agent, a 4,6-diamino cresol.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in conjunction with the accompanying drawing wherein:

FIGURE 1 is a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process, for the production of positive silver prints, the thickness of the various materials being exaggerated; and

FIG. 2 is a view similar to that of FIGURE 1 illustrating the association of elements during one stage of the performance of another diffusion transfer process, for the production of positive silver prints.

It has now been found that a 4,6-diamino-ortho cresol silver halide developing agent may be employed in diffusion transfer processes to provide high speed transfer prints of exceptional quality, either alone or in combination with other silver halide developers, particularly hydroquinone or one of its derivatives.

It has been found unexpectedly that the use of 4,6-diamino-ortho cresol provides a much more rapid rate of silver transfer than does the use of Amidol. 4,6-diamino-ortho cresol has unexpectedly also been found to give silver transfer images exhibiting extremely low structure, thereby providing silver transfer images of unexpectedly superior acuity. In addition to providing unobvious high Diffusion Transfer Exposure Indices, when employed as the sole developing agent, 4,6-diamino-ortho cresol has been found to be very useful as an additive developer used in small concentrations with hydroquinones and other developing agents. 4,6-diamino-ortho cresol also forms an oxidation product possessing less color than that of Amidol, thereby markedly reducing or avoiding any transfer image stain.

The developing agent of the present invention may be employed in the form of its acid addition salt, such as the hydrochloride, where desired.

In particular, the silver halide developing agent of the present invention is highly useful in so-called "high speed" diffusion transfer processes wherein high quality silver transfer prints are obtained from a silver halide emulsion which has been substantially underexposed in relation to its A.S.A. rating. Such an exposure provides a latent image having a density gradient confined to the low exposure or toe region of the negative material's characteristic curve.

The "speed" of a photosensitive material comprises generally an empirically derived relative measurement which may be defined as a value representing the reciprocal of the exposure required to produce a given result. Any precise definition of "speed," therefore, is based upon the selection of a particular result as the standard reference point. A precise quantitative measure of speed has

been developed from the work of L. A. Jones et al., as reported in Mees, *The Theory of the Photographic Process*, the Macmillan Company, New York, 1944, chapters XIX and XXII. This work suggested a system in which negative sensitive materials are assigned a speed that is in terms of the exposure required to give a negative image from which a positive print of specified quality can be produced.

Based on this work, The American Standards Association, Incorporated, has established standards for rating sensitive materials for speed. Under such standards, emulsion speed is considered as a value inversely proportional to the minimum exposure which must be incident upon the negative material, from the scene element of minimum brightness in which detail is visible, in order that a print of excellent quality can be made from the resultant negative. These standards specify techniques for plotting the characteristic H and D curve of a negative material, that is, the curve relating the logarithm of the original exposure of the negative to density in said negative. The value of speed derived from the standard characteristic curve so determined is specified as equal to the reciprocal of the exposure, E, on the characteristic curve at which the slope is 0.3 times the average slope for a log exposure range of 1.5 of which E is the minimum exposure. The precise method for determining speed in this manner is described in detail in the publication of The American Standards Association, Incorporated, pH 2.5—1954, and titled, "American Standard Method for Determining Photographic Speed and Exposure Index."

The A.S.A. speed rating is to be distinguished from what is termed the A.S.A. Exposure Index, for use with exposure meters and calculators. The A.S.A. Exposure Index is determined by the formula: A.S.A. Exposure Index=A.S.A. Speed/4. The exposure index so obtained indicates generally the correct exposure rating to which an A.S.A. calibrated exposure meter must be set in order that it give correct exposure data for producing pictures of satisfactory high quality.

The A.S.A. speed rating is to be further distinguished from what may be termed "Diffusion Transfer Process Exposure Index." In such processes, the exposure index may be based on a curve relating original exposure of the negative to the density in the resultant positive. It has been found experimentally that the Diffusion Transfer Exposure Index of a silver transfer process may be determined by plotting a characteristic curve of the reflection density of the positive as a function of the log exposure of the negative, determining the exposure in meter-candle-seconds (m.s.c.) at the point on this curve corresponding to a density of 0.50, and dividing the constant, 4.0, by the exposure so determined. The exposure index so obtained indicates generally the correct exposure rating of a silver transfer process to which an exposure meter, calibrated to the A.S.A. Exposure Index, must be set in order that it give correct exposure data for producing transfer prints of satisfactory high quality, and is sometimes referred to as the "equivalent A.S.A. exposure index."

