United States Patent Office 3,345,16[illegible]
Patented Oct. 3, 196[illegible]

3,345,169

PHOTOGRAPHIC PROCESS

Hugh G. McGuckin, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed May 25, 1965, Ser. No. 458,750
19 Claims. (Cl. 96—29)

ABSTRACT OF THE DISCLOSURE

Photographic nuclei for use in the diffusion transfer process having improved stability are prepared by treating silver precipitating nuclei with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum, gold and mixtures thereof, such as potassium chloroplatinite, potassium chloropalladite, etc.

This invention concerns the silver halide diffusion transfer process and improved nuclei for use in the diffusion transfer process.

The solvent transfer or diffusion transfer system is described in Rott U.S. Patent 2,352,014 as a photographic process in which an exposed silver halide emulsion is developed in the presence of a silver halide solvent and contacted against a receiving support having thereon silver precipitating nuclei. The soluble silver halide complex diffuses (image-wise) from the undeveloped areas of the silver halide emulsion to the nuclei where silver is precipitated to form a positive image.

Various substances have been disclosed in the art for use as silver precipitating agents in the diffusion transfer process as disclosed in British Patent 868,243. The nuclei include metals such as colloidal silver, salts of metals or metalloids such as silver sulfide, nickel sulfide, and the like. However, it has been desirable to produce nuclei and solvent transfer images having better stability than are produced by the previously described nuclei. Moreover, it has been desirable to find a method of treating the previously known nuclei to render them more stable but at the same time to preserve the photographic characteristics of the nuclei.

Many of the nuclei which have been found to be particularly suitable for use in the diffusion transfer process have had to be prepared fresh prior to coating, since they have often had poor stability on standing. For instance, when a dispersion of the nuclei was permitted to stand, the dispersion would appear to lose density, possibly due to a bleaching effect so that the nuclei would no longer be of practical use.

Particularly useful nuclei used in the transfer process are known as Carey Lea silver. This colloidal silver material has been described by Luppo-Cramer, Koll, Zeitschrift, vol. 8, p. 240 (1911). However, Carey Lea silver has a noticeable yellow tint, particularly when dispersed in a colloid medium. It has also been difficult to tone images formed on Carey Lea silver. Therefore, positive images formed on a receiver containing practical amounts of Carey Lea silver can only be partially tone-modified to produce neutral images. These characteristics have limited the usefulness of Carey Lea silver as nuclei and it has been desirable to find a means of eliminating the yellow color while maintaining the high nucleating activity characteristics.

Photographic images obtained by the diffusion transfer process have in some instances been unstable over a period of time so that various treatments have been employed to improve the stability, such as after-baths, coating treatments, etc. Most of these treatments have been intended to remove the processing chemicals which were retained by the print. However, it has been appreciated that the

stability of the print is related to the stability of the nuclei and it has been desirable to find a method of treating the nuclei which would improve the stability of the print obtained therefrom.

I have found a method of treating silver precipitating nuclei for use in a diffusion transfer process which gives them improved stability without adversely affecting the photographic properties of the nuclei.

One object of this invention is to provide improved nuclei for use in the diffusion transfer system. Another object is to provide a method of treating nuclei which results in improved stability over previously known nuclei. A further object is to provide a method of treating Carey Lea silver nuclei to increase their usefulness as developing centers for the formation of images by diffusion transfer.

A further object of this invention is to provide a photographic element useful in forming images by the diffusion transfer process, which element provides for the production of images which will have improved stability. An additional object is to provide images obtained by physical development which will be stable to conditions of high humidity and elevated temperatures. Another object of my invention is to provide a treatment for sites for physical development which combine desirable features of different types of nuclei. These and other objects will become clear from the description of my invention which follows.

The above objects are obtained by treating silver precipitating nuclei with a noble metal in the ionic form. Particularly useful forms of the noble metal are the alkali metal salts of halo-noble metal acids, such as potassium chloroplatinite, potassium chloropalladite, etc. Gold chloride may also be used.

The results achieved by toning Carey Lea silver nuclei with an ionic form of a noble metal are surprising, since it has been hitherto impossible to form neutral toned images by physical development on Carey Lea silver nuclei. When a conventional toning agent such as a triazole was supplied to the diffusion transfer processing system employing Carey Lea silver, only partial toning of the resulting image was obtained. Moreover, the toned nuclei of this invention have, surprisingly, resulted in solvent transfer images having higher maximum density, more nearly neutral tone, improved tonal reproduction, longer stability, etc., than produced by the previously described nuclei.

The photographic element embodying the toned nuclei is prepared by coating a suspension of the toned nuclei in a colloid such as gelatin on a suitable support such as baryta-coated paper after which this element can be used as a receiving sheet for use in the diffusion transfer process. The nuclei may also be coated on a transparent polymeric support such as polyethylene terephthalate. In a particularly useful embodiment 1.35 milliequivalents of nickel sulfide nuclei treated with 1.27 milliequivalents of potassium chloropalladite in 2000 milligrams of gelatin is coated per square foot of support.

In another example of the utility of this nucleated support, the nucleated support having the toned nuclei thereon is overcoated with a substantially unhardened silver halide emulsion. After exposure the emulsion is developed with a silver halide diffusion transfer type developing solution containing a silver halide developer such as hydroquinone and also containing a silver halide complexing agent such as sodium thiosulfate. The undeveloped silver halide, complexed with the thiosulfate, diffuses to the nucleated underlayer where an image is formed which is positive with respect to the negative image formed in the silver halide emulsion. The unhardened silver halide emulsion is then removed by washing in warm water.

In carrying out the toning operation, the nuclei to be toned are formed in a conventional manner by the re-

action of two salts in a medium permitting the precipitation of the desired nuclei. For instance, nickel sulfide may be prepared from solutions of nickel nitrate and sodium sulfide and then suspended or dispersed in a suitable medium such as gelatin. However, these nuclei have been found to be unstable on standing and it has been customary for these nuclei to be prepared fresh prior to coating. For instance, when a dispersion of the nuclei was permitted to stand, the dispersion would appear to lose density so that the nuclei would no longer be of practical use. This is termed "fading." According to this invention, the nuclei prepared according to conventional methods are treated with an ionic form of a noble metal. For instance, the nickel sulfide prepared as above would then be treated with a compound of a noble metal such as potassium chloroplatinite, which supplies an ionic form of the noble metal, preferably in a gram equivalent ratio of about 1:1 to the nickel sulfide. The treated nuclei have a changed appearance in that the dispersion is now of a brownish color but it is found to be stable as compared with a dispersion of the untreated black nickel sulfide nuclei which fades badly after standing for 40 hours and after two weeks becomes colorless.

In a desirable embodiment the nuclei have an average particle size of about 7 A. units to 2,500 A. units. These nuclei include those known in the silver halide diffusion transfer art, such as, for example, metallic sulfides, polysulfides, selenides, and polyselenides, heavy metals and heavy metal salts, including stannous halides, and fogged silver halide. Heavy metal sulfides such as lead, silver, zinc, antimony, cadmium, and bismuth sulfides are particularly useful, either alone or in admixture, or as complex salts with thioacetamide, dithio-oxamide, or dithiobiuret. The heavy metal may be silver, gold, platinum, palladium or mercury. Of course, the particular noble metal used as a treating compound would be other than the metal used for the nuclei. It will be appreciated that mixtures of the noble metals may be used as a treating compound if desired.

For convenience in treating, the nuclei are prepared in a suitable suspending medium such as in a colloid suspension of gelatin. After the nuclei have been prepared, they are reacted with a noble metal in ionic form. In a particularly useful treatment, the noble metal is reacted in a gram equivalent relationship of about 1:1. However, other gram equivalent relationships of nuclei to noble metal within the range of 3:1 to 1:2 may be used. After treating the nuclei in the dispersion, the colloidal dispersion can then be coated on a suitable support.