Both the A.S.A. Exposure Index and the Diffusion Transfer Exposure Index can be judged or rated according to sensitometric criteria with exposure, that is, the luminance flux reaching a unit area of the photosensitive surface, being measured in m.c.s. The equivalence of the foregoing methods of determining rated A.S.A. Exposure Indices and Diffusion Transfer Exposure Indices can be readily established by obtaining a standardized silver transfer positive and determining the illumination, by measuring with an exposure meter calibrated according to an A.S.A. standard which includes a computer in which has been entered the shutter duration and f-stop of the camera, found necessary to provide the standard transfer print.

In the subsequent discussion, the term "A.S.A. Exposure Index" is intended to signify the exposure index determined in accordance with the aforementioned Amer-

ican Standards Association specifications. The term "Diffusion Transfer Exposure Index" is intended to signify, in reference to diffusion transfer processes, or the materials used therein, the exposure index as determined in the aforementioned manner. Both designations, in one sense, serve the same purpose. The A.S.A. Exposure Index of the negative is based upon the exposure to which the negative must be subjected in order to obtain a good photograph of a predetermined subject by conventional processing, whereas the Diffusion Transfer Exposure Index is based upon the exposure to which a negative for use in a silver diffusion transfer process must be subjected in order to obtain a good positive by that process. Both, therefore, are direct guides to the exposure setting which must be made in a camera in order to obtain proper exposure. Nevertheless, the two definitions of exposure must be carefully distinguished from each other because, although the A.S.A. Exposure Index is related qualitatively to the production of a positive of high quality, it is a term which describes the character of a negative material. This negative material, nevertheless, may be employed, for example, in a silver diffusion transfer process of the present invention to effect a Diffusion Transfer Exposure Index vastly different from the A.S.A. Exposure Index of the negative material. In the novel diffusion transfer processes of the present invention, a positive print of satisfactory high quality is produced from a negative material subjected to exposures less, in some cases many times less, than recommended by its rated A.S.A. Exposure Index. Such an exposure provides a latent image having a density gradient confined to the low exposure or toe region of the negative material's characteristic curve.

Referring now to the drawing, FIGURE 1 illustrates one assemblage and process of the present invention in the performance of a diffusion transfer process for the production of positive silver prints. As depicted in the drawing, an aqueous alkaline fluid layer 12 of a silver halide developing agent chosen in accordance with the present invention and a suitable silver halide solvent are spread between photosensitive emulsion layer 11 which is superposed on support 10 and image-receiving layer 13 which is affixed to support layer 14. Image-receiving layer 13 preferably contains silver precipitating agents or nuclei such as the silver precipitating nuclei disclosed in U.S. Patent No. 2,698,237. Support layer 14 may comprise an opaque material where a reflection print is desired or may comprise a transparent material where a transparency is desired.

Fluid layer 12 may be obtained by distribution of the processing composition in a substantially uniform manner between photosensitive emulsion layer 11 and image-receiving layer 13, for example, in accordance with the procedures disclosed in U.S. Patent No. 2,543,181. For example, one or more rupturable containers may be attached to either photosensitive emulsion layer 11 and/or image-receiving layer 13 such that upon superposition of the respective layers 11 and 13 said container or containers are so positioned as to be capable, upon rupture, of releasing their contents in a substantially uniform layer between and in contact with the opposed surface of each of said layers. Rupture of the container or containers and spreading of the contents thereof may be accomplished, for example, by compression between a pair of opposed, suitably gapped, rollers.

For clarity, the developing agent, the degree to which the photosensitive layer is exposed, and the character of the silver-receptive layer will be described in detail hereinafter.