Carey Lea silver, as conventionally prepared according to Luppo-Cramer, has a characteristic yellow color. In carrying out the invention of toning Carey Lea silver, the Carey Lea silver is, for convenience, suspended in a solution of a colloid such as an aqueous gelatin solution, and treated with a noble metal in its ionic form such as potassium chloropalladite preferably in about a ratio of 1:1. The normally yellow Carey Lea silver after appropriate toning is completely free of any yellow color. The toned Carey Lea silver suspended in gelatin is coated on a suitable support such as transparent cellulose acetate film support and permitted to dry.

The element is then brought into contact with the developing exposed silver halide emulsion in the presence of a silver halide complexing agent to form a positive image on the Carey Lea silver nuclei. The positive image on the nuclei is completely free of any yellow cast over the entire density scale whereas untreated Carey Lea silver when used in the same process results in a product having the characteristic yellow background cast of the Carey Lea silver nuclei. Lower concentrations of the toned Carey Lea silver may be used to obtain the same print density as the concentrations used with the untoned yellow Carey Lea silver.

The particular colloid material which is used is not critical but may be any of those customarily used for silver halide emulsions including the proteinaceous colloids such as gelatin, casein, zein, etc. Other colloids such as albumen, collodion, hydrolyzed cellulose acetate, polyvinyl alcohol, polyacrylates, etc., may be used. In the event that a hydrophobic medium is desired, a polymeric binder may be used. However, these are preferably used as a polymeric latex such as a styrene-butadiene latex or the like. Of course, mixtures may be used of a latex and hydrophilic colloid.

The silver halide emulsion which is used is not critical but may be any of those customarily used in the silver halide process such as silver chloride, bromide, iodide, chlorobromide, chloroiodide, chlorobromoiodide, etc. These emulsions may be sensitized by chemical or spectral sensitizers, and may contain other addenda.

The supports upon which the nuclei are used are not critical but depend upon the purpose desired. They may include paper, glass, metals, such as aluminum, etc., transarent polymeric materials such as cellulose esters, polyolefins such as polyethylene, polyesters, polystyrene, polyamides, etc. They may be reflection type supports such as those having a pigmented reflection coating such as baryta or the like.

The amount of treated nuclei which is coated on the support may vary depending upon the desired result and upon the particular silver halide emulsions employed. However it may vary from 0.025 milligram to 20 milligrams per square foot of support.

The silver halide developers which are employed in carrying out the silver halide diffusion transfer process are those conventionally used such as hydroquinone, other dihydroxybenzene and naphthalene compounds, paraphenylene diamine type developers, etc. It will be appreciated that auxiliary developing agents may also be used, such as those conventionally known in the art including the pyrazolidone-type developers, etc.

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

EXAMPLE 1

A nickle sulfide nuclei solution stabilized with potassium chloropalladite was prepared as follows:

The solution consisted of 300.0 ml. of 0.006 N NiS nuclei prepared in 2.0 percent gelatin, to which was added 60.0 ml. of 0.017 NK_2PdCl_4 in a 2.1 percent gelatin. (Unless otherwise stated, all percentages are by weight.)

The solution demonstrated excellent resistance to fading after more than 15 months' refrigeration keeping, whereas a control solution of untreated NiS nuclei faded badly after 1 week.

EXAMPLE 2

A coating containing nickel sulfide nuclei stabilized with K_2PdCl_4 (Pd/NiS) was prepared as follows:

The web material, coated on polyethylene terephthalate support, consisted of, on each square foot, 1.35 milliequivalents of NiS nuclei treated with 1.27 milliequivalents of K_2PdCl_4 in 2000 mg. of gelatin.

The preparation was as follows:

Nuclei solution

Seven and one-half milliliters of 10% gelatin and 1.95 ml. of 1.00 N sodium sulfide were added to 231.1 ml. of distilled water at 40° C. A solution comprised of 1.95 ml. of 1.00 N $Ni(NO_3)_2$ in 50.0 ml. of distilled water was next added with good stirring. This was followed by the addition of 7.5 ml. of 6% gelatin. Three hundred milliliters of 0.0062 N potassium chloropalladite were combined with 300 ml. of the above mixture.