The processing composition preferably comprises a film-forming transfer processing composition. It may comprise, for example, one or more of the developing agents in accordance with the present invention, an alkali such as sodium hydroxide, a silver halide complexing agent such as sodium thiosulfate, and a high molecular weight film-forming thickening agent such as sodium car-

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boxymethyl cellulose. All these materials are preferably in aqueous solution. These photographic agents are preferably contained in solution in the processing composition prior to the spreading thereof as layer 12, but they may be in part or in whole added to the processing composition as it is spread between the photosensitive emulsion 11 and image-receiving layer 13, said agents being so located on, in, or adjacent to a surface of one or both of said layers as to be dissolved by or otherwise interacted with the liquid agent when the latter wets said layers.

In carrying out the aforementioned transfer process, the photosensitive emulsion 11 is exposed to a predetermined subject matter to form therein a latent image of said subject matter. The exposed emulsion is superposed on image-receiving layer 13 and the photographic processing composition 12 spread between the opposed surfaces of said emulsion 11 and said image-receiving layer 13. Reagents permeate into the photosensitive emulsion 11, developing the latent image contained therein and forming a soluble silver complex of unexposed silver halide. Soluble silver complex is transported from photosensitive emulsion layer 11, at least in part, by imbibition, to print-receiving stratum 13 and the silver of the complex is precipitated thereon and/or therein to provide the desired positive image formation. The laminate formed by the spreading of the processing composition as layer 12 between photosensitive emulsion layer 11 and print-receiving layer 13 is kept intact for approximately 10 seconds to 1½ minutes, preferably 10 seconds, and at the termination of this time interval the print-receiving layer 13 is dissociated from photosensitive emulsion 11 as, for example, by manual stripping.

A further transfer process of the present invention for the production of positive silver prints is illustrated in FIG. 2 and comprises a spreader sheet 15, a layer of relatively viscous processing composition 12, a photosensitive emulsion layer 11 superposed on image-receiving layer 13 which is, in turn, superposed on a support layer 14. As stated in connection with the description of FIGURE 1, image-receiving layer 13 preferably contains silver precipitating nuclei and support layer 14 may comprise either an opaque or transparent material.

Fluid composition layer 12 may be obtained by spreading a photographic processing composition, for example, in a manner disclosed in U.S. Patent No. 2,698,244. As disclosed in the aforementioned patent, the liquid processing composition may be disposed in a rupturable container so positioned in regard to the appropriate surface of photosensitive emulsion layer 11 that, upon compression by spreader sheet 15, a substantially uniform layer 12 of processing composition is distributed over the external surface of said photosensitive emulsion 11, with respect to image-receiving layer 13.

In carrying out the last-mentioned transfer process, the photosensitive emulsion 11 is exposed to a predetermined subject matter to form therein a latent image of said subject matter. A substantially uniform distribution of processing composition 12 is distributed on the external surface of said emulsion 11, as for example, according to the previously described procedure. Processing composition reagents permeate into photosensitive emulsion 12, developing the latent image contained therein according to the point-to-point degree of exposure thereof. Substantially contemporaneous with the development of the latent image, an imagewise distribution of soluble silver complex is formed from unexposed and undeveloped silver halide within said emulsion. At least part of said silver complex, solubilized, is transferred, by imbibition, to print-receiving stratum 13. The transferred silver complexes are reacted therein to provide a positive, reversed image of the latent image. Subsequent to formation of the positive image in image-receiving layer 13, dissociation of said layer from emulsion layer 11 may be effected.

Where desired, the image-receiving layer 13 may be dissociated from emulsion layer 11 by stripping the emul-

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sion from the surface thereof. A conventional stripping layer may be provided to facilitate separation of emulsion layer 11 from image-receiving layer 13 subsequent to transfer processing. Sufficient abrasion-resistant properties may be provided to image-receiving layer 13 as to alleviate any necessity of subsequently overcoating the external surface of said image-receiving layer 13 with a transparent abrasion-resistant water-soluble plastic to prevent subsequent laceration and resultant degradation of the positive image. Image-receiving layer 13 may also comprise sufficient integral dimensional stability as to alleviate the necessity of a separate support layer 14.