Coating solution

Twenty grams of gelatin were dissolved in 160 ml. of distilled water. While holding at 40° C., 8.3 ml. of the nuclei solution were added. A hardener and coating aid were also included. The final volume was then adjusted to 200.0 ml. with distilled water.

An exposed high speed silver bromoiodide negative was then processed using the above web according to following procedure. The web prepared as above was soaked for 3 minutes at 90° F. in a solution containing:

Methylaminoethanol-SO_2 addition product, 19% SO_2 by weight	ml	160.0
Hydroquinone	grams	15.0
Sodium thiosulfate, pentahydrate	do	40.0
Potassium iodide	do	0.4
2-methyl-1-phenyl-3-pyrazolidone	do	2.0
3-mercapto-1,2,4-triazole	do	0.05

Water to make 1.2 liters.

The soaked web was squeegeed free of surface liquid and rolled into intimate contact with the exposed photographic film. The film-web sandwich was stored in the dark for 20 minutes at room temperature. After this time, the film and processing web were separated. The negative image was completely processed, and a good density neutral-toned positive image was formed in the processing web.

EXAMPLE 3

Other metal sulfide nuclei were stabilized with K_2PdCl_4 as follows:

Solutions consisting of 75.0 ml. of 0.0065 N metal sulfide nuclei were prepared in 0.4% gelatin, diluted both 1:1 and 3:1 with 0.0062 N K_2PdCl_4. Untreated nuclei solutions were also prepared as controls. Nuclei were prepared of the following metal sulfides: copper sulfides, zinc sulfide, cobalt sulfide, nickel sulfide, lead sulfide and silver sulfide.

All solutions were incubated 2 weeks at 130° F. Throughout this time physical changes in the nuclei were observed. Generally, considerable improvement in resistance to fading was noted after 2 weeks with those solutions which had been treated with K_2PdCl_4, whereas the untreated samples with the exception of Ag_2S had faded badly. No apparent change in density or color was observed after 2 weeks with CuS, ZnS, CoS or NiS nuclei diluted 1:1 with .0062 N K_2PdCl_4.

The results were as follows:

Nuclei Type	Time of Observation			
	Fresh	After 15 hours	After 4 days	After 2 weeks
Control:				
CuS	Red-brown	Turned green; faded	Badly faded	Badly faded.
ZnS	Opalescent-white	Turned clear	No change	Milky.
CoS	Black	No change	White-silvery	Badly faded.
NiS	do	Slight fading	Badly faded	Do.
PbS	Red-brown	No change	White precipitate	Black prec.
Treatment 3:1:				
Cus	Brown	do	No change	Do.
ZnS	do	do	do	Do.
CoS	do	do	Fading; blue prec.	Badly faded.
NiS	do	do	No change	No change.
PbS	do	do	do	Do.
Treated 1:1:				
Cus	do	do	do	Do.
ZnS	do	do	do	Do.
CoS	do	do	Slight fading	Do.
NiS	do	do	No change	Do.
PbS	do	do	White precipitate	Some fading.
Ag_2S	do	White precipitate [1]	No change	No change.

[1] This precipitate is probably silver chloride formed by the reaction of silver ion and the chloride ion from the chloropalladite solution.

Web coatings were prepared with these nuclei fresh and after 2 weeks' incubation at 130° F. showed no loss in nuclei activity, based on sensitometric data.

EXAMPLE 4

Physically developed images having improved stability obtained by means of palladium treated nickel sulfide (Pd/NiS) nuclei were prepared as follows:

Samples of unwashed positive images physically developed on equivalent concentrations of untreated NiS nuclei and palladium treated nickel sulfide nuclei were incubated for 4 days at 90° F., 90% RH.

Coatings were prepared as described in Example 2, bu at one-fourth the nuclei concentration per square foo Precessing conditions were identical to those of Exampl 2. The NiS sample lost considerable density (1.0) an increased in positive speed, whereas the positive on Pd NiS nuclei lost much less density (0.22) and increase only slightly in speed. There was also less yellow stai and almost no visible mottle on the Pd/NiS sample whil the NiS sample showed both a bad stain and mottle.

EXAMPLE 5

Metal sulfide nuclei stabilized with other noble meta salts were prepared as follows:

Separate solutions were prepared, which consisted o 0.00 N NiS nuclei dispersed in 2.0% gelatin and 0.4% gelatin to which were added an equal volume of .0048 N potassium chloroplatinite (K_2PtCl_4) and an equal volume of .0088 N gold chloride ($AuCl_3$) respectively.

These nuclei solutions demonstrated improved resistance to fading after 3 days' incubation at 130° F., whereas a control solution of untreated NiS nuclei faded badly after less than 1 day incubation at 130° F.

EXAMPLE 6

(Pd/NiS) nuclei were prepared in a polyvinyl alcohol (PVA) derivative as follows:

The solution consisted of 0.0065 N NiS nuclei prepared in 0.4% PVA derivative to which was added an equal volume of 0.0062 N K_2PdCl_4. This solution showed no apparent density loss up to 13 days keeping at 130° F., whereas a control solution of untreated NiS nuclei was completely clear after 4 days.

EXAMPLE 7

A wash-off solvent transfer material containing (Pd/NiS) nuclei was prepared as follows:

The material consisted of, on each square foot, 3.4 milliequivalents of Pd/NiS nuclei coated in 100 mg. of hardened gelatin over cellulose acetate support. This layer was overcoated with 400 mg. of an unhardened slow silver bromoiodide emulsion. A coating aid was included in both layers.

A good density neutral toned positive image was produced by immersing the above coating in a solvent-containing developer which included the tone modifying agents for 2 minutes at room temperature and washing off the unhardened emulsion layer under warm water.

EXAMPLE 8

A web material was prepared coated over a cellulose acetate support, consisting of, on each square foot, 2.4 mg. of Carey Lea silver treated with 1.9 mg. of K_2PdCl_4 in 100 mg. of gelatin. A hardener and coating aid were included.

A good-density neutral-toned positive image was obained by soaking the web and a high-speed bromoiodide egative emulsion for 10 seconds at room temperature in he following developer:

Methylaminoethanol-SO_2 addition product, 10% SO_2 by weight	g--	130.0
Hydroquinone	g--	20.0
Sodium thiosulfate·$5H_2O$	g--	20.0
Potassium bromide	g--	10.0
1-phenyl-3-pyrazolidone	g--	2.0
3-mercapto-1,2,4-triazole	g--	0.3
3,8-dithiadecane - 1,10-bis(N - methylpiperidinium p-toluene sulfonate)	g--	1.0
Isopropanol	ml--	100.0
Water to make 1.0 liter.		

The web and negative were brought in contact for 3 minutes at room temperature. The positive image in the web was completely free of any yellow cast over the entire density scale. A positive made in a similar manner using a Carey Lea silver web which had not been modified by the K_2PdCl_4 showed some toning in the dense areas due to the presence of the mercaptotriazole, but it had the characteristic yellow background cast of the Carey Lea silver nuclei.

EXAMPLE 9

A web material was prepared coated over a polyethylene terephthalate support, consisting of, on each square foot, 0.5 mg. of Carey Lea silver treated with 0.40 mg. of K_2PdCl_4 in 2000 mg. of gelatin.

The preparation was as follows:

Nuclei solution

At room temperature the following were combined:

Carey Lea silver (approximately 25.0 mg. silver per ml. of solution)	ml--	5.0
Distilled water	ml--	100.0
1% K_2PdCl_4 in water	ml--	10.0
5% gelatin at 40° C. (added immediately)	ml--	100.0

Coating solution

Photographic grade gelatin	grams--	20.0
Nuclei solution	ml--	8.62
Distilled water	ml--	171.38
Total volume	ml--	200.0

A hardener and coating aid were included.

The dried web material prepared as above was soaked in a developer having the following formula:

	Grams
Methylaminoethanol-So_2 addition product, 19% SO_2 by weight	100.0
Hydroquinone	15.0
Sodium thiosulfate·$5H_2O$	40.0
2-methyl-1-phenyl-3-pyrazolidone	2.0
3-mercapto-1,2,4-triazole	0.3
3,8-dithiodecane - 1,10-bis(N - methylpiperdinium p-toluene sulfonate)	1.0
Water to make 1.0 liter.	