In the last-mentioned processes, spreading of the liquid processing composition on the external surface of photosensitive emulsion layer 11 is preferably effected by rupture of a suitably positioned frangible container and distribution of its processing composition contents by means of a converted cellulose acetate spreader sheet, that is, a cellulose acetate sheet the surface of which has been converted to cellulose. When employed, the converted cellulose acetate spreader sheet may exhibit an adhesive capacity for the processing composition in excess of the adhesive capacity exhibited by the photosensitive emulsion. A means is thus provided for effecting dissociation of the processing composition from contact with the photosensitive emulsion, subsequent to image formation, by dissociating the spreader sheet from its proximate relationship to the external emulsion surface.

It will be apparent that the facility with which the photosensitive emulsion layer is dissociated from contact with the print-receiving layer may be increased by providing a conventional stripping layer interposed between said emulsion and said print-receiving layer. The stripping layer may be coated on the surface of the print-receiving element and a photosensitive emulsion thereafter coated on the external surface of said stripping layer.

While distribution of the processing composition in diffusion transfer processes has been described utilizing a frangible container, it will be apparent that said container provides a convenient means of distributing the liquid processing composition to permit the processing to be effected within a suitable camera apparatus. The diffusion transfer processes of this invention may be otherwise effected. For example, a photosensitive element, after exposing in a suitable apparatus and while preventing further exposure thereafter to actinic radiation, may be removed from such apparatus and permeated with the liquid processing composition as, for example, by coating, spraying, flowing etc., the composition on said photosensitive element or otherwise wetting said element with a composition, following which the permeated, exposed, photosensitive element, still without additional exposure to actinic radiation, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

The rupturable containers may be constructed in accordance with the disclosures set forth in U.S. Patent No. 2,634,886. Containers of this type are generally constructed from a blank comprising a flexible, deformable, three-ply sheet material comprising, respectively, an outer layer of kraft paper, a layer of metal foil and an inner layer or liner of a thermoplastic resin. The container blank is folded upon itself such as to provide a fluid-containing cavity and a container exhibiting a sealed passage adjacent to an edge thereof which may be substantially uniformly unsealed throughout a predetermined length of the seal passage upon application of stress to the container. The passage may be formed by the utilization of differential adhesion.

As previously noted, the print-receiving stratum preferably contains silver precipitating agents or nuclei, whose presence during the transfer process has a desirable effect on the amount and character of the silver precipitated during positive print formation. Examples of such silver precipitating agents are the metallic sulfides and selenides,

thiooxalates, and thioacetamides, and colloidal metals disclosed in U.S. Patent No. 2,698,237. It is also desirable, as disclosed in that patent, to provide, as the vehicle for the silver precipitating agents, a macroscopically continuous film that consists of submacroscopic agglomerates of minute particles of a suitable water-insoluble, inorganic, preferably siliceous, material such as silica aerogel. The use of such a vehicle for the precipitating agents tends to aggregate the silver that is precipitated into its most effective condition for print formation.

Silver halide solvents suitable for incorporation in the processing composition include conventional fixing agents such as sodium thiosulfate, sodium thiocyanate, ammonium thiosulfate, or associations of cyclic imides and nitrogenous bases such as associations of barbiturates or uracils and ammonia or amines. Of these, the conventional fixing agents specified are preferred. Preferably, the solution also contains a film-forming material such as a water-soluble plastic, starch or gum imparting a viscosity of from 1000 to 200,000 centipoises at a temperature of 20° C. in order to permit the solution to be readily controlled during and after spreading.

It will be apparent that the relative proportions of the agents of the developer composition set forth herein may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, silver halide solvents, etc., other than those specifically mentioned. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of developing agent may be varied over a wide range and when desirable the developing agent may be disposed in the photosensitive element prior to the exposure of the emulsion. The developing agent may be disposed in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

The preferred pH of the developing agent containing solution is generally in excess of 12, for the most favorable results. The concentration of developer preferably ranges from about 1 to 8% and that of the solvent from 0.3 to 10%, by weight.

The emulsion layer designated in the drawing as 10 may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both the synthetic types and those derived from naturally occurring products.