Contact was then made with a high-speed bromoiodide negative for 20 minutes at room temperature. Complete fixation of the negative was achieved. The positive image in the web was neutral.

EXAMPLE 10

A web material, coated over a polyethylene terephthalate support, was prepared consisting of, on each square foot, 0.5 mg. of Carey Lea silver treated with 0.80 mg. of K_2PtCl_4.

The preparation was as follows:

Nuclei solution

At room temperature the following were combined:

	Ml.
Carey Lea silver (approximately 25.0 mg. silver per ml. of solution)	5.0
Distilled water	90.0
1% K_2PtCl_4 in water	20.0
5% gelatin at 40° C.	100.0

Coating solution

The coating solution was identical to that described in Example 9 except 8.62 ml. of Pt^{++} treated nuclei were added instead of 8.62 ml. of Pd^{++} treated nuclei.

Processing tests were carried out as described in Example 9 and produced approximately the same results.

EXAMPLE 11

A web material was prepared, coated over a polyethylene terephthalate support, consisting of, on each square foot, 0.5 mg. of Carey Lea silver treated with 0.60 mg. of gold chloride ($AuCl_3$).

The preparation was as follows:

Nuclei solution

	Ml.
Carey Lea silver (approximately 25.0 mg. silver per ml. solution)	5.0
Distilled water	100.0
1% $AuCl_3·2H_2O$ in water	15.0
5% gelatin at 40° C.	100.0

Coating solution

The coating solution was identical to that described in Example 9 except 8.62 ml. of Au^{+++} treated nuclei were added instead of 8.62 ml. of Pd^{++} treated nuclei.

Processing tests were carried out as described in Example 9 and also produced approximately the same results.

The sensitometric properties of the image which is physically developed on the nuclei are known to be a function of the type of nuclei used. Nuclei treated by the method and materials of my invention surprisingly enough maintain the sensitometric characteristics of the untreated nuclei yet show improved stability which is characteristic of the treated nuclei. The values for the gradient, D_{max}, and toe speeds of positive images produced on treated nuclei correspond very nearly to those values obtained on control coatings containing untreated nuclei. The following example illustrates this effect with nickel sulfide nuclei which were treated with potassium chloropalladite.

EXAMPLE 12

Nuclei prepared as in Example 2 with and without treatment by potassium chloropalladite were prepared. A control coating containing palladium sulfide nuclei was prepared by using 7.5 ml. of 10 percent gelatin and 1.5 ml. of 1.00 N sodium sulfide to which were added 231 ml. of distilled water at 40° C. A solution comprised of 1.95 ml. of 1.00 N potassium chloropalladite in 50 ml. of distilled water was added with vigorous stirring. This was followed by the addition of 7.5 ml. of 6 percent gelatin.

Following the procedure described in Example 2, coatings of the three types of nuclei were prepared at the same coverages as in Example 2 and used for processing. A comparison of the sensitometric curves of positive images for the three types of nuclei, (1) untreated nickel sulfide, (2) nickel sulfide nuclei, and (3) palladium sulfide nuclei, showed the following results. The image produced using the palladium sulfide nuclei was of considerably lower toe speed having a long drawn-out sweep to the toe portion of the characteristic curve. Contrast was lower and the D_{max} was considerably lower than corresponding values for the other two types of nuclei.

The aforementioned sensitometric properties produced in coatings containing treated and untreated nuclei were very nearly alike having the same values within narrow limits. The above results would indicate that my invention does not involve simply the conversion of the nuclei of one type to nuclei of the second type. In the above case it is not simply a conversion of nickel sulfide nuclei to palladium sulfide nuclei since the sensitometric properties of the former are maintained and the stability characteristics of the latter are produced.