The photosensitive emulsion stratum may comprise a commercially available silver halide gelatin emulsion such as sold by Eastman Kodak Company under the trade names "Microfile," "Spectrum Analysis," "Contrast Process," "SXX aero Recon," "Verichrome," "Royal Pan," "Royal X Pan," or "Tri X Pan," or sold by E. I. du Pont under the trade names "Fine Grain Pan," "High Speed Pan," "Arrow Pan," or "Superior 3," or sold by Ansco under the trade name "Triple S. Pan," or sold by Gevaert under the trade name "Gevapan."

As previously stated, the silver halide developing agent of the present invention may also be used in small quantities with other silver halide developers, for example, hydroquinone or one of its derivatives, to produce high speed prints of exceptional quality by diffusion transfer processes.

The present invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative employment and evaluation of the silver halide developing agent of this invention in high speed diffusion transfer processes which, however, are not limited to the details therein set forth and are intended to be illustrative only.

#### Example I

A silver iodobromide emulsion was exposed and advanced in superposed relationship with an image-receiv-

ing element, comprising a silver-receptive stratum containing silver precipitating nuclei, between a pair of pressure applying rollers to spread a processing composition which comprised 0.4 gram of 4,6-diamino-ortho cresol added to 10 cc. of a solution comprising:

	Grams
Hydroxyethyl cellulose (high viscosity) -----	366
Sodium sulfite -----	260
Sodium thiosulfate -----	741
10 Sodium hydroxide -----	425
Water to make 9 liters.	

between the exposed emulsion and the image-receiving element. After an imbibition period of approximately 60 seconds, the emulsion, together with the layer of processing composition, was stripped from the image-receiving element to uncover a silver transfer image which possessed a maximum density of 1.35, a minimum density of 0.02, and a shoulder speed of 0.00015 m.c.s. The Diffusion Transfer Exposure Index obtained was 4800.

#### Example II

The process of Example I was repeated except that the processing composition employed comprised 0.4 gram of Amidol added to 10 cc. of the aforementioned solution. The resultant silver transfer image exhibited a maximum density of 1.43, a minimum density of 0.07, and a shoulder speed of 0.00037 m.c.s. The Diffusion Transfer Exposure Index obtained was 1450.

#### Example III

The process of Example I was repeated except that the processing composition employed comprised 0.3 gram of tertiary-butyl hydroquinone and 0.1 gram of 4,6-diamino-ortho cresol added to 10 cc. of the aforementioned solution and that the emulsion, together with the layer of processing composition, was stripped from the image-receiving element after an imbibition period of 30 seconds. The resultant silver transfer image exhibited a shoulder speed of 0.00016 m.c.s. The Diffusion Transfer Exposure Index obtained was 1180.

#### Example IV

The process of Example III was repeated except that the 4,6-diamino-ortho cresol was absent from the processing composition. The Diffusion Transfer Exposure Index obtained was substantially below 50.

#### Example V

The process of Example III was again repeated except that 0.1 gram of Amidol was employed in place of the 4,6-diamino-ortho cresol. The Diffusion Transfer Exposure Index obtained was 384 and the resultant silver transfer image exhibited a maximum density of 1.57, a minimum density of 0.25, and a shoulder speed of 0.00040.

As used in the above examples, the "shoulder speed" is the minimum amount of exposure in meter-candle-seconds which can be used to expose the negative emulsion and give a transfer image in which there is the minimum contrast which the eye can distinguish, i.e., there is visible detail in the shadow regions of the transfer image. This exposure level is determined at the point on the shoulder portion of the previously-described characteristic curve of the positive transfer image where the slope is 0.4.

The chief function of a photographic negative material as used in pictorial photography is to reproduce as density differences the luminance differences existing in the object photographed. The minimum useful exposure will, therefore, be that required to reproduce the minimum difference existing in the shadow regions of the object by means of some minimum density difference in the resulting image.

When the developing agent designated is used in high speed diffusion transfer processes, the region of the A.S.A. characteristic curve of the negative used in accordance

with the present invention lies at a relatively low exposure level and corresponds to an exposure gradient predominantly below approximately 0.015 m.c.s. Ordinarily, the fog level in such a case is at a point on the characteristic curve that corresponds to an exposure gradient predominantly above approximately 0.005 m.c.s.

It has been determined that, under the proper conditions, the activity of the silver halide developing agent, in accordance with the present invention, is concentrated in the extreme outer layer of the silver halide stratum. This phenomenon is probably due to the fact that the activity of the developer is so rapid that oxidation of the developer occurs before it is able to penetrate very deeply into the silver halide stratum. In comparison, the silver halide developing agent of conventional silver diffusion transfer processes is active in deeper layers of the silver halide stratum.

As illustrated in the aforementioned specific examples the photosensitive emulsions of the present processes are underexposed in relation to their respective A.S.A. Exposure Index to produce therein a weak latent image having an exposure gradient predominantly in the toe region of the A.S.A. density versus log exposure curve of the photosensitive emulsion. The emulsion is therefore exposed to produce a latent image lying in the toe region of the A.S.A. characteristic curve for the negative emulsion such that, by the standard A.S.A. development method, it would be impractical to develop the emulsion such as to provide a useful conventional negative image. By means of the compositions, products and processes of the present invention, one may advantageously employ a photosensitive emulsion having a stated A.S.A. Exposure Index and provide said emulsion with an effective exposure that ordinarily would require a photosensitive emulsion having a higher A.S.A. Exposure Index to provide an acceptable positive print resultant therefrom.

With conventional developing practices, good negatives can be obtained only from an emulsion that has been sufficiently exposed within the range of exposures specified for the emulsion. Underexposed emulsions result in a negative having only an image from which it is impractical to obtain a satisfactory print by conventional processes.

The present invention obviates the problem of constructing a satisfactory negative from an underexposed emulsion, for example, by intensification, hypersensitization, latensification techniques, so as to obtain a satisfactory positive print. In addition, the present invention provides satisfactory positive images from both underexposed and adequately exposed conventional silver halide photosensitive emulsions. As previously mentioned, a convenient measure of the amplification of image development, obtained according to the present disclosure, over the results obtained from conventional development practices, is in terms of increase in the speed or quantum excitation sensitivity of the emulsion as indicated by the results previously set forth, over the normal specified speed of the same emulsion as determined by the results of standard development practice.

It will be recognized that the steps of the instant processes may, where desired, be combined with such conventional speed-increasing steps as the aforementioned hypersensitization, latensifications, etc. In particular, pre-fogging has been used to excellent advantage.

Since certain changes may be made in the above products, processes and compositions 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.

We claim:

1. The photographic process which comprises the steps of selectively exposing a photosensitive gelatino silver halide emulsion with an illuminance flux incident thereon predominantly below 0.015 meter-candle-seconds; de-

veloping exposed silver halide in said photosensitive emulsion with an aqueous alkaline solution containing 4,6-diamino-ortho cresol and a silver halide solvent; substantially contemporaneous with said development, contacting unexposed and undeveloped silver halide therein with said silver halide solvent and forming thereby an imagewise distribution of a soluble silver complex in the unexposed areas of said emulsion, as a function of the point-to-point degree of exposure thereof; transferring from said emulsion, at least in part, by imbibition, said imagewise distribution of soluble silver complex to a print-receiving layer, containing silver precipitating nuclei, in superposed relationship to said emulsion; and there precipitating silver complex to provide thereby a reversed, positive, full scale silver print of the latent image.

2. The photographic process of claim 1 including the step of separating said print-receiving layer from its superposed relationship with said photosensitive emulsion at some stage subsequent to positive print formation.

3. The photographic process which comprises the steps of selectively exposing a photosensitive gelatino silver halide emulsion with an illuminance flux incident thereon not substantially in excess of 0.015 meter-candle-seconds; developing exposed silver halide in said photosensitive emulsion with an aqueous solution comprising 4,6-diamino-ortho cresol and a silver halide solvent, in the presence of a silver precipitating agent distributed in a layer contiguous with said silver halide emulsion; substantially simultaneously with said development, contacting undeveloped and unexposed silver halide therein with said silver halide solvent and forming thereby an imagewise distribution of a soluble silver complex in the unexposed areas of said emulsion, as a function of the point-to-point degree of exposure thereof; transferring from said emulsion, at least in part, by imbibition, said imagewise distribution of soluble silver complex to said contiguous layer; and there precipitating said silver complex to provide thereby a reversed, positive silver print of the latent image exhibiting a full pictorial density range.