The noble metal salts useful in my invention are those of the group which include gold, platinum, palladium, etc. Ionic species of the metals are used to promote the interaction of the noble metal ion with the nuclei to be treated. Complexes of noble metals with the halogens, cyanides, etc., are typical of the more readily available compounds. For example, sodium, potassium, and ammonium salts of bromoaurates, chloroaurates, cyanoaurates, and corresponding platinites, palladites, etc., represent some useful embodiments of noble metal compounds which provide the ionic form of the noble metal which may be used in carrying out my invention.

The extent of treatment of the nuclei by the ionic form of a noble metal used to demonstrate the particular advantages of my invention is dependent somewhat on the individual noble metal and the conditions of treatment.

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.

I claim:

1. A photographic element for use in the photographic diffusion transfer process comprising a support having thereon silver precipitating nuclei reacted with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold and mixtures thereof in which the noble metal is other than any metal comprising said silver precipitating nuclei.

2. A photographic element of claim 1 in which the said nuclei are selected from the class consisting of sulfides, polysulfides, selenides and polyselenides of metals, heavy metals, heavy metal salts, complex compounds of heavy metal sulfides with thioacetamide, dithio-oxamid and dithio-biuret, and mixtures thereof.

3. A photographic element of claim 1 in which the said nuclei are selected from the class consisting of Carey Lea silver, the sulfides of cadmium, cobalt, copper, lead, nickel, silver, and zinc, and mixtures thereof.

4. A photographic element of claim 1 in which the said noble metal has a minimum positive valence.

5. A photographic element of claim 1 in which the support has thereon nickel sulfide nuclei reacted with a solution of an alkali metal chloropalladite.

6. A photographic element of claim 1 in which the support has thereon cobalt sulfide nuclei reacted with an alkali metal chloropalladite.

7. A photographic element of claim 1 in which the support has thereon zinc sulfide nuclei reacted with a compound having as an anion $(PdCl_4)^=$.

8. A photographic element of claim 1 in which the support has thereon Carey Lea silver reacted with an alkali metal chloroplatinite.

9. A photographic element of claim 1 in which the support has thereon Carey Lea silver reacted with gold trichloride.

10. Nuclei for use in a photographic diffusion transfer process comprising silver precipitating nuclei reacted with an ionic compound comprising a noble metal selected from the class consisting of palladium, platinum and gold and mixtures thereof in which the noble metal is other than any metal comprising said silver precipitating nuclei.

11. Nuclei of claim 10 in which the said silver precipitating nuclei are selected from the class consisting of sulfides, polysulfides, selenides and polyselenides of metals; heavy metals; heavy metal salts, complex compounds of heavy metal sulfides with thioacetamide, dithio-oxamid and dithio-biuret, and mixtures thereof.

12. Nuclei of claim 10 wherein the said silver precipitating nuclei are selected from the class consisting of Carey Lea silver, the sulfides of cadmium, cobalt, copper, lead, nickel, silver, and zinc, and mixtures thereof.

13. Nuclei of claim 10 in which the said noble metal has a minimum positive valence.

14. Nuclei of claim 10 comprising nickel sulfide silver precipitating nuclei reacted with a solution of an alkali metal chloropalladite.

15. Precipitating nuclei of claim 10 comprising cobalt sulfide nuclei reacted with an alkali metal chloropalladite.

16. Precipitating nuclei of claim 10 comprising zinc sulfide nuclei reacted with a compound having as an anion $(PdCl_4)^=$.

17. Precipitating nuclei of claim 10 comprising Carey Lea silver reacted with an alkali metal chloroplatinite.

18. Precipitating nuclei of claim 10 comprising Carey Lea silver reacted with gold trichloride.

19. A process of obtaining an image by the diffusion transfer process which process comprises developing an exposed silver halide emulsion in the presence of a diffusion transfer type silver halide developer and contacting the developing silver halide emulsion against silver halide precipitating nuclei disposed on a support, which nuclei have been reacted with an ionic compound comprising a noble metal selected from the class consisting of platinum, palladium, gold and mixtures thereof, and which noble metal is other than a metal comprising said nuclei.

References Cited

UNITED STATES PATENTS

2,698,237 12/1954 Land ---------- 96—76

NORMAN G. TORCHIN, *Primary Examiner.*

R. E. MARTIN, *Assistant Examiner.*