4. The photographic process which comprises the steps of selectively exposing a photosensitive gelatino silver halide emulsion layer with an illuminance flux incident thereon not substantially in excess of 0.015 meter-candle-seconds; spreading an aqueous solution of 4,6-diamino-ortho cresol and a silver halide solvent, in the presence of a silver precipitating agent, between said emulsion layer and a second layer; effecting thereby development of said emulsion; substantially contemporaneous with said development, contacting undeveloped and unexposed silver halide therein with said silver halide solvent and thereby providing an imagewise distribution of a soluble silver complex in the unexposed areas of said emulsion as a function of the point-to-point degree of exposure thereof; and transferring from said emulsion, at least in part, by imbibition, said imagewise distribution of soluble silver complex to provide a positive print in the presence of said silver precipitating agents, said positive print exhibiting a full pictorial density range.

5. The photographic process which comprises the steps of selectively exposing a photosensitive gelatino halide emulsion with an illuminance flux incident thereon not substantially in excess of 0.015 meter-candle-seconds; developing exposed silver halide in said photosensitive emulsion with an aqueous solution of at least two silver halide developing agents, at least one of said silver halide developing agents being 4,6-diamino-ortho cresol and a silver halide solvent; substantially simultaneous with said development, contacting undeveloped and unexposed silver halide therein with said silver halide solvent and thereby forming an imagewise distribution of a soluble silver complex in the unexposed areas of said emulsion, as a function of the point-to-point degree of exposure thereof; transferring from said emulsion, at least in part, by imbibition, said imagewise distribution of soluble silver complex to a print-receiving layer, containing a silver

precipitating agent, in contiguous relationship to said emulsion; and there precipitating said silver complex to provide thereby a positive silver print exhibiting a full pictorial density range.

6. The photographic process of claim 5 wherein said solution has a pH in excess of 12.

7. The photographic process which comprises the steps of selectively exposing a photosensitive gelatino silver halide emulsion layer with an illuminance flux incident thereon not substantially in excess of 0.015 meter-candle-seconds; spreading an aqueous alkaline solution of 4,6-diamino-ortho cresol and a silver halide solvent between said emulsion layer and a second layer, said second layer comprising a silver-receptive stratum which comprises a silver precipitating agent and a siliceous material; effecting thereby development of said emulsion and, substantially contemporaneous with said development, contacting undeveloped and unexposed silver halide therein with said silver halide solvent and thereby providing an image-wise distribution of a soluble silver complex in the unexposed areas of said emulsion, as a function of the point-to-point degree of exposure thereof; transferring from said emulsion, at least in part, by imbibition, said imagewise distribution of soluble silver complex to said second layer to provide a positive print exhibiting a full pictorial density range.

8. The photographic process which comprises the steps of exposing a photosensitive gelatino silver halide emulsion with a light flux incident thereon not substantially in excess of the exposure range delineated by the toe region of said emulsion's characteristic H and D curve, determined according to A.S.A. Standard pH 2.5—1954; developing exposed silver halide in said photosensitive emulsion with an aqueous solution of 4,6-diamino-ortho cresol and a silver halide solvent; contacting undeveloped silver halide with said silver halide solvent and forming thereby an imagewise distribution of soluble silver complex in the unexposed areas of said emulsion; transferring from

said emulsion, at least in part, said imagewise distribution of soluble silver complex to a print-receiving element, containing silver precipitating agents, in superposed relationship to said emulsion; and precipitating said silver complex to provide thereby a reversed, positive print possessing a characteristic curve with a slope greater than the slope of said H and D curve, said positive's characteristic curve determined by plotting the reflection density of the positive print as a function of the log exposure of the negative.

